Ab Initio Molecular Orbital Study of Cation−π Binding between the Alkali-Metal Cations and Benzene

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We present optimized geometries and binding energies for alkali-metal cation complexes with benzene. Results are obtained for Li^+ through Cs^+ at the RHF/6-311G* and MP2/6-311+G* levels of theory with K^+, Rb^+, and Cs^+ represented by relativistic ECPs and associated valence basis sets. RHF/6-311G* frequencies are used to verify the optimized geometries are minima and used to calculate binding enthalpies. The effects of basis-set superposition error (BSSE) are estimated at both the RHF and MP2 levels. We obtain BSSE-corrected MP2/6-311+G* binding enthalpies (in kcal/mol) of 35.0 (Li^+), 21.0 (Na^+), 16.0 (K^+), 13.3 (Rb^+), and 11.6 (Cs^+). The distances (Å) between the center of the benzene ring and the cation are 1.865 (Li^+), 2.426 (Na^+), 2.894 (K^+), 3.165 (Rb^+), and 3.414 (Cs^+). Additional single-point CCSD(T)/6-311+G*//MP2/6-311+G* and CCSD(T)/6-311+G(2d,2p)//MP2/6-311+G* calculations indicate that the MP2/6-311+G* results are well converged with regard the extent of electron correlation, whereas small changes in binding energy are still observed when larger basis sets are used. Additional calculations using local and nonlocal density functional theory are included for comparison.

Introduction

An important breakthrough in the understanding of molecular recognition was the realization of the significance of cation−π interactions.[1,2] Experimental evidence of such interactions between the alkali cations and arenes was reported some years ago.[3−6] However, it is only recently that the importance of these interactions has been widely appreciated.[7] A particularly noteworthy aspect of cation−π interactions is that their strength is several times greater than other interactions commonly involved in molecular recognition, such as hydrogen bonding and dispersive (van der Waals) attractions, due to the full positive charge on the cation. Thus, π systems offer binding sites that are strong enough to compete with the more traditionally viewed coordinating groups, such as amines, alcohols, and ethers. Although cation−π interactions are often associated with biological systems, they also have been observed in the coordination chemistry of the alkali cations.[8]

Our interest in cation−π binding stems from our efforts to design ligands that selectively bind radioactive elements, e.g., ^{137}Cs, and thus remove them from waste streams. In particular, our research is focused on the development and application of molecular mechanics force field methods in the rational design of new separation agents.[9−12] One family of compounds that show great promise as separation agents are the calixarenes, which are able to bind cations inside a cavity formed from aromatic rings.[8,13,14] Key to our ability to rationally design new ligands is a thorough understanding of the interactions of the cations with the π electrons present in these systems. Force-field parametrization requires the energetics and structures of the complexes that form between aromatic systems and the alkali-metal cations.

As a first step toward modeling the cation−π interactions in calixarenes, we chose to study the binding of the alkali-metal cations to benzene. Prior theoretical studies of alkali-metal binding to benzene have been limited; the levels of theory used have not been extensive enough to quantify the basis set and correlation requirements needed to obtain accurate values of the gas-phase binding geometries and energies. In addition, prior studies have not included cesium, and thus a complete set of results for the entire series of alkali metals has not been reported. In this paper we present a comprehensive ab initio molecular orbital and density functional theory (DFT) study of cation−π bonding between the alkali-metal cations and benzene. The geometries and binding energies are obtained at the RHF/6-311G* and MP2/6-311+G* levels of theory. Data from additional DFT calculations done at the SVWN/TZ94p and BP86/TZ94p levels are included for comparison. Frequency calculations are used to determine zero-point and vibration energies and, thus, the binding enthalpies and entropies. The effects of the incomplete basis set (basis-set superposition error (BSSE)) is investigated at both the RHF and MP2 levels. The importance of higher order correlation and more flexible basis sets is also presented. We find that the use of higher levels of theory leads to quantitatively different results than those obtained in previous studies.

Prior Molecular Orbital Calculations. One of the earliest theoretical studies of alkali metal−benzene interactions reported RHF/STO-3G calculations of Na^+−benzene complexes.[6] That study examined several possible geometries of the Na^+−benzene complex, concluding that the C_{6v} conformation in which the Na^+ interacts with the center of the π-electron cloud was the most stable. They also presented an electrostatic calculation showing why Na^+ lies on the 6-fold axis of benzene. Kumpf and Dougherty[2] report the interaction energies of benzene complexed with Li^+ through Rb^+ at the RHF (restricted Hartree−Fock) level with the 6-31G** basis set on C and H and STO-3G on the cations. The interaction of Na^+ with benzene was recalculated by Mecozzi, West, and Dougherty at the RHF/6-31G** and MP2/6-31G**//RHF/6-31G** levels of theory.[15]

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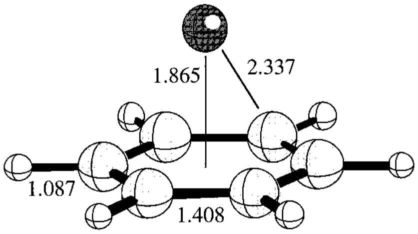

Figure 1. MP2/6-311+G* optimized geometry of the Li^+−benzene complex. Selected distances in Å.

In that study the authors concluded the BSSE was small, as were zero-point and thermal corrections to the binding energies. MP2/6-31G* geometries and binding energies for Li^+, Na^+, and K^+ binding to benzene have also been reported by Caldwell and Kollman.[16] These authors were particularly interested in modeling cation−π interactions with a classical force field and indicated that nonadditive (polarization) effects were needed in order to reproduce the quantum mechanical (and experimental) data. This observation is consistent with the results of Sunner et al. who showed the importance of the quadrupole moment of benzene in calculating the electrostatic interaction correctly.[6]

Theoretical Details

The geometries of benzene and the alkali metal−benzene complexes were initially optimized at the restricted Hartree−Fock (RHF) level. The 6-311G* basis set was used for H, C, Li, and Na. The valence basis sets and effective core potentials (ECPs) of Hay and Wadt were used for K, Rb, and Cs.[17] The Hay−Wadt valence basis sets are a (5s5p)/[3s2p] contraction to which we added the energy-optimized polarization (d) functions suggested by Glendening and co-workers.[18] The exponents of these functions are 0.48 for K, 0.24 for Rb, and 0.19 for Cs. The Hay−Wadt formalism treats the $(n - 1)$ shell of core electrons explicitly while representing the rest of the core by the ECP. Relativistic (mass−velocity and Darwin) corrections are included in the Rb and Cs ECPs. For simplicity, we term this level of theory RHF/6-311G*. We assumed D_{6h} symmetry for benzene and C_{6v} symmetry for the cation−benzene complexes (Figure 1). The raw binding energy (ΔE_e) was determined from the difference between the total energy of the complexes and the sum of the total energies of the corresponding isolated cations and benzene. Estimates of the basis-set superposition error in the binding energy were obtained at the RHF/6-311G* level of theory using the counterpoise correction method.[19]

Frequency calculations were done at the RHF/6-311G* level to verify that the geometries were minima on the potential-energy surface and to obtain the zero-point (ΔE_{ZPE}) and thermal energy corrections ($\Delta E_{Thermal}$) needed for the calculation of enthalpies. The RHF/6-311G* frequencies were scaled[20] by 0.893 to approximately account for the effects of correlation and anharmonicity. Binding enthalpies were then calculated as follows: $\Delta H = \Delta E_e + \Delta E_{ZPE} + \Delta E_{Thermal} + \Delta(PV)$, where $\Delta(PV) = nRT = -0.593$ kcal/mol at 298.15 K and ΔE_e includes the BSSE correction. The translational energy of the cation is $^3/_2RT$. The enthalpies were calculated at temperatures that correspond to the conditions under which experimental data, with which we compare, were obtained. Entropies were also obtained using the RHF/6-311G* frequency calculations.

Starting from the RHF/6-311G* geometries and force constants, we then reoptimized benzene and the complexes using second-order Møller Plesset perturbation theory (MP2).[21] The MP2 optimizations used the 6-311+G* basis set on H, C, Li, and Na. The valence basis sets and associated ECPs described above were used for K, Rb, and Cs. We term this level of theory MP2/6-311+G*. The frozen-core calculations excluded the electrons in the C 1s, and Na 1s, 2s, and 2p shells from the correlation treatment. Glendening and co-workers[18] found that failure to include the $(n - 1)$ electron shell of the metal can give poor geometries and binding energies for cation−water complexes. We did not find this to be a significant problem in the calculation of cation−benzene interactions, as an optimization of the Na^+−benzene complex including all electrons gave a geometry and binding energy similar to a frozen-core calculation (see below). Counterpoise corrections were also obtained at the MP2/6-311+G* level of theory. There is some evidence that counterpoise corrections overestimate the BSSE, leading to underestimation of binding energies. This issue is explored in detail for the Li^+−benzene complex (see below). Predictions of the binding enthalpies were calculated as noted above from the BSSE-corrected MP2/6-311+G* binding energies and the scaled RHF/6-311G* thermodynamic data.

To test the effect that a more complete basis set and a more extensive treatment of electron correlation would have on the results, the binding energy was also calculated at the CCSD(T)/6-311+G*, CCSD(T)/6-311+G(2d,2p), and MP2/aug-cc-pVTZ[22,23] levels for the Li^+ complex, using the MP2/6-311+G* geometries.[24] We report the MP2, MP3, MP4, and CCSD energies obtained from the CCSD(T) calculations as well. We used Gaussian94 for all the calculations.[25]

Density functional theory has been shown to be a useful method for obtaining energetic and structural information about a variety of chemical systems.[26−30] Nonlocal DFT has been shown to reliably reproduce the energetics of the group IIB dication complexes with water clusters[31] as compared to MP2 results.[32] The DFT calculations were done as follows. Geometries were optimized and frequencies calculated[33] at the local (Slater exchange and Vosko−Wilk−Nusair correlation,[34] SVWN) and nonlocal (Becke exchange[35−37] and Perdew correlation,[38] BP86) levels for the separated atomic ions and benzene and for the complexes (no symmetry was used). We initially used a polarized triple-ζ basis set (TZ94p)[39] on all atoms except Cs, which was represented by a pseudopotential. These calculations were performed with the program DGauss.[40−43] Surprisingly, the optimizations using the Rb TZ94p basis set and Cs pseudopotential gave binding distances that were much too short. We thus reoptimized these complexes using the Hay−Wadt ECPs and basis sets (described above) on Rb and Cs. We report only these results. The Rb and Cs optimizations were done with Gaussian94.

Results and Discussion

Geometries. The predicted M^+−C, M^+−centroid, and C−C distances are reported in Tables 1−4 (RHF, MP2, SVWN, and BP86). As expected, the M^+−C and M^+−centroid distances exhibit a steady increase as the size of the cation increases. At the RHF/6-311G* level, the M^+−centroid distance in the Li^+ complex is 1.892 Å, expanding to 3.605 Å in the Cs^+ complex. The M^+−centroid distances become shorter when the effects of electron correlation are included. This difference becomes greater as the cation size increases. At the MP2/6-311+G* level, the Li^+−centroid distance is 0.027 Å shorter than the RHF value whereas the Cs^+−centroid distance is 0.191 Å shorter.

The M^+−centroid distance at the SVWN/TZ94p level range from 1.805 Å for Li^+ to 3.308 Å for Cs^+. The M^+−centroid distances are longer at the BP86/TZ94p level, ranging from 1.879 Å for Li^+ to 3.498 Å for Cs^+. The BP86/TZ94p values

TABLE 1: RHF/6-311G* Optimized C−C Bond Distances (Å), C−H Out-of-Plane Angle (deg), M$^+$−C and M$^+$−Centroid Distances (Å), M$^+$ Partial Charges (|*e*|), Energies and Enthalpies (kcal/mol), and Entropies (cal/mol K) for the Benzene−Cation Complexes[a]

cation	C−C[b]	C−H (OOP)	M$^+$−C	M$^+$−centroid	q(M$^+$)	ΔE_{BSSE}	ΔE_{e}	ΔE_{ZPE}	ΔH_0	ΔS	ΔH_{T}	ΔH_{Exp}
Li$^+$	1.394	0.43	2.350	1.892	0.634	1.06	−38.7	1.68	−37.0	−25.16	−37.7	−37.9[c]
Na$^+$	1.392	1.73	2.840	2.475	0.839	1.12	−23.5	0.85	−22.7	−22.35	−22.7	−28.0[d]
K$^+$	1.390	1.88	3.299	2.992	0.975	0.34	−14.8	0.62	−14.2	−20.56	−14.1	−18.3[c]
Rb$^+$	1.389	1.89	3.568	3.286	0.976	0.30	−12.2	0.53	−11.6	−20.04	−11.6	
Cs$^+$	1.388	1.87	3.820	3.605	0.980	0.26	−10.1	0.48	−9.6	−19.40	−9.6	

[a] Frequency data were scaled by 0.893. Enthalpies and entropies calculated at 298.15 (Li$^+$, Rb$^+$, and Cs$^+$), 500 (K$^+$), and 610 K (Na$^+$). Experimental binding enthalpies are included for comparison. [b] RHF/6-311G* C−C bond length in benzene is 1.386 Å. [c] Reference 46. [d] Reference 48. [e] Reference 6.

TABLE 2: MP2/6-311+G* Optimized C−C Bond Distances (Å), C−H Out-of-Plane Angle (deg), M$^+$−C and M$^+$−Centroid Distances (Å), M$^+$ Partial Charges (|*e*|), and Energies and Enthalpies (kcal/mol) for the Benzene−Cation Complexes[a]

cation	C−C[b]	C−H (OOP)	M$^+$−C	M$^+$−centroid	q(M$^+$)	ΔE_{BSSE}	ΔE_{e}	ΔH_0	ΔH_{T}	ΔH_{Exp}[c]
Li$^+$	1.408	0.52	2.337	1.865	0.496	4.17	−36.0	−34.3	−35.0	−37.9[c]
Na$^+$	1.406	1.87	2.804	2.426	0.806	3.04	−21.9	−21.0	−21.0	−28.0
Na$^+$ (Full)	1.405	1.76	2.777	2.396	0.797	3.74	−22.5	−21.6	−21.6	−28.0
K$^+$	1.404	2.52	3.217	2.894	0.979	1.79	−16.7	−16.1	−16.0	−18.3
Rb$^+$	1.404	2.51	3.462	3.165	0.976	1.98	−13.9	−13.3	−13.3	
Cs$^+$	1.403	2.41	3.691	3.414	0.974	2.11	−12.1	−11.6	−11.6	

[a] Enthalpies calculated at 298.15 (Li$^+$, Rb$^+$, and Cs$^+$), 500 (K$^+$), and 610 K (Na$^+$) from the RHF frequency data. Experimental binding enthalpies are included for comparison. All values are obtained from frozen-core calculations, with additional data reported for an all-electron (full) MP2 calculation of the Na$^+$ complex. [b] MP2/6-311+G* C−C bond length in benzene is 1.400 Å. [c] See footnotes in Table 1.

TABLE 3: SVWN Optimized C−C Bond Distances (Å), C−H Out-of-Plane Angle (deg), M$^+$−C and M$^+$−Centroid Distances (Å), M$^+$ Partial Charges (|*e*|), and Energies and Enthalpies (kcal/mol) for the Benzene−Cation Complexes[a]

cation	C−C[b]	C−H (OOP)	M$^+$−C	M$^+$−centroid	q(M$^+$)	ΔE_{e}	ΔE_{ZPE}	ΔH_0	ΔS	ΔH_T	ΔH_{Exp}[c]
Li$^+$	1.402[b]	0.6	2.286	1.805	0.869	−40.1	1.95	−38.1	−29.25	−39.0	−37.9
Na$^+$	1.401[b]	1.5	2.693	2.301	1.077	−27.4	0.93	−26.4	−26.29	−26.8	−28.0
K$^+$	1.398[b]	1.9	3.102	2.769	1.043	−19.1	0.75	−18.3	−24.94	−18.5	−18.3
Rb$^+$	1.392[d]	2.2	3.349	3.046	0.979	−16.3	0.59	−15.7	−22.06	−15.9	
Cs$^+$	1.391[d]	2.2	3.588	3.308	0.987	−14.1	0.54	−13.6	−21.22	−13.6	

[a] Enthalpies calculated at 298.15 (Li$^+$, Rb$^+$, and Cs$^+$), 500 (K$^+$), and 610 K (Na$^+$) from the SVWN frequency data. Experimental binding enthalpies are included for comparison. [b] C−C bond length in benzene is 1.394 Å. [c] See footnotes in Table 1. [d] C−C bond length in benzene is 1.388 Å.

TABLE 4: BP86 Optimized C−C Bond Distances (Å), C−H Out-of-Plane Angle (deg), M$^+$−C and M$^+$−Centroid Distances (Å), M$^+$ Partial Charges (|*e*|), and Energies and Enthalpies (kcal/mol) for the Benzene−Cation Complexes

cation	C−C	C−H (OOP)	M$^+$−C	M$^+$−centroid	q(M$^+$)	ΔE_{e}	ΔE_{ZPE}	ΔH_0	ΔS	ΔH_T	ΔH_{Exp}[c]
Li$^+$	1.415[b]	0.3	2.352	1.879	0.898	−34.5	1.56	−33.0	−27.92	−33.6	−37.9
Na$^+$	1.413[b]	1.0	2.803	2.421	1.040	−21.6	0.81	−20.8	−24.83	−21.0	−28.0
K$^+$	1.411[b]	2.1	3.290	2.972	1.010	−13.5	0.54	−13.0	−21.61	−13.0	−18.3
Rb$^+$	1.405[d]	2.1	3.520	3.228	0.970	−11.5	0.55	−11.0	−20.44	−11.0	
Cs$^+$	1.404[d]	2.2	3.770	3.498	0.976	−9.5	0.52	−9.0	−19.85	−9.0	

[a] Enthalpies calculated at 298.15 (Li$^+$, Rb$^+$, and Cs$^+$), 500 (K$^+$), and 610 K (Na$^+$) from the BP86 frequency data. Experimental binding enthalpies are included for comparison. [b] C−C bond length in benzene is 1.407 Å. [c] See footnotes in Table 1. [d] C−C bond length in benzene is 1.401 Å.

are similar to the MP2 values, differing by 0.014 Å for Li$^+$, −0.005 Å for Na$^+$, +0.078 Å for K$^+$, +0.063 Å for Rb$^+$, and +0.084 Å for Cs$^+$.

Previous predictions of the M$^+$−centroid distances come from the RHF calculations by Dougherty, which used the 6-31G* basis set on H and C and STO-3G on the alkali metal.[2] Dougherty's M$^+$−centroid distances of 1.96 (Li$^+$), 2.41 (Na$^+$), 2.88 (K$^+$), and 2.96 Å (Rb$^+$) can be compared to our RHF/6-311G* values of 1.89, 2.48, 2.99, and 3.29 Å for the same atoms. Although both levels of theory give the same trend, differences as large 0.3 Å are apparent.

Predictions of the M$^+$−centroid distances also were reported at the MP2/6-31G* level by Kollman.[16] The M$^+$−centroid distances of 1.90 (Li$^+$), 2.42 (Na$^+$), and 2.85 Å (K$^+$) compare to our MP2/6-311G* values of 1.87, 2.43, and 2.89 Å for the same atoms. In this case, the agreement between the MP2 calculations with two different basis sets is quite close, the largest difference being 0.05 Å.

As previously observed, complexation of an alkali cation to benzene results in longer C−C bond lengths.[6] For isolated benzene at the RHF/6-311G* level, we obtain a C−C bond distance of 1.386 Å. When the cations bind to benzene, the C−C bond length is slightly increased, consistent with donation of electron density from the ring to the cation. The most notable effect is seen in the Li$^+$ complex, in which the C−C bond length is increased by 0.008 Å. The lengthening of the C−C bond is less pronounced as the size of the cation increases; the C−C bond lengthening is 0.006 Å in the Na$^+$ complex but only 0.002 Å in the Cs$^+$ complex. At the MP2/6-311+G* level, correlation lengthens the C−C bond distance in benzene to 1.400 Å, 0.015 Å longer than predicted at RHF/6-311G*. The C−C bonds in the metal complexes show a lengthening similar to that obtained at the RHF/6-311G* level. The BP86/TZ94p calculations show a similar C−C bond lengthening with Li$^+$ complex lengthening by 0.008 Å, decreasing to 0.003 Å for Cs$^+$. Previous studies have not reported C−C bond lengths, so we can make no comparisons.

In all cases, the presence of the cation results in the hydrogens bending out of the plane of the benzene carbons, away from the cation. The out-of-plane (OOP) angles from the RHF-6-311G* optimizations range from 0.4° for Li^+ to 1.9° for Rb^+. The OOP angles generally increase as we move down the periodic table, but as shown in Table 1, the trend is not exact. Similarly, the OOP angles range from 0.5° for Li^+ to 2.5° for Rb^+ at the MP2/6-311+G* level and 0.3° for Li^+ to 2.2° for Cs^+ at the BP86/TZ94p level. The fact that the OOP angles increase with increasing M−centroid distance and decreasing change in the benzene C−C distances is somewhat surprising. A possible explanation for this behavior is that the smaller cations are effectively screened by the negative charge of the π-electron cloud and, thus, do not interact strongly with the hydrogens. As the M^+−centroid distance increases, the positive charge may be less effectively screened by the π-electrons, leading to an increasingly repulsive interaction with the hydrogens, forcing the hydrogens further out of plane.

Binding Energies. Energetic data are also presented in Tables 1−4. We first consider binding energies corrected for BSSE (ΔE_e). The RHF/6-311G* binding energies are strongly dependent on the size of the cation, ranging from −38.7 kcal/mol for Li^+ to −10.1 kcal/mol for Cs^+. The inclusion of correlation (MP2/6-311+G*) increases the predicted values of ΔE_e, with the difference between the RHF and MP2 binding energies increasing with cation size. Thus, whereas the MP2/6-311+G* ΔE_e for Li^+ is −36.0 kcal/mol, only 2.7 kcal/mol less than the RHF/6-311G* value, ΔE_e for Cs^+ is −12.1 kcal/mol, binding about 2 kcal/mol weaker than the RHF calculations indicate.

The SVWN/TZ94p values for ΔE_e are similar to the MP2 values. In contrast, the BP86/TZ94p calculations give the weakest binding of all the levels of theory. If we compare with the BSSE-corrected MP2 binding energies, the BP86/TZ94p calculations predict binding that is weaker by as much as 3.2 kcal/mol.

Previous calculations have not reported binding energies corrected for BSSE nor ZPE and thermal effects, thus we can only compare the raw energy values. At the RHF/6-31G*/STO-3G level, Dougherty obtained binding energies of −39.5 (Li^+), −24.4 (Na^+), −19.2 (K^+), and −15.8 kcal/mol (Rb^+).[2] Our RHF/6-311G* calculations for the same cations predict raw binding energies of −39.8, −24.6, −15.1, and −12.4 kcal/mol. Whereas the theoretical values are very similar for Li^+ and Na^+, our larger basis-set calculations with ECPs predict significantly weaker binding for K^+ and Rb^+. Dougherty later obtained a binding energy of −27.1 kcal/mol for the Na^+−benzene complex at the RHF level using the 6-31G* basis set on all atoms.[15]

The MP2/6-31G* calculations from Kollman predict ΔE_e values of −43.8 (Li^+), −29.5 (Na^+), and −15.0 kcal/mol (K^+).[16] Our MP2/6-311+G* calculations for the same cations give raw energies of −40.2, −24.9, and −18.5 kcal/mol. Our values differ from Kollman's by as much as 4 kcal/mol.

As expected, the BSSE corrections are less at the RHF level than for the MP2 calculations, despite the increase in the basis-set size. As expected, ΔE_{BSSE} is larger for the Li^+ and Na^+ complexes, in which the M^+−C distance is shorter, and the ECP is not used to represent the core electrons of the cation. The BSSE corrections at the RHF/6-311G* level range from 0.26 to 1.12 kcal/mol, as much as 5% of the value of the corresponding binding energies. The MP2 ΔE_{BSSE} values are more significant, varying from 4.17 to 1.79 kcal/mol. Thus, BSSE corrections can be as large as 15% of the raw binding energies at the MP2/6-311+G* level of theory. We have not included BSSE corrections at the DFT results because such corrections are usually smaller at this level of theory.[43]

TABLE 5: ΔE_e for Li^+−Benzene at the CCSD(T)/6-311+G* and CCSD(T)/6-311+G(2d,2p) Levels[a]

	basis set		
	6-311+G*		6-311+G(2d,2p)[b]
correlation	ΔE_0	ΔE_{BSSE}	ΔE_0
MP2	−40.17	4.17	−37.06
MP3	−40.50	3.91	−37.62
MP4(d)	−40.24	3.99	−37.28
MP4(dq)	−40.20	3.66	−37.60
MP4(sdq)	−40.04	3.56	−37.56
CCSD	−39.88	3.55	−37.45
CCSD(T)	−39.95	4.01	−37.11

[a] ΔE_{BSSE} calculated at the CCSD(T)/6-311+G* and MP2/6-311+G(2d,2p) levels only. All energies in kcal/mol. [b] ΔE_{BSSE} at MP2/6-311+G(2d,2p) = 1.62 kcal/mol.

TABLE 6: Low-Lying Vibrational Frequencies (cm^{-1}) of M^+−Benzene Complexes Calculated at the RHF/6-311G*, SVNW/TZ94p, and BP86/TZ94p Levels

	e mode			a mode		
cation	RHF	SVWN	BP86	RHF	SVWN	BP86
Li^+	280	319	248	381	450	357
Na^+	123	126	99	185	217	182
K^+	94	98	58	125	151	94
Rb^+	80	94	73	90	110	86
Cs^+	74	88	70	75	93	72

The ΔE_{ZPE} and $\Delta E_{Thermal}$ values are comparable to ΔE_{BSSE}. These contributions to the enthalpy are largest for the Li^+ complex (a total of 1.01 kcal/mol), decreasing to 0.49 kcal/mol for the Cs^+ complex. Considering BSSE, zero-point, and thermal corrections, we predict binding enthalpies that range from −37.7 (Li^+) to −9.6 kcal/mol (Cs^+) at the RHF level. At the MP2 level, the predicted values of ΔH range from −35.0 for the Li^+ complex to −11.6 kcal/mol for the Cs^+ complex. Note that the differences between the RHF and MP2 values of ΔH are not constant across the series of cations. Thus, while the MP2/6-311+G* ΔH for Li^+ is less than that obtained at the RHF/6-311G* level, the reverse is true for Cs^+.

At the BP86/TZ94p level, the binding enthalpies range from −33.6 for Li^+ to −9.0 kcal/mol for Cs^+. The BP86/TZ94p binding enthalpies are in fair agreement with the MP2 values; the largest discrepancy of 3.0 kcal/mol occurs with K^+. The SVWN/TZ94p enthalpies are the largest of all the calculated values, with the value for Na being 5.2 kcal/mol greater than the MP2 prediction.

Frequencies and Estimated Binding Entropies. The M^+−benzene complexes exhibit three low-frequency modes corresponding to the motion of the cation: a degenerate bend parallel to the benzene plane and a stretch away from the benzene plane. The RHF/6-311G* and DFT frequencies of these modes are given in Table 6. The symmetric stretch of the cation from the benzene plane is generally higher than the degenerate mode, although the values converge to a similar value with increasing atomic number. This is consistent with the lengthening of the M^+−centroid distance, suggesting that the interaction of the benzene with the cation is less directed for the heavier cations.

Predicted values for the entropy of the cations, benzene, and the M^+−benzene complexes were obtained at the RHF/6-311G*, SVWN/TZ94p, and BP86/TZ94p levels of theory. The entropies were needed in order to make an accurate comparison of our calculated enthalpies with experimental values. The calculated entropies for benzene (64.46 (RHF), 64.56 (SVWN), and 64.49 cal/mol K (BP86) at 298.15 K) are in excellent agreement with the experimental value (64.36 cal/mol K[44]). The agreement is not unexpected considering that the entropy of benzene is dominated by the translational and rotational contributions. The entropies of the complexes are somewhat approximate, because we have used harmonic frequencies in the calculation of ΔS, whereas the low-frequency modes involving the cations are likely to be very anharmonic. The calculated change in entropy associated with cation binding is given in Table 1 (RHF) and Tables 3 and 4 (SVWN and BP86). At the RHF/6-311G* level, we obtain the following entropy changes: Li^+, −25.16 at 298.15 K; Na^+, −22.35 at 610 K; K^+, −20.56 at 500 K; Rb^+, −20.04 at 298.15 K; and Cs^+, −19.40 at 298.15 K.

Additional Calculations To Test Basis-Set and Correlation Convergence. As stated earlier, there is an indication that failure to correlate the 2*s* and 2*p* electrons in Na^+ can lead to poor geometries and binding energies for Na^+−water clusters.[18] To explore the accuracy of the standard frozen-core approximation used in Gaussian94, we also did the required optimizations and calculations of the BSSE for the Na^+−benzene complex using the 6-311+G* basis set and including all electrons in the MP2 treatment. The results, given in Table 2, show that in this case the frozen-core approximation does not lead to large errors. The difference in the C−C bond length is 0.0015 Å. The differences in the M^+−C and M^+−centroid distances are both ∼0.03 Å. Although the value of ΔE_e is more than 1 kcal/mol larger than the frozen-core calculation predicts, this effect is countered by an increase in ΔE_{BSSE}. Thus, the predicted value of ΔH is only 0.6 kcal/mol greater than the value obtained from the frozen-core calculation, about a 3% difference. These results are consistent with the DFT calculations where all electrons are correlated. However, it is possible that core correlation is more important for the heavier cations. [45] We leave this area for future investigation.

We also tested the effect of higher order correlation corrections on the binding energies. Thus, we did CCSD(T)/6-311+G* single-point calculations of the Li^+−benzene system using the MP2/6-311+G* geometries. The results, shown in Table 5, indicate little change in the value of ΔE_e as the correlation treatment becomes more complete. Particularly noteworthy is the difference between the MP2 and CCSD(T) values, which amounts to only 0.22 kcal/mol. The values of ΔE_{BSSE} are very similar for the different correlation treatments, ranging from 3.55 (CCSD(T)) to 4.17 kcal/mol (MP2).

To ensure that the basis set was adequate for the CCSD(T) calculation and to test the basis-set dependence of the MP2 results, we also obtained CCSD(T)/6-311+G(2d,2p) single point energies at the MP2/6-311+G* geometries. As before, there is no indication that a correlation treatment above MP2 is needed to describe these systems accurately; the MP2 and CCSD(T) predictions of ΔE_e differ by only 0.05 kcal/mol. For the more expensive 6-311+G(2d,2p) calculations, we only estimated the BSSE at the MP2 level, assuming, as was demonstrated with the 6-311+G* basis set, that ΔE_{BSSE} does not vary greatly with the extent of electron correlation. The predicted values of ΔE_e are all ∼3 kcal/mol less with the larger basis set, but there is also a decreased ΔE_{BSSE} (1.62 kcal/mol at MP2/6-311+G(2d,-2p) versus 4.17 kcal/mol at MP2/6-311+G*). Thus, the BSSE corrected values of ΔE_e are about 0.5 kcal/mol lower when the larger basis set is used.

Comparison with Experimental Data. Although there has been no direct measurement of ΔH for the formation of the Li^+−benzene complex, the determination of a ΔG value allows ΔH to be estimated from a calculated entropy. Woodin and Beauchamp report a ΔG_{298} value of −29.7 kcal/mol for Li^+−benzene formation.[46] This value was obtained by ion cyclotron resonance spectrometric measurements of equilibria for reactions involving the transfer of Li^+ from one base to another. The thermodynamic ladder is anchored by a value of −27.3 kcal/mol for Li^+−H_2O. There is some uncertainty associated with this value because it is based on an extrapolation of $Li(H_2O)_n$ ΔG_{298} values to $n = 1$. Recent data allow us to check the Li^+−H_2O value prior to estimating a ΔH_{298} value for Li^+−benzene.

Feller and co-workers have computed thermodynamic values for the formation of Li^+−H_2O at the MP4/complete basis-set extrapolation level.[47] They obtain $\Delta H_{298} = -34.0$ kcal/mol, $\Delta S_{298} = -22.63$ cal/mol-K, and $\Delta G_{298} = -27.3$ kcal/mol, confirming the Li^+−H_2O reference point.

We obtain values for ΔS_{298} of −25.16 (RHF) and −27.92 cal/mol K (BP86), which compare to the estimate of −27.52 cal/mol K used by Woodin and Beauchamp. Combining the experimental ΔG_{298} value of −29.7 kcal/mol with our RHF ΔS_{298} value of −25.16 cal/mol-K allows us to estimate a ΔH_{298} of −37.2 kcal/mol for the formation of the Li^+−benzene species. Use of the BP86 ΔS yields a ΔH_{298} of −38.0 kcal/mol. For comparison, Woodin and Beauchamp report a value for ΔH_{298} of −37.9 kcal/mol. At the MP2/6-311+G* level, we obtain a ΔH_{298} of −35.0 kcal/mol. Our best calculated value of ΔH_{298} for Li^+−benzene is −34.5 kcal/mol at the 6-311+G(2d,2p)/CCSD(t) level, using the reported BSSE correction of 1.62 kcal/mol. There is little difference between either of the these enthalpies. Both enthalpies are several kcal/mol below either of the estimated ΔH_{298} values derived from Woodin and Beauchamp's G_{298}. The values in best agreement with the experimental measurements are the RHF and SVWN results, which are probably the least reliable levels of theory, thus the disagreement between the experimental and theoretical binding enthalpy for Li^+ was explored at an even higher level of theory.

As noted earlier, counterpoise corrections may overestimate the BSSE. In particular, it has been found that calculations of binding energies at the MP2/aug-cc-pVTZ level give values closer to the complete basis-set limit if BSSE corrections are ignored.[47] Using the MP2/6-311+G* geometries, the binding energy calculated at the MP2 level, with the aug-cc-pVTZ basis set on C and Li and cc-pVTZ on H, is −37.1 kcal/mol. This leads to a ΔH of −36.1 kcal/mol, closer to the experimental value of −37.9 kcal/mol.

In addition, we can obtain a better estimate of the effects of core correlation, which might be underrepresented with the 6-311+G* basis set. We thus calculated the binding energy again using Dunning's cc-pVTZ basis set with core-valence functions added for C and Li. Single-point energies were obtained with both the frozen-core approximation and with all electrons included in the correlation treatment. The difference in binding energy between these two sets of calculations, −1.39 kcal/mol, can be taken as an estimate of core correlation effects. Including this correction in the MP2/aug-cc-pVTZ calculation of the enthalpy gives $\Delta H = -37.5$ kcal/mol, in near agreement with experiment. The cost of these calculations was quite large, prohibiting us from using the cc-pVTZ basis set with both diffuse and core−valence functions and from doing optimizations with the larger basis sets. We were also unable to do similar calculations for the rest of the alkali metals, due to computational cost and lack of similar basis sets for the heavier cations. However, it is possible that such costly calculations may be needed in order to obtain close agreement with experiment.

Castleman and co-workers report a Δ*H* value of −28.0 ± 1.5 kcal/mol and a Δ*S* value of −31.0 ± 3.0 cal/mol-K for the formation of Na^+−benzene.[48] These values were obtained from van't Hoff plots of equilibrium constants determined by high-pressure mass spectrometric measurements over a temperature range of 570−650 K. Therefore, we have corrected our calculated thermodynamic values to the average temperature (610 K) over this range for comparison with these data. At 610 K, we obtain a Δ*H* of −21.0 kcal/mol at the MP2/6-311+G* level and a Δ*S* of −22.35 cal/mol-K from the RHF/6-311G* frequencies. Our results suggest that the experimental value for Δ*S* is too high by 6−9 eu. The inclusion of anharmonicity in our calculations would further lower Δ*S*, not raise it.

Kebarle and co-workers report a Δ*H* value of −18.3 kcal/mol and a Δ*S* value of −22.4 cal/mol-K for the formation of K^+−benzene.[6] These values were obtained from van't Hoff plots of equilibrium constants determined by high-pressure mass spectrometric measurements over a temperature range of 400−600 K. Although previous theoretical papers have compared calculated results to an experimental Δ*H* value of −19.2 kcal/mol, which was reported in the same study, Kebarle and co-workers noted that experimental complications make this value too large and they provide the corrected Δ*H* value of −18.3 kcal/mol as an *upper limit* for the measurement. As with sodium, we have calculated thermodynamic values corresponding to the average temperature (500 K) over the experimental temperature range. We obtain a Δ*H* of −16.0 kcal/mol at the MP2/6-311+G* level and a Δ*S* of −20.04 cal/mol-K from the RHF/6-311G* frequencies.

Summary and Conclusion

We have presented an ab initio molecular orbital study of *π*-cation interactions between the alkali-metal cations and benzene. We find that all levels of theory indicate that binding energies become weaker as we move down the Periodic Table, consistent with previous studies. We also find that the relative energies predicted by the MP2 calculations differ from those calculated at the RHF level. Thus, some treatment of correlation is important for accurate predictions of the binding energies. However, the similarity between the MP2 and CCSD(T) results (and indeed, with all the higher order correlation methods presented) is small, and thus calculations at the MP2 level appear adequate. This result is consistent with previous studies of Li^+-(H_2O) binding energies. We also find that the energies have not fully converged with regard to basis-set size at the MP2/6-311+G* level, and even larger basis sets are needed to obtain limiting values. However, the energy difference between the 6-311+G* and 6-311+G(2d,2p) levels is not large when BSSE corrections are included. The BSSE is substantial at the MP2/6-311+G* level and should be taken into account. The binding energies at the local DFT level are larger than the MP2 values, with the largest percent difference found for Na^+. The SVWN/TZ94p binding energies for the three heavier cations are 15−20% larger than the MP2 values. At the BP96/TZ94p level, the binding energies are in good agreement with the MP2 values but are ∼20% too low for the heavier cations. These results suggest that with the basis sets used in these studies, the BP86 and SVWN methods are not yet giving quantitative agreement with the MP2 results. However, the BP86/TZ94p geometries are in reasonable agreement with the MP2 values, suggesting that DFT geometries might be used as starting points for the more expensive MP2 calculations. We generally predict binding enthalpies that are significantly lower than the experimental values. Considering the extensive test of theoretical methods we have presented, we feel that further experimental work may be needed to definitively establish absolute alkali metal−benzene binding energies. Our results prove that the interactions between the alkali-metal ions and benzene are indeed strong enough to compete with other coordinating donor groups such as amines, ethers, and alcohols. An important implication of this result is that the arene constituents present in calixarenes and other multidentate ligands may play a larger role in the coordination of cationic hosts than previously recognized. We intend to investigate this facet of cation recognition with force-field techniques. The geometries and interaction energies we obtained for the cation−benzene complexes are now being used for force-field parametrization.

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