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Anisole as an Ambidentate Ligand: Ab Initio Molecular Orbital Study of Alkali Metal Cations Binding to Anisole

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We present optimized geometries and binding energies for alkali metal cation complexes with anisole (methoxybenzene). 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 that the optimized geometries are minima and to calculate binding enthalpies. The effects of basis set superposition error (BSSE) are estimated at both the RHF and MP2 levels. We find that the alkali metals bind to anisole in two ways, either predominantly through interactions with the aromatic ring or with the ether oxygen. For binding to the ring, we obtain BSSE-corrected MP2/6-311+G* binding enthalpies (in kcal/mol) of −38.1 (Li^+), −23.6 (Na^+), −18.3 (K^+), −15.4 (Rb^+), and −13.6 (Cs^+). The average distances (in Å) between the ring carbons and the cations are 2.33 (Li^+), 2.79 (Na^+), 3.20 (K^+), 3.44 (Rb^+), and 3.70 (Cs^+). For binding to the ether oxygen, the BSSE-corrected MP2/6-311+G* binding enthalpies (in kcal/mol) are −37.6 (Li^+), −25.2 (Na^+), −19.4 (K^+), −16.4 (Rb^+), and −14.3 (Cs^+). The distances (in Å) between the ether oxygen and the cations are 1.82 (Li^+), 2.24 (Na^+), 2.62 (K^+), 2.87 (Rb^+), and 3.10 (Cs^+). Although the differences in binding energy between the two sites are small, the cations generally prefer to bind to the oxygen.

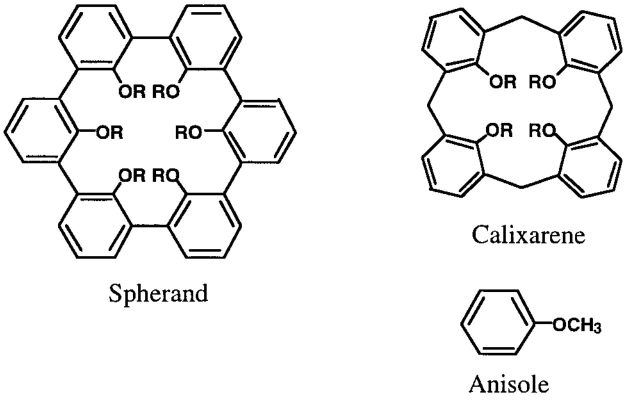
Introduction

The structural design of metal-selective ligands is a challenging endeavor.[1−7] The goal is to combine two or more donor groups to form a spatial array of binding sites that are both complementary and preorganized for the targeted metal ion. The ability to design an ideal multidentate binding cavity requires knowledge of how the metal ion interacts with individual donor groups. This information includes the preferred geometry at the metal center, the preferred metal−donor atom distance, and the preferred orientation of the donor group relative to the metal. The structural preferences for a specific metal ion−donor group can be incorporated into molecular mechanics models to provide a convenient tool for the analysis of ligand binding site organization.[8−12] Unfortunately, structural design criteria are not available for many ligand donor groups of interest. In the current paper, we focus on anisole as a ligand donor group for the alkali cations.

Anisole (methoxybenzene) represents a simple analogue of the main structural component found in calixarene and spherand macrocycles (Scheme 1). The prototype calixarene structure, a cyclic oligomer of phenol groups linked at the 2 and 6 positions by methylene spacers, has proven to be an attractive framework for the construction of new ligands.[13−16] The preparation of calixarene derivatives often involves the substitution of the phenol hydrogens to form ether linkages. Thus, the phenyl−O−CH_2X moiety is a ubiquitous subunit in calixarene derivatives. Although there have been extensive studies of the synthesis and ion-binding properties of these macrocycles,[17−19] the relationship between ligand structure and metal ion binding affinity remains obscure. This situation can be improved by first understanding how an analogue of the primary building block for these ligands, anisole, interacts with metal ions.

Prior theoretical studies of anisole metal complexes have been limited to the alkali and alkaline earth cations. To obtain geometries and potential energy surfaces for force field development, Hay et al.[20] performed RHF/STO-3G calculations on isolated anisole metal complexes in which the metal ion (Li^+−Rb^+, Mg^{2+}−Sr^{2+}) was coordinated to anisole through the oxygen atom. At this level of theory, with the M−O distances constrained to the average values observed in crystal structures, a minimum energy configuration was obtained in which the anisole was planar and the metal ion remained in the plane of the ligand. Force field parameters, M−O−C angles and M−O−C−C dihedral angle preferences, were assigned to favor this orientation. The resulting model well reproduces the structures of benzocrown ether complexes in which the alkoxy substituents maintain a planar orientation with respect to benzene.[20−22] However, as we will show herein, a planar geometry for oxygen-coordinated anisole is not obtained at higher levels of theory.

SCHEME 1



The anisole arene ring provides another potential site for metal ion complexation. Crystal structure data reveal the presence of bonding interactions between alkali cations and a variety of arene donors,[23] including the arene rings present in calixarenes.[24]

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Although there have been no prior theoretical studies of the interaction between the alkali cations and the anisole arene ring, π-complexes between alkali cations and a variety of arenes have been examined.[25−30] In a previous paper, we reported the results of density functional theory (DFT) and high-level ab initio molecular orbital (MO) calculations on benzene complexes with Li$^+$−Cs$^+$.[30] The binding enthalpies at the MP2/6-311+G* level of theory, −11.6 kcal/mol (Cs$^+$) to −35.0 kcal/mol (Li$^+$), confirm that the π-cation interaction in benzene is strong enough to complete with more conventional ligand donor groups, such as alcohols, ethers, and amines.

In this paper, we present a comprehensive ab initio MO study of the bonding between the alkali cations and anisole. The results reveal anisole to be an ambidentate ligand offering two sites, oxygen and arene, for cation binding. Geometries and binding energies are obtained at the RHF/6-311G* and MP2/6-311+G* levels of theory. Frequency calculations are used to determine zero-point and vibrational energies and thus the binding enthalpies. The effects of the incomplete basis set are investigated at both the RHF and MP2 levels.

Theoretical Details

The geometries of anisole and the alkali metal−anisole 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.[31] The Hay−Wadt valence basis sets are a (5s5p)/[3s3p] contraction to which we added the energy-optimized polarization (d) functions suggested by Glendening and co-workers.[32] 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*. Although no symmetry was assumed in preliminary optimizations, it became apparent that the complexes involving binding to the ether oxygen had C_s symmetry. We thus used C_s symmetry in all the calculations reported here. The complexes in which the metals bind to the ring have C_1 symmetry. The raw binding energy 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 anisole. Estimates of the basis set superposition error (BSSE) in the binding energy were obtained at the RHF/6-311G* level of theory using the counterpoise correction method.[33] The BSSE-corrected binding energies are referred to as ΔE_e.

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 by 0.893[34] to approximately account for the effects of correlation and anharmonicity. Binding enthalpies at 298.15 K were then calculated as follows: $\Delta H_{298} = \Delta E_e + \Delta E_{ZPE} + \Delta E_{Thermal} + \Delta(PV)$, where $\Delta(PV) = \Delta nRT = -0.593$ kcal/mol at 298.15 K. The translational energy of the cation is $3/2RT$.

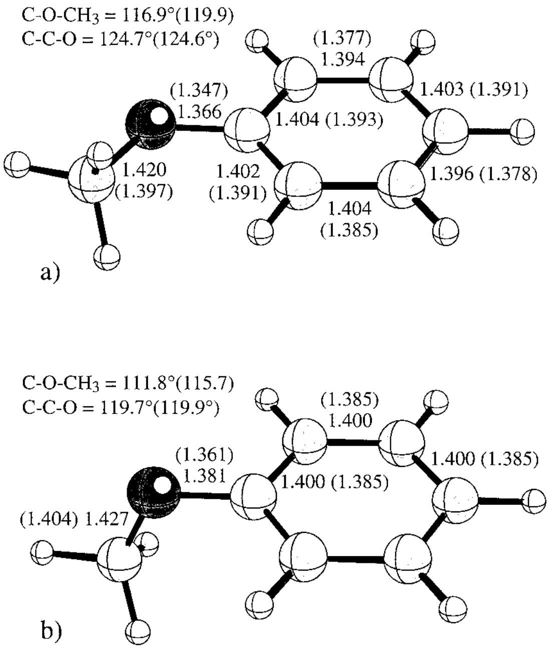

Figure 1. (a) MP2/6-311+G* optimized geometry of the ground state of anisole. (b) MP2/6-311+G* optimized geometry of the transition state for rotation about the C−C−O−CH$_3$ torsion angle. Selected distances in angstroms and angles in degrees. RHF/6-311G* values of the internal coordinates are in parentheses.

Starting from the RHF/6-311G* geometries and force constants, we then reoptimized anisole and the complexes using second-order Møller−Plesset perturbation theory (MP2).[35] 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[32] 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 our previous study of cation−benzene interactions, in which an optimization of the Na$^+$−benzene complex including all electrons gave a geometry and binding energy similar to a frozen core calculation. We thus used the frozen core scheme described above for all the Na$^+$−anisole results reported here. Counterpoise corrections were also obtained at the MP2/6-311+G* level of theory. Predictions of the binding enthalpies were obtained as discussed above from the BSSE-corrected MP2/6-311+G* binding energies and the scaled RHF/6-311G* thermodynamic data. We used Gaussian 94 for all the calculations.[36]

In our previous study of alkali metal cation binding to benzene,[30] we found small changes in binding energies when more extensive treatments of electron correlation (CCSD(T)), and when considerably more flexible basis sets (aug-cc-pVTZ), including core-valence functions, were used. Lacking experimental data with which we could judge the accuracy of our results, we choose to not attempt such computationally expensive calculations at this point.

Results and Discussion

Geometries of Anisole Conformers. We first consider the conformational flexibility of anisole. Previous theoretical studies have obtained results very similar to ours.[37,38] In Figure 1a we show the MP2 optimized geometry for the ground state of anisole. Selected values of internal coordinates involving heavy atoms are given. Corresponding values obtained at the RHF/6-311G* level of theory are given in parentheses. Conjugation of the lone pairs on O with the π-system results in the heavy atoms of the side chain lying in the plane of the ring. Selected values of internal coordinates involving heavy atoms are given.

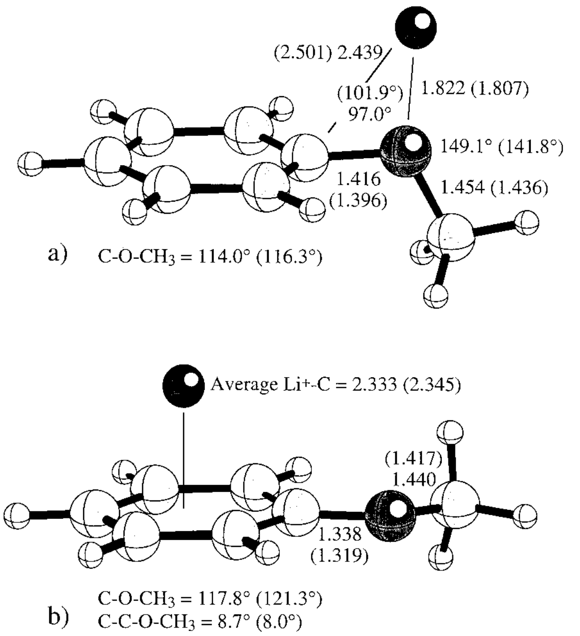

Figure 2. (a) MP2/6-311+G* optimized geometry of the Li^+ binding to the anisole oxygen. (b) MP2/6-311+G* optimized geometry of the Li^+ binding to the anisole ring. Selected distances in angstroms and angles in degrees. RHF/6-311G* values of the internal coordinates are in parentheses.

TABLE 1: MP2/6-311+G* and RHF/6-311G* Optimized Values (Angstroms and Degrees) of Internal Coordinates for the Alkali Metals Binding to Oxygen

	CH_3-O	$O-C$	M^+-O	M^+-C	CH_3-O-C	M^+-O-C	M^+-O-CH_3
				RHF/6-311G*			
Li^+	1.436	1.396	1.807	2.501	116.3	101.9	141.8
Na^+	1.429	1.386	2.211	2.769	115.9	98.0	146.1
K^+	1.424	1.379	2.629	3.121	115.6	97.4	147.1
Rb^+	1.422	1.376	2.880	3.339	115.5	97.0	147.6
Cs^+	1.421	1.374	3.123	3.569	115.4	97.3	147.3
				MP2/6-311+G*			
Li^+	1.454	1.416	1.822	2.439	114.0	97.0	149.1
Na^+	1.449	1.406	2.244	2.763	113.1	95.6	151.2
K^+	1.444	1.397	2.617	2.963	112.7	89.8	157.5
Rb^+	1.443	1.394	2.868	3.179	112.4	89.6	158.0
Cs^+	1.442	1.395	3.104	3.379	112.4	89.0	158.6

Corresponding values obtained at the RHF/6-311G* level of theory are given in parentheses. When the cations bind to the π system, the methoxy group bends slightly out of the plane of the ring (see below). In contrast, when the alkali metals bind to the oxygen, the methoxy group is orthogonal to the ring. Although such an arrangement is a stable minimum energy point when the metals bind, it is a transition state for bare anisole, being 1.89 kcal/mol higher in energy than the ground state at the MP2/6-311+G* level of theory. The MP2 geometry of the transition state conformer is given in Figure 1b.

Geometries of Alkali Metals Binding to the Methoxy Oxygen. The MP2/6-311+G* optimized geometry of the Li^+–anisole complex in which the Li^+ binds to oxygen is shown in Figure 2a. Internal coordinates for the optimized geometries for all the complexes (Li^+-Cs^+) are given in Table 1. In all cases, binding of the metal results in a complex of C_s symmetry, with the methoxy group rotating orthogonal to the ring. We were not able to locate any other stable minimum in which the alkali metal was bound to the oxygen.

The trends in internal coordinates over the series of alkali metals are as expected and the same as we observed in our previous study of alkali metal–benzene complexes. [30] The M^+-O distances exhibit a steady increase as the size of the cation increases. At the RHF level, the M^+-O distance in the Li^+ complex is 1.807 Å, expanding to 3.123 Å in the Cs^+ complex. The M^+-O distances for the Li^+ and Na^+ cases are slightly longer when the effects of electron correlation are included. However, the reverse is true for the heavier metals. Thus, at the MP2 level, the Li^+-O distance is 1.822 Å, whereas the Cs^+-O distance is 3.104 Å.

The $C-O-CH_3$ bond angles are not greatly affected by the binding of the metal to oxygen if we compare them to the geometry of anisole in which the methoxy group is orthogonal to the ring. Thus, the MP2 $C-O-CH_3$ angle of 111.8° in bare anisole (transition state geometry) is 113.9° in the Li^+ complex, contracting to 112.4° in the Cs^+ complex. In contrast, the $C-O$ and $O-CH_3$ bond lengths are both significantly longer in the complexes. The MP2 $C-O$ bond length in the Li^+ complex is 1.416 Å, much longer than the value of 1.381 predicted for bare anisole. Although the $C-O$ bond length becomes shorter for the larger metals, it is still 1.395 Å in the Cs^+ complex. The same effect is seen in the RHF data. In this case, the $C-O$ bond distances range from 1.396 (Li^+) to 1.374 Å (Cs^+), whereas we obtain a value of 1.361 Å in the orthogonal conformer of bare anisole. The $O-CH_3$ bond is similarly lengthened by the presence of the metal, the MP2 values ranging from 1.454 Å in the Li^+ complex to 1.442 Å in the Cs^+ complex. These bond lengths compare to the value of 1.427 Å in uncomplexed anisole. Again, the trend is duplicated at the RHF level, with predictions of $O-CH_3$ bond lengths ranging from 1.436 (Li^+) to 1.421 Å (Cs^+). This bond length is 1.404 Å in the orthogonal conformation of anisole.

As the size of the alkali metal increases, the metal moves closer to the ring. Although the cation is clearly bound to the oxygen, it appears that the larger cations are also attracted to the π-electron density of the ring. This effect is illustrated by the values of the $C-O-M^+$ bond angle, which become smaller as we move down the periodic table. In the Li^+ complex, this angle is 97.0°. Thus, Li^+ is 2.439 Å from the nearest ring carbon, whereas the Li^+-O distance is 1.822 Å. In contrast, in the Cs^+ complex, the $C-O-Cs^+$ angle contracts to 89.0°, placing Cs^+ 3.379 Å from the ring carbon, more similar to the 3.104 Å distance to oxygen. For this aspect of the geometry, the RHF data behave quite differently; all of the $C-O-M^+$ angles are larger than 90° at the RHF level. The angle in the Li^+ complex is 101.9°, contracting to 97.0 for Rb^+, and then expanding slightly to 97.3° for Cs^+. It appears that at the RHF level there is much less tendency for the metal to be attracted to the π-electron density while binding to oxygen.

In contrast to the large changes observed in the internal coordinates of the methoxy group, there is almost no change in the $C-C$ bond lengths in the ring with the binding of the different cations. The average $C-C$ bond length is 1.400 Å in the Li^+ complex and 1.401 Å in the Cs^+ complex. These values compare to an average $C-C$ bond length of 1.401 in anisole. A similarly small effect is seen in the RHF data.

Geometries of Alkali Metals Binding to the Ring. The optimized geometry of the Li^+–anisole complex in which the cation binds to the ring is shown in Figure 2b. Optimized values of the internal coordinates for all of the complexes are given in Table 2. When the alkali metal cations bind to the ring, anisole tends to be more nearly planar. In the Li^+ complex, the $C-C-O-CH_3$ torsion angle is 8.7° at the MP2 level. The angle bends farther out of plane for the larger cations; it is 21.7° when Cs^+ binds to the ring. Considering that the internal coordinates of the organic discussed above have tended to be closer to those of the free molecule as the size of the metal increases, the trend

TABLE 2: MP2/6-311+G* and RHF/6-311G* Optimized Values (Angstroms and Degrees) of Internal Coordinates for the Alkali Metals Binding to the Ring

	CH_3-O	$O-C$	M^+-C	CH_3-O-C	$C-C-O-CH_3$	C−H OOP
			RHF/6-311G*			
Li^+	1.417	1.319	2.345	121.3	8.0	0.43
Na^+	1.413	1.328	2.831	120.8	12.1	1.73
K^+	1.411	1.335	3.288	120.5	17.0	1.88
Rb^+	1.409	1.337	3.553	120.3	17.9	1.89
Cs^+	1.408	1.339	3.807	120.2	18.7	1.87
			MP2/6-311+G*			
Li^+	1.440	1.338	2.333	117.8	8.7	0.52
Na^+	1.436	1.346	2.793	117.8	11.6	1.87
K^+	1.434	1.352	3.196	117.4	17.8	2.52
Rb^+	1.422	1.356	3.440	117.2	19.7	2.51
Cs^+	1.432	1.359	3.703	117.2	21.7	2.41

in the $C-C-O-CH_3$ dihedral angle is in oposition to what we would expect.

Similar to the M^+-O bond lengths when the metal cations bind to oxygen, the distances between the metal and the ring carbons also increase as the size of the cation becomes larger. The cations do not bind exactly in the center of the ring, but tend to be displaced slightly. We did not observe any trend in this displacement from the center of the ring and assume it is the result of a relatively flat potential energy surface for binding to the π system. Thus, we simply report the average of the six M^+-C distances. For the Li^+ complex, the average Li^+-C distance is 2.333 Å at the MP2 level. This distance expands to 3.703 Å in the Cs^+ complex. The corresponding distance calculated previously for the Cs^+−benzene complex is 3.691 Å. The M^+-C distances tend to be longer at the RHF level, and the difference between the RHF and MP2 values increases for the larger metals. The average M^+-C distances are within 0.02 Å of the distances obtained for alkali metal cation binding to benzene at the same level of theory.[30] Despite the close similarity in distances, the binding energies are significantly greater for the anisole complexes than for the benzene complexes (see below).

The $C-O-CH_3$ angles are similar to those in the planar conformation of anisole. The largest angle is predicted for Li^+ (117.8°), decreasing to 117.1° for Cs^+. The $C-O-CH_3$ angle is 116.9° in anisole at the MP2 level. The RHF values of the $C-O-CH_3$ angle tend to be larger by about 3° and also trend toward the angle obtained for planar anisole with increases in cation size. The MP2 C−O bond length is 1.338 Å in the Li^+ complex, increasing to 1.359 Å for Cs^+. We saw above that cation binding to the oxygen caused significant increases in the C−O bond length. In contrast, binding to the ring results in shorter C−O bond lengths; the MP2 value in planar anisole is 1.366 Å. For the $O-CH_3$ bonds we obtain the same behavior as we did for oxygen binding. The $O-CH_3$ bonds are all longer than in planar anisole (1.420 Å), ranging from 1.440 (Li^+) to 1.433 Å (Cs^+).

In all cases, the binding of the cation to the ring results in the hydrogens bending slightly out of the plane of the ring 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 2, the trend is not exact. Similarly, the OOP angles range from 1.2° for Li^+ to 2.8° for Cs^+ at the MP2 level. The fact that the OOP angles increase with increasing M^+−carbon distance and decreasing change in the ring 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^+−carbon distances increase, the positive charge may be less effectively screened by the π electrons, leading to an increasingly repulsive interaction with the hydrogens, forcing the hydrogens out of plane. The similar trend in OOP angles was found in our previous study of cation biding to benzene.[30] These interactions may also explain the increased bending of the methoxy group out of the plane of the ring as the size of the metal cation increases.

Binding Energies of Alkali Metals Binding to the Methoxy Oxygen. Energetic data for the alkali metals binding to the methoxy oxygen are presented in Table 3. We first consider binding energies corrected for BSSE (ΔE_e). The RHF binding energies are strongly dependent on the size of the cation. For binding to the oxygen the values range from −40.4 kcal/mol for Li^+ to −12.9 kcal/mol for Cs^+. The inclusion of correlation (Table 3) decreases the predicted binding energies for Li^+ and Na^+, whereas it increases the binding energies for the heavier metals. Thus, whereas the MP2 binding energy for Li^+ coordinated to oxygen is −38.1 kcal/mol, about 2 kcal/mol less than the RHF value, the binding energy for Cs^+ is −14.4 kcal/mol, about 2 kcal/mol stronger than the RHF calculations indicate.

As expected, the BSSE corrections are less at the RHF level than for the MP2 calculations, despite the increase in the basis set size. Also, as expected, ΔE_{BSSE} is larger for the Li^+ and Na^+ complexes, in which the M^+-C or M^+-O distance is shorter, and the ECP is not used to represent the core electrons of the cation. The BSSE corrections at the RHF level range from 0.45 to 1.63 kcal/mol for binding to oxygen. Thus, BSSE is as large as ∼4% of the corresponding binding energy. The MP2 ΔE_{BSSE} values are more significant, varying from 2.11 to 3.19 kcal/mol. In this case, BSSE corrections can be as large as ∼18% of the binding energy.

The combined effect of the ΔE_{ZPE} and $\Delta E_{thermal}$ corrections is approximately the same as that of the RHF BSSE. These contributions to the enthalpy are largest for the Li^+ complex (1.05 kcal/mol), decreasing to 0.69 kcal/mol for the Cs^+ complex. Considering BSSE, zero-point, and thermal corrections, we predict binding enthalpies that range from −40.0 kcal/mol (Li^+) to −12.8 (Cs^+) at the RHF level. At the MP2 level, the predicted values of ΔH range from −37.7 kcal/mol for the Li^+ complex to −14.3 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^+.

The MP2 binding enthalpies can be compared to those obtained in a prior study of the alkali cation complexes with dimethyl ether.[39] These calculations, performed at the MP2 level with a similar 6-31+G* hybrid basis set, gave binding enthalpies (in kcal/mol) of −38.2 (Li^+), −25.9 (Na^+), −18.8 (K^+), −15.8 (Rb^+), and −13.6 (Cs^+). Thus, binding strengths to the anisole oxygen are similar to those observed with dimethyl ether oxygen; 0.5 kcal/mol weaker with Li^+ and 0.7 kcal/mol stronger with Cs^+.

Binding Energies of Alkali Metals Binding to the Arene Ring. Energetic data for the alkali metals binding to the arene ring are given in Table 4. We again first consider the BSSE-corrected binding energies (ΔE_e). As we demonstrated above for cation binding to oxygen, the binding energies are strongly dependent on cation size. For binding to the ring the RHF values range from −41.0 kcal/mol for Li^+ to −11.3 kcal/mol for Cs^+. As before, electron correlation decreases the predicted binding energies for Li^+ and Na^+, whereas it increases the binding for the heavier metals (Table 4). The MP2 binding energy for Li^+

TABLE 3: RHF/6-311G* and MP2/6-311+G* Binding Energies and Enthalpies (kcal/mol) for the Alkali Metals Binding to Oxygen (Frequency Data Scaled by 0.893, Enthalpies Calculated at 298.15 K)

	RHF/6-311G*					MP2/6-311+G*			
cation	ΔE_{BSSE}	ΔE_{e}	$\Delta E_{\mathrm{ZPE+thermal}}$	ΔE_{298}	ΔH_{298}	ΔE_{BSSE}	ΔE_{e}	ΔE_{298}	ΔH_{298}
Li^+	1.63	−40.4	1.05	−39.4	−40.0	2.89	−38.1	−37.1	−37.7
Na^+	1.33	−27.2	0.80	−26.4	−27.0	2.11	−25.4	−24.6	−25.2
K^+	0.48	−18.4	0.73	−17.7	−18.3	2.91	−19.6	−18.8	−19.4
Rb^+	0.45	−15.4	0.70	−14.7	−15.3	3.03	−16.5	−15.8	−16.4
Cs^+	0.45	−12.9	0.69	−12.2	−12.8	3.19	−14.4	−13. 7	−14.3

TABLE 4: RHF/6-311G* and MP2/6-311+G* Energies and Enthalpies (kcal/mol) for the Alkali Metals Binding to the Ring (Frequency Data Scaled by 0.893, Enthalpies Calculated at 298.15 K)

	RHF/6-311G*					MP2/6-311+G*			
cation	ΔE_{BSSE}	ΔE_{e}	$\Delta E_{\mathrm{ZPE+thermal}}$	ΔE_{298}	ΔH_{298}	ΔE_{BSSE}	ΔE_{e}	ΔE_{298}	ΔH_{298}
Li^+	1.09	−41.0	1.38	−39.6	−40.2	4.18	−38.9	−37.6	−38.1
Na^+	1.14	−25.1	0.96	−24.2	−24.8	3.05	−24.0	−23.0	−23.6
K^+	0.31	−16.2	0.85	−15.4	−16.0	2.31	−18.6	−17.8	−18.3
Rb^+	0.31	−13.4	0.83	−12.6	−13.2	2.55	−15.6	−14.8	−15.4
Cs^+	0.29	−11.3	0.81	−10.4	−11.0	2.77	−13.8	−13.0	−13.6

coordinated to the ring is −38.9 kcal/mol, about 2 kcal/mol less than the RHF value, whereas the binding energy for Cs^+ is −13.8 kcal/mol, about 2.5 kcal/mol stronger than at the RHF level.

The BSSE corrections for binding to the ring are less than those for binding to oxygen at the RHF level. The reverse is true for the MP2 calculations. The RHF ΔE_{BSSE} corrections range from 0.29 to 1.14 kcal/mol for binding to ring, the value for Li^+ being almost 0.5 kcal/mol less than the corresponding value for oxygen binding. In the worst case (Na^+), the BSSE represents ∼4% of the binding energy. The MP2 ΔE_{BSSE} values vary from 2.31 to 4.18 kcal/mol. At this level of theory, the BSSE accounts for ∼17% of the binding Cs^+ energy.

As before, the sum of the E_{ZPE} and $\Delta E_{\mathrm{thermal}}$ corrections is approximately the same as that of the RHF BSSE. These contributions to the enthalpy are largest for the Li^+ complex (1.38 kcal/mol), decreasing to 0.81 kcal/mol for the Cs^+ complex. At the RHF level of theory, we predict binding enthalpies that range from −40.2 (Li^+) to −11.0 (Cs^+) kcal/mol. The MP2 enthalpies range from −38.1 kcal/mol for the Li^+ complex to −13.6 kcal/mol for the Cs^+ complex. As was the case for binding to oxygen, the differences between the RHF and MP2 values of ΔH are not constant across the series of cations. The MP2 enthalpies for Li^+ and Na^+ are less than those predicted at the RHF level, whereas the reverse is true for the other cations.

Over this series of metal cations we expect there to be a systematic change in the binding energies. It is commonly assumed that the binding energy is a function of the cation charge (+1 in all cases) and some measure of the binding distance. Using nonlinear least-squares regression, we fit the binding energy data to an equation of the form $\Delta H = a/r^n + c$, where r is the average M^+-C distance in Å and n gives the dependency of the binding energy on the interatomic distance. For the MP2 data for ring binding we obtain $\Delta H = -554.1/r^{3.4} - 7.4$. For the MP2/6-311+G* enthalpies to the oxygen we obtain $\Delta H = -123.5/r^{2.1} - 3.6$. The correlation coefficients (R^2) in all cases are larger than 0.99, indicating an excellent fit of the equation to the theoretical data.

In a previous paper, we presented calculations for alkali metal cation binding to benzene.[30] These calculations gave 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^+). Thus, binding to the anisole ring is predicted to be more favorable than binding to the benzene ring by ∼3.1 (Cs^+) to 2.0 (Li^+) kcal/mol. This increased binding enthalpy may be due to the additional electrostatic attraction of the cations to the oxygen when the cation is bound to the ring. Alternately, we may consider stronger binding results from electron donation to the ring (activation) by the methoxy substituent, as is commonly invoked in electrophilic aromatic substitution.

Transition State for Cation Movement between the Two Binding Sites. Although there are clearly two binding sites for each alkali metal, in both cases the position of the cation with respect to anisole is quite similar. This is particularly true for the larger cations, which tend toward similar M^+-O and M^+-C distances. As noted above, the relative binding energies of the two sites are also similar. Thus, it seemed likely that there was not a large barrier to cation movement between the two sites. The relative ease with which cations could switch binding sites has implications for ligand design.

We determined the transition state for the movement of Na^+ between the two binding sites. The MP2/6-311+G* geometry of the transition state is shown in Figure 3. The transition state geometry more closely resembles that of the cation binding to the ring. The Na^+ has moved toward the oxygen, but is still closer to the ring carbons. The shortest M^+-C distance is 2.588 Å to C1. The two M^+-C2 distances are longer; 3.136 Å for the carbon nearest the methyl group, and 2.678 Å for the other carbon. Viewed from the top (Figure 3b), we see that rather than passing over a single carbon as it moves, the cation passes between two of the ring carbons. The values of the $C-O-CH_3$ angle and $C-C-O-CH_3$ torsion are also more similar to those when Na^+ binds to the ring. In contrast, the $C-O$ and $O-CH_3$ bond lengths are very close to those predicted for cation binding to oxygen. There is also a significant movement of the oxygen out of the plane of the ring (∼7°) in the transition state.

At the RHF level, the BSSE-corrected energetic barrier to movement between the ring-bound and oxygen-bound geometries is only 0.7−0.8 kcal/mol (ΔH_{298}). At the MP2 level we predict a barrier of 0.91 kcal/mol. Whereas the enthalpy of the complex in which Na^+ is bound to oxygen is lower by 2.3 kcal/mol (RHF) or 1.6 kcal/mol (MP2), the barriers to movement for the reverse process are correspondingly greater.

Conclusions

We find that anisole is an ambidentate ligand. Two distinct modes for cation binding involve coordination predominantly through either the ether oxygen or the arene ring. Comparison of the binding energies reveals that the two binding modes yield complexes of almost equal strength. At the MP2 level of theory, Li^+ prefers the arene site by 0.45 kcal/mol, whereas Cs^+ prefers the oxygen site by 0.71 kcal/mol. The similarity of these binding energies suggests the possibility of previously unrecognized

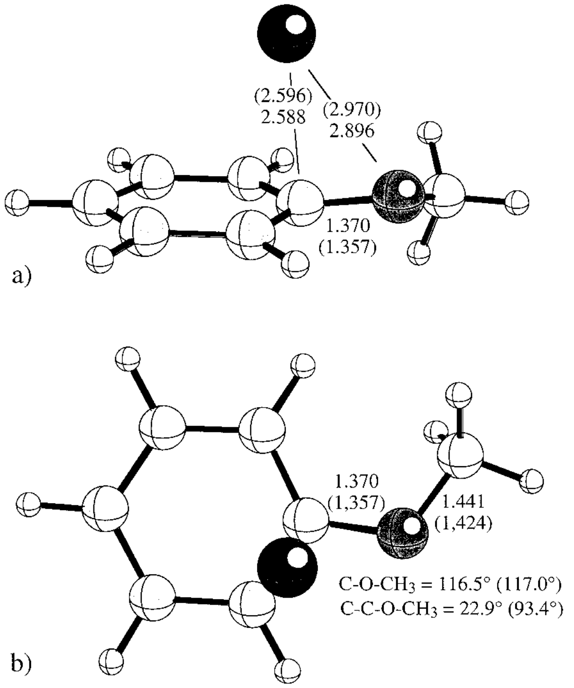

Figure 3. (a) MP2/6-311+G* optimized geometry of the transition state for Na^+ moving between the ring and oxygen binding sites. (b) Top view. Selected distances in angstroms and angles in degrees. RHF/6-311G* values of the internal coordinates are in parentheses.

metal−ion binding modes in ligands composed of cyclic oligomers of anisole subunits, e.g., calixarenes and spherands. A theoretical study to identify the possible alkali cation complexes with tetramethoxycalix[4]arene is now in progress.

We predict that the cations are significantly more tightly bound to the anisole ring than they are to benzene. This suggests that the electron-releasing effects of the methoxy substituent may have a role in the binding energies. The low barrier calculated for the movement of Na^+ between the ring and oxygen binding sites indicates that the potential energy surface for binding is relatively flat. Thus, the cation can occupy a position anywhere between the two minimum energy geometries (ring and oxygen) we calculated and still strongly interact with the ligand.

As expected, we find that the BSSE corrections can significantly alter the binding energies and should be included. The BSSE is particularly large at the MP2 level for cation binding to the anisole ring. We also find that the relative energies predicted by the MP2 calculations differ notably from those calculated at the RHF level. Thus, as we found in our prior study of π-complexes of the alkali cations with benzene, some treatment of correlation is important for accurate predictions of the binding energies.

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