Preference for $Na^+-\pi$ Binding over Na^+-Dipole Binding in Na^+-Arene Interactions

Michelle Watt, JiYoung Hwang, Kevin W. Cormier, and Michael Lewis*

Department of Chemistry, Saint Louis University, 3501 Laclede Avenue, Saint Louis, Missouri 63103

Received: March 17, 2009

The cation binding of dipolar aromatics was investigated employing computational techniques. In most cases, cation binding at the π region of the aromatic (the cation$-\pi$ interaction), which can be thought of as a cation−quadrupole interaction, is preferred over cation binding at the negative end of the dipole moment. Surprisingly, in some cases, the cation−dipole complex is not even a minimum on the potential energy surface.

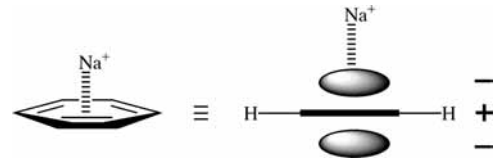
Introduction

Cation$-\pi$ interactions of aromatics[1] are important in a wide range of biological and chemical fields including enzyme−substrate recognition,[2] catalyst development,[3] and nanomaterial design.[4] Cation$-\pi$ interactions have been investigated in the gas phase,[1a,c] the solution phase,[1a,c] and in the solid state,[1b] and the interaction is generally understood via the quadrupole moment of the aromatic.[1a] In general, for electron-rich arenes, the negative areas of the quadrupole moment coincide with the aromatic π-cloud regions, as shown for benzene and Na^+ in Scheme 1. Many studies have investigated Na^+-arene complexes to probe the basic nature of cation$-\pi$ interactions. The gas-phase Na^+ binding of benzene has been investigated experimentally[5] and computationally,[6] and the Na^+ binding of numerous monosubstituted aromatics has been measured, including fluorobenzene,[7] benzonitrile,[8] toluene,[9] aniline,[10] and phenol.[11]

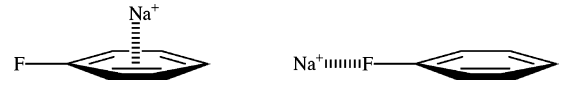
As a means of describing the relative strength of the cation$-\pi$ interaction, Dougherty sites[12] the work of Kebarle which shows the gas-phase binding of the $K^+-C_6H_6$ complex is −19 kcal/mol while the binding of the K^+-H_2O complex is −18 kcal/mol.[13] Thus, the cation$-\pi$ interaction is competitive with the cation−dipole interaction. Lisy and co-workers found similar results in their gas-phase competitive solvation experiments where they show the benzene$-K^+$ complex is strong enough for benzene to displace some water molecules from the K^+-water complex.[14] The same result was not found for Na^+; benzene will not displace water from the Na^+-water complex. Despite the findings of Kebarle and Lisy, there remains a common belief that the multipole moment expansion (point charge, dipole, quadrupole, octapole, ...) is perturbative, and therefore the attraction between a cation and a molecular multipole should decrease along the series dipole, quadrupole, octapole, and so forth. In other words, cation$-\pi$ binding, which is a cation−quadrupole interaction, should be weaker than the cation−dipole binding, even though Anslyn and Dougherty have pointed out in their recent text that this is not the case.[15]

While the comparison of the $K^+-C_6H_6$ and K^+-H_2O complexes is an elegant demonstration of the strength of cation$-\pi$ binding, we sought to gain a more direct comparison of the relative strengths of cation$-\pi$ and cation−dipole complexes in aromatic complexes by comparing the Na^+ binding of monosubstituted aromatics where the cation is either bound to the aromatic π cloud or to the negative end of the aromatic dipole moment. Toward this end, we have calculated the Na^+ binding of aromatics with the general formula C_6H_5X where X = F (**1**), Cl (**2**), Br (**3**), I (**4**), CN (**5**), NO_2 (**6**), BH_2 (**7**), CH_3 (**8**), SiH_3 (**9**), NH_2 (**10**), PH_2 (**11**), OH (**12**), and SH (**13**), and

SCHEME 1: Cation$-\pi$ Complex of Na^+ and Benzene



SCHEME 2: Cation$-\pi$ (Cation−Quadrupole) and Cation−Dipole Complexes for Na^+-Fluorobenzene



in each case, we have investigated the binding to the π region of the aromatic (the cation−quadrupole complex) and to the negative end of the molecular dipole moment. Scheme 2 illustrates the two types of complexes for fluorobenzene.

Computational Methods and Theoretical Approach

All calculations were performed using the Gaussian03 suite of programs.[16] The first approach we employed to investigate the difference in binding energy between cation$-\pi$ and cation−dipole complexes was to optimize the geometries for the cation−arene complexes with the cation either starting over the π cloud or at the negative end of the molecular dipole moment. All structures were optimized at the MP2(full)/6-311G** level of theory, and the absence of imaginary frequencies confirmed they were minima on the potential energy surface (PES). The ΔE_0, ΔH_0, and ΔH_{298} binding energies were determined for each structure using the following equations:

$$\Delta E_0 = \left[E(Na^+ - C_6H_5X) - (E(C_6H_5X) + E(Na^+))\right];$$

energies (E) were corrected for basis set superposition error (BSSE) using the counterpoise method[17]

$$\Delta H_0 = \Delta E_0 + [ZPVE(Na^+-C_6H_5X) - (ZPVE(C_6H_5X) + ZPVE(Na^+))];$$

ZPVE ≡ zero-point vibrational energy

$$\Delta H_{298} = \Delta H_0 + [E_{thermal}(Na^+-C_6H_5X) - (E_{thermal}(C_6H_5X) + E_{thermal}(Na^+))];$$

$E_{thermal}$ ≡ translational, rotational and vibrational energy at 298 K

The above approach found PES minima for the cation$-\pi$ and cation−dipole complexes of most $Na^+-C_6H_5X$ complexes;

* Corresponding author. E-mail: LewisM5@slu.edu.

10.1021/jp902400h CCC: $40.75
Published on Web 05/04/2009

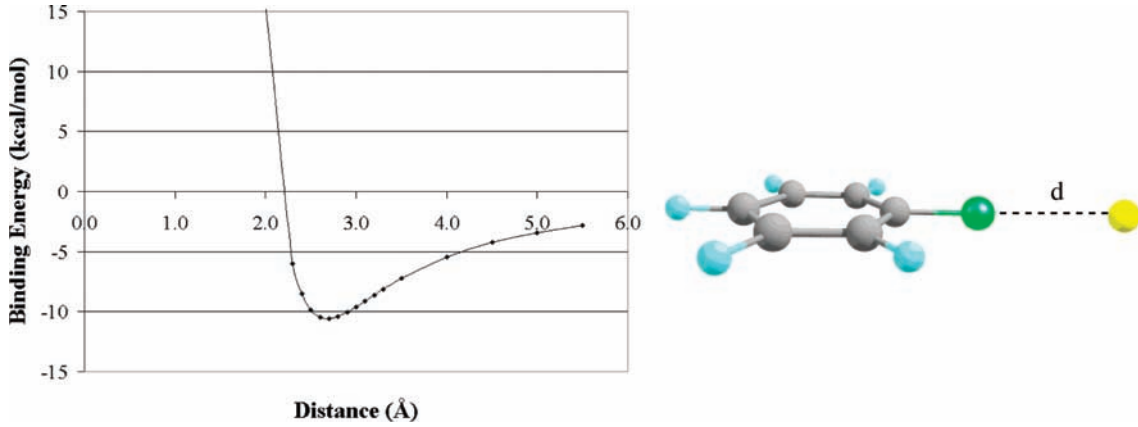


Figure 1. Determination of ΔE_0 for $Na^+-C_6H_5Cl$ cation−dipole complex at the MP2(full)/6-311G** level of theory (Na: yellow. Cl: green. C: gray. H: blue).

TABLE 1: Cation Binding Energies[a] of $Na^+-C_6H_5X$ Complexes where Optimizations began with Na^+ Interacting with the Dipole or the π-Cloud

C_6H_5X	Na^+ starting at dipole				Na^+ starting at π cloud				
X =	ΔE_0	ΔH_0	ΔH_{298}	optimized structure[b]	ΔE_0	ΔH_0	ΔH_{298}	optimized structure[b]	experimental values
F (**1**)	−18.14	−17.60	−17.05	dipole	−17.68	−16.33	−16.07	Pi	$\Delta H_0 = -16.7 \pm 0.8$[d] $\Delta H_{298} = -16.9 \pm 1.0$[d]
Cl (**2**)	−15.64	−14.60	−14.18	C_{ipso}	−17.89	−16.52	−16.29	Pi	
Br (**3**)	−17.34	−16.22	−15.81	C_{ipso}	−18.31	−16.88	−16.68	Pi	
I (**4**)	−18.46	−17.61	−17.14	C_{ipso}	−19.83	−18.55	−18.29	Pi	
CN (**5**)	−32.05	−30.86	−30.49	dipole	−12.73	−11.55	−11.23	Pi	$\Delta H_0 = -32.7 \pm 1.4$[e]
NO_2 (**6**)	−31.03	−30.30	−29.94	dipole	−31.03	−30.30	−29.94	dipole	
BH_2 (**7**)	−15.83	−15.01	−14.64	dipole	−18.96	−17.91	−17.59	Pi	
CH_3 (**8**)	−23.62	−21.89	−21.77	Pi	−23.62	−21.89	−21.77	Pi	$\Delta H_0 = -26.8 \pm 0.8$[f] $\Delta H_{298} = -27.2 \pm 1.1$[f]
SiH_3 (**9**)	−21.53	−20.30	−20.09	Pi	−21.53	−20.30	−20.09	Pi	
NH_2 (**10**)	−32.21	−30.25	−30.14	dipole[c]	−27.22	−25.45	−25.34	Pi	$\Delta H_0 = -28.7 \pm 0.6$[g]
PH_2 (**11**)	−19.75	−18.70	−18.41	dipole	−21.52	−20.19	−20.02	Pi	
OH (**12**)	−26.87	−25.61	−25.34	dipole[c]	−22.48	−20.80	−20.69	Pi	$\Delta H_0 = -23.5 \pm 0.8$[h] $\Delta H_0 = -24.5 \pm 0.8$[i] $\Delta H_{298} = -24.8 \pm 0.9$[i]
SH (**13**)	−19.90	−18.84	−18.59	dipole	−20.94	−19.86	−19.65	Pi	

[a] Cation binding energies ΔE_0, ΔH_0, and ΔH_{298} in kcal/mol. [b] Dipole: structure optimized with Na^+ at the negative end of the molecular dipole. C_{ipso}: structure optimized with Na^+ above the ipso-carbon atom. Pi: structure optimized with Na^+ above the aromatic π cloud. [c] Binding energies from cation-lone pair complexes of phenol and aniline, representing cation−dipole complexes of local dipoles. [d] Reference 7. [e] Reference 8. [f] Reference 9. [g] Reference 10. [h] Reference 11a. [i] Reference 11b.

however, for five cation−dipole complexes (C_6H_5X: X = Cl, Br, I, CH_3 and SiH_3) and one cation−π complex ($C_6H_5NO_2$), there was no PES minima at the MP2(full)/6-311G** level of theory. Since our goal was to compare cation−π and cation−dipole binding energies, we obviously needed a method to obtain these values. The approach we employed involved holding the structure of the monosubstituted aromatic constant and varying the distance of the Na^+ from the negative end of the dipole moment for the cation−dipole complexes, as shown in Figure 1 for $Na^+-C_6H_5Cl$. Of course, for the $Na^+-C_6H_5NO_2$ cation−π complex, we varied the distance between the Na^+ and the center of the π cloud. As was the case for the optimizations, these calculations used the MP2(full)/6-311G** level of theory, and they were corrected for BSSE. The binding energy (ΔE_0) was taken as the minimum on the PES (Figure 1). As a means of quantifying the veracity of the approach shown in Figure 1, we used it to calculate ΔE_0 for the $Na^+-C_6H_5F$ cation−dipole complex. Varying the distance between the negative end of the C_6H_5F dipole moment and the Na^+ gives $\Delta E_0 = -17.05$ kcal/mol, and this is about 6% less than the −18.14 kcal/mol value obtained from optimization.

Results and Discussion

Before analyzing the results, comparing our calculated Na^+ binding enthalpies and the Na^+-benzene binding enthalpy to experimentally measured values will serve to illustrate the suitability of the MP2(full)/6-311G** level of theory for performing this study. There have been three experimentally measured Na^+-benzene binding enthalpies: $\Delta H_0 = -28.0 \pm 0.1$ kcal/mol,[5a] $\Delta H_{298} = -22.5 \pm 1.5$ kcal/mol,[5b] and $\Delta H_{298} = 21.5 \pm 1.0$ kcal/mol.[5c] Recent high-level computational work supports the accuracy of the latter two values; the calculated Na^+-benzene binding energy is $\Delta E_0 = -21.5$ kcal/mol at the MP2 level with the Sadlej basis set[6a] and $\Delta E_0 = -22.95$ kcal/mol at the CCSD(T) level with complete basis set approximation.[6b] At the MP2(full)/6-311G** level of theory, the Na^+ binding energy is $\Delta H_{298} = -24.51$ kcal/mol, just outside the experimental range for the smaller two values. The ΔE_0, ΔH_0, and ΔH_{298} cation−π and cation−dipole binding energies obtained from MP2(full)/6-311G** optimization and frequency calculations are collected in Table 1, along with the experimentally measured Na^+ binding enthalpies (ΔH_0 and ΔH_{298}), in the cases where they have been determined. The MP2(full)/6-311G** calculated Na^+ binding energies of fluorobenzene, benzonitrile, aniline, and phenol are in excellent agreement with the experimental values, and only for toluene is the agreement poor. Still, the fact that the MP2(full)/6-311G** theoretical level gives Na^+-arene binding enthalpies in excellent agreement with experiment for four of the five aromatics in Table 1 and benzene supports its use in this study.

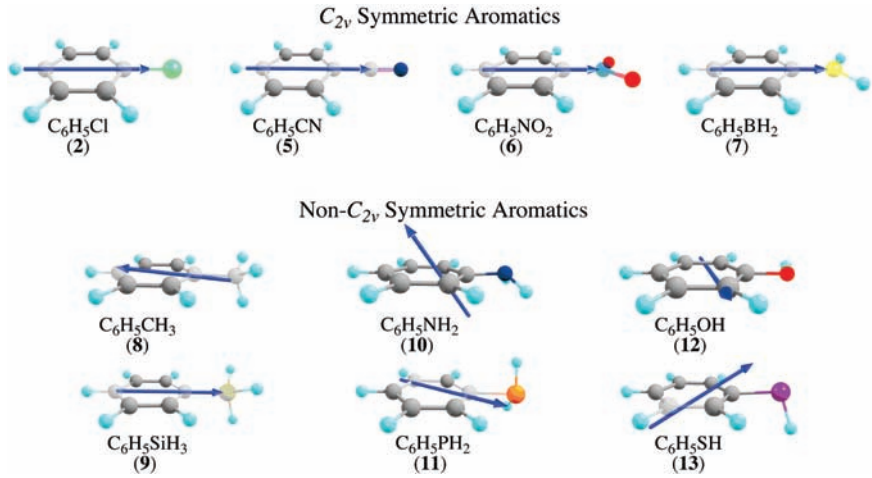


Figure 2. MP2(full)/6-311G** calculated dipole moments for monosubstituted aromatics **1**−**13**. (C: gray. H: light blue. Cl: green. N: dark blue. O: red. B: yellow. Si: olive. P: orange. S: purple.)

In order to determine where the negative ends of the C_6H_5X molecular dipole moments were so we could calculate the ΔE_0 values for the cation−dipole complexes, we first needed to calculate the molecular dipole moments of each aromatic, and these are given in Figure 2 (where chlorobenzene is used to illustrate the halo-benzenes). The calculated dipole moments of the C_{2v} symmetric halo-benzenes (**1**−**4**), benzonitrile (**5**), nitrobenzene (**6**) and phenylborane (**7**) are as expected: symmetry dictates that the dipole moment is along the C_2 axis. Toluene (**8**), phenylsilane (**9**), aniline (**10**), phenylphosphine (**11**), phenol (**12**), and phenylthiol (**13**) are all less symmetric, and thus the dipole moment is not along the C_{para}−H and C_{ipso} bonds. For toluene and phenylsilane, the dipole moment is largely along the C_{para}−H and C_{ipso}−X bonds, and the main difference between the two is the direction: the negative end of the dipole moment is at (or near) the C_{para}−H region for toluene, and it is near the silyl-group for phenylsilane. The structures of aniline and phenylphosphine are quite different with respect to the orientation of the $-NH_2$ and $-PH_2$ groups, and, likewise, the structures of phenol and phenylthiol are different with respect to the orientation of the −OH and −SH groups. While this fact has been noted elsewhere,[18] for the sake of the work presented here, it is important to note this results in $C_6H_5NH_2$ and $C_6H_5PH_2$, and in C_6H_5OH and C_6H_5SH, having dipole moments with very different directions. In all four cases, the dipole moment is far from being along the C_{para}−H and C_{ipso} bonds. For aniline, the negative end of the molecular dipole moment is very near the π region, and placing the Na^+ at this position does not give a cation−dipole complex but instead gives the cation−π complex. For phenol, the negative end of the molecular dipole moment is between the ortho and meta carbon atoms, and this too would obviously not be a likely place to find a cation−dipole complex. Thus for aniline and phenol, we placed the cation near the nitrogen or oxygen lone pair(s) in order to determine the binding energy of the most likely cation−π complex competitor. It is reasonable to still consider this a cation−dipole complex as the Na^+ interacts with a local dipole rather than with the molecular dipole.

Optimizations that led to cation−π complexes are termed Pi in Table 1 and optimizations that led to cation−dipole complexes are denoted dipole. When the optimization of the Na^+−arene complexes were started with the cation over the π cloud, the resulting minima corresponded to the cation−π complex in all cases except for nitrobenzene, where the cation moved to the negative end of the molecular dipole. In contrast,

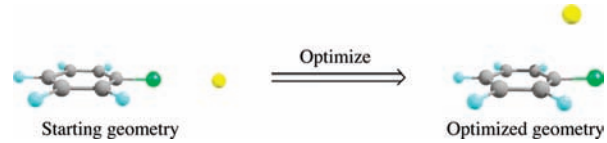


Figure 3. MP2(full)/6-311G** optimization of Na^+−C_6H_5Cl complex where Na^+ starts at the negative end of the molecular dipole moment. (Na: yellow. Cl: green. C: gray. H: blue.)

TABLE 2: ΔE_0 Cation Binding Energies of Na^+−C_6H_5X Complexes Determined by Holding the Aromatic Constant and Varying the Distance between the Na^+ and the Negative End of the Dipole or the π Cloud

C_6H_5X, X =	structure[a]	ΔE_0 (kcal/mol)
Cl	dipole	−9.24
Br	dipole	−8.35
I	dipole	−5.67
CH_3	dipole	−3.49
SiH_3	dipole	−6.32
NO_2	Pi	−11.47

[a] Structures labeled "dipole" varied the distance between the Na^+ and the negative end of the molecular dipole moment. The structure labeled "Pi" varied the distance between the Na^+ and the center of the π cloud.

when the cation started at the negative end of the dipole moment, there were five cases where optimization did not lead to the cation−dipole complex. The optimizations of chloro-, bromo-, and iodobenzene, where the Na^+ started at the negative end of the molecular dipole moment, finished with the cation directly above the C_{ipso} carbon (shown in Figure 3 for the Na^+−chlorobenzene complex). For toluene and phenylsilane, the optimizations where Na^+ started at the negative end of the molecular dipole moment finished with the cation directly above the aromatic π cloud, the cation−π complex.

Table 2 shows the cation−dipole ΔE_0 Na^+ binding energies for chloro-, bromo-, and iodobenzene, toluene, and phenylsilane, along with the cation−π ΔE_0 binding energy for nitrobenzene. As described above, we calculated these values by holding the aromatic constant and varying the distance between the Na^+ and the molecular dipole moment, for the cation−dipole complexes, or the aromatic π cloud, for the cation−π complex. These calculations were performed only for the aromatics that did not have cation−dipole or cation−π PES minima, and we use them here to compare cation−dipole and cation−π binding energies. If both the cation−dipole and the cation−π complexes

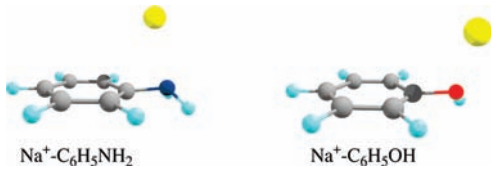


Figure 4. MP2(full)/6-311G** optimized structures of Na^+ binding to the lone pair of aniline and phenol. (Na: yellow. N: dark blue. O: red. C: gray. H: light blue.)

are minima on the MP2(full)/6-311G** PES, then we compare the ΔH_{298} value in Table 1. If either complex is not a PES minimum, then we will compare the ΔE_0 value of the PES minimum in Table 1 with the ΔE_0 value of the constrained complex in Table 2. For instance, in comparing the cation−dipole and cation−π binding energies of chlorobenzene, we use the optimized cation−π complex in Table 1 and the constrained cation−dipole complex in Table 2.

For the seven C_{2v} symmetric aromatics (**1**−**7**), the negative end of the dipole moment is at the substituent. Of these, the cation−dipole complex is slightly more stable than the cation−π complex for fluorobenzene, by 0.98 kcal/mol on the ΔH_{298} PES, and it is significantly more stable for cyano- and nitrobenzene, by 19.26 kcal/mol on the ΔH_{298} PES and 19.56 kcal/mol on the ΔE_0 PES, respectively. For the Cl-, Br-, and I-substituted benzenes, the cation−π complex is more stable by 8.65, 9.96, and 14.16 kcal/mol on the ΔE_0 PES, and for phenylborane, the cation−π complex is 2.95 kcal/mol more stable on the ΔH_{298} PES. Only for the $Na^+-C_6H_5BH_2$ complex is the cation−dipole complex even a minimum on the PES. The $Na^+-C_6H_5X$ (X = Cl, Br, I) complexes do have a second minimum; when the optimization of these complexes began with the cation at the negative end of the C_6H_5X dipole moment, the optimized structure has the Na^+ above the C_{ipso} position. Still, the cation−π complex is more stable than these complexes by 2.11, 0.87, and 1.15 kcal/mol for C_6H_5Cl, C_6H_5Br, and C_6H_5I on the ΔH_{298} PES.

The cation−dipole complexes for toluene and phenylsilane are not minima on the MP2(full)/6-311G** PES. Calculating the cation−dipole binding energies as described in Figure 1 shows the cation−π complex is more stable than the cation−dipole complex by 20.13 kcal/mol for toluene and 15.21 kcal/mol for phenylsilane on the ΔE_0 PES. The MP2(full)/6-311G** optimized Na^+-lone pair, or cation-local dipole, complexes for $C_6H_5NH_2$ and C_6H_5OH are shown in Figure 4, and they are both PES minima.[19] This complex is 4.80 kcal/mol more stable than the cation−π complex for aniline, and for phenol, it is 4.65 kcal/mol more stable than the cation−π complex. The negative end of the molecular dipole moment for phenylphosphine is at the phosphorus lone pair (Figure 2), and optimizing the Na^+ complex with the cation at this position leads to a cation−dipole complex that is a PES minima. Still, the cation−π complex is more stable by 1.61 kcal/mol. The negative end of the dipole moment for phenylthiol is also at the heteroatom lone pair, and optimizing the cation at this position gives a minimum on the $Na^+-C_6H_5SH$ PES. However, as was the case for phenylphosphine, the cation−π complex is more stable by 1.06 kcal/mol. Thus, for toluene and phenylsilane, the cation−π complex is significantly more stable than the cation−dipole complex; for aniline and phenol, the cation−dipole complex is slightly more stable, and for phenylphosphine and phenylthiol, the cation−π complex is slightly more stable.

Our Na^+−phenol and Na^+−aniline results conform to previous experimental work on these complexes. Lisy has investigated Na^+•phenol•$(H_2O)_n$ clusters via gas-phase infrared spectroscopy and molecular orbital theory and found phenol preferentially binds Na^+ at the lone pair, the cation−dipole complex, rather than at the π cloud, the cation−π complex.[20] Our results, with the cation−dipole complex being more stable than the cation−π complex, support this view. Rodgers investigated the Na^+ complexes of *N*-methylaniline and *N*,*N*-dimethylaniline using mass spectrometry and molecular orbital theory and, in both cases, found the cation−π complex was more stable than the cation−dipole complex.[19] The cation−π complex was preferred by 2.3 kcal/mol for *N*,*N*-dimethylaniline and 1.2 kcal/mol for *N*-methylaniline on the ΔE_0 PES at the MP2(full)/6-311+G(2d,2p)//B3LYP/6-31G* level of theory. We find the cation dipole complex is 4.99 kcal/mol more stable than the cation−π complex for Na^+−aniline on the ΔE_0 PES, and this fits the general trend of the cation−dipole complex increasing in favor with decreasing *N*-methylation, although the magnitude is somewhat larger than might be expected.

Conclusions

Kebarle[13] and Lisy[14] demonstrated that the cation−π complex between K^+ and benzene is as strong as the cation−dipole complex between K^+ and water. Here, we showed that in dipolar monosubstituted aromatics Na^+ generally prefers to bind to the aromatic π cloud over the negative end of the dipole moment. Of the 13 aromatics studied, only cyano- and nitrobenzene have cation−dipole complexes that are significantly more stable than their respective cation−π complex, by over 19 kcal/mol. The cation−dipole complexes of fluorobenzene, aniline, and phenol are slightly more stable than the cation−π complexes, by between 1 and 5 kcal/mol. The remaining eight aromatics all have cation−π complexes that are more stable than their respective cation−dipole complex. For phenylborane, phenylphosphine, and phenylthiol, the cation−π complex is slightly more stable than the cation−dipole complex, by between 1 and 3 kcal/mol. Chlorobenzene, bromobenzene, iodobenzene, toluene, and phenylsilane all have cation−π complexes that are more stable than the cation−dipole complexes by between 8 and 21 kcal/mol. Another important point is that, while the cation−π complex is a minimum on the cation binding PES of every aromatic except nitrobenzene, the cation−dipole complex is not a PES minimum for toluene, phenylsilane, chloro-, bromo-, and iodobenzene. Thus, in the absence of highly electron-withdrawing substituents, the cation−π interaction is either highly competitive with, or dominant over, the cation−dipole interaction.

Acknowledgment. This work was partially supported by the National Center for Supercomputing Applications under CHE050039N and utilized the cobalt system.

Supporting Information Available: Computational data is available free of charge via the Internet at http://pubs.acs.org.

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JP902400H