J. Phys. Chem. A **2001,** *105,* 769−773

The Origin of the Cation/π Interaction: The Significant Importance of the Induction in Li^+ and Na^+ Complexes

Seiji Tsuzuki,* Masaru Yoshida, Tadafumi Uchimaru, and Masuhiro Mikami

National Institute of Advanced Industrial Science and Technology and National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565, Japan

Received: September 15, 2000

The interaction energies of the cation/π complexes (cation = Li^+, Na^+, and K^+, π system = benzene, toluene, ethylbenzene, and *tert*-butylbenzene) were calculated at the MP2/6-311G** level. The electrostatic (E_{es}) and induction (E_{ind}) energies were calculated with distributed multipoles and distributed polarizabilities model. Induction and electrostatic interactions are the major source of the attraction. The E_{ind} values of the Li^+/π complexes are 2.5−2.8 times larger than the E_{es}. The E_{ind} values of the Na^+/π complexes are 40−80% larger than the E_{es}. The induction energy is approximately proportional to R^{-4}. The thin structure of the benzene, which enables the cation to have the short contact with carbon atoms of benzene, is essential for the large E_{ind}. More polarizable cyclohexane is not a better cation binder than benzene. The E_{ind} value of the Li^+/cyclohexane complex is considerably smaller than that of the Li^+/benzene complex. The Li^+/cyclohexane complex has larger intermolecular separation, and therefore has the smaller E_{ind}. The small E_{ind} and negligible E_{es} of the Li^+/cyclohexane complex are the causes of the smaller binding energy of the Li^+/cyclohexane complex. The *tert*-butylbenzene complexes have larger binding energies than the benzene complexes. The larger E_{ind} in the *tert*-butylbenzene complexes are the cause of the larger binding energy.

Introduction

The cation/π interaction, the strong attractive non covalent interaction between the cation and π system, is an important driving force in molecular recognition.[1,2] During these two decades the cation/π interaction has been observed in many biological systems such as the binding site of acetylcholine esterase[3−5] and alkylamine dehydrogenase.[6,7] The cation/π interaction is important for the selectivity of K^+ channel[8,9] and for the helix stability.[10] The cation/π interaction is also important for the supramolecular recognition[11] by artificial host molecules such as cyclophanes[3,12] and for the structure control of catenanes.[13,14]

A detailed understanding of the origin of the cation/π interactions is significantly important for many fields of chemistry and biology.[1,2] A lot of experimental[15−25] and theoretical studies[9,26−37] have been reported about the geometries and the binding energies of the cation/π complexes, while only a few studies were reported about the origin of the cation/π interaction.[27,29−32,36] Dougherty and co-workers stated that a complete quantitative description of the cation/π interaction can be obtained only by considering a number of fundamental intermolecular forces. They also reported that the electrostatic interaction plays a prominent role and that the magnitude of the electrostatic energy explains the variation in cation/π binding energies.[30,31] Their calculations suggested that the electrostatic energy is roughly 50% of the total interaction energy of the Na^+/benzene complex. The electrostatic energy changes greatly by the substituents of the benzene ring. The electrostatic energy is only about 10% in some Na^+ complexes.[30,31]

Ma and Dougherty stated that non electrostatic terms were always important for the cation/π interaction.[2] It is likely that the induction (polarization) is also an important source of the attraction in the cation/π complexes, since the electric field produced by the cation is very strong. They also suggested the importance of polarizability of the aromatics.[2] Unfortunately it is still not clear how largely the induction contributes to the attraction. Recently, Cubero et al. carried out intermolecular perturbation theory calculations to evaluate the magnitude of the induction energies in several Na^+/π complexes.[32] They reported that the electrostatic energy was larger (more negative) than the induction energy in the Na^+/benzene complex. They also reported that the induction energy was larger than the electrostatic energy in some Na^+/π complexes, in which the electrostatic energy was small due to the electron withdrawing substituents attached to the aromatic ring. Although their calculations were impressive, unfortunately they used a small 6-31G** basis set, which is too small to quantitatively evaluate molecular polarizabilies and the induction energies. A large basis set is necessary to accurately evaluate molecular polarizability by ab initio molecular orbital method.[38−40] In this paper we have calculated the interaction energies of some Li^+/π, Na^+/π, and K^+/π complexes using a large basis set and evaluated the electrostatic and induction energies of the complexes. We have shown that the induction energy is the major source of the attraction in the Li^+/π and Na^+/π complexes and the induction is a commonly important interaction in cation/π complexes. In addition we have demonstrated that large substituents lead to increase the induction energy and the binding energy of cation/π complex.

Computational Method

The Gaussian 98 program[41] was used for the ab initio molecular orbital calculations. The 6-311G** basis set[42] was used. Electron correlation was corrected by the MP2 method.[43,44] Basis set superposition error (BSSE)[45] was corrected for all calculations using the counterpoise method.[46] The geometries of the complexes were optimized at the MP2/6-311G** level.

---

* Corresponding author. E-mail: tsuzuki@nimc.go.jp.

10.1021/jp003287v CCC: \$20.00

The complex formation slightly deformed the geometries of the π systems. The distributed multipoles[47,48] of the π systems were obtained from the MP2/6-311G** wave functions of monomers using CADPAC version 6.[49] The geometries of monomers in the complexes were used for the calculations of the distributed multipoles. The electrostatic and induction energies of the complexes were calculated by ORIENT version 3.2.[50] The electrostatic energy was calculated as the interaction between the cation and the distributed multipoles of the π system. The induction energy was calculated as the interaction between the distributed polarizable sites [51] of the π system and the electric field produced by the cation. The anisotropic polarizabilities $\alpha_{xx} = \alpha_{yy} = 14$ and $\alpha_{zz} = 7$ au were put on the carbon atoms of benzene rings (The z-axis is parallel to the 6-fold axis.).[52] The $\alpha_{xx} = \alpha_{yy} = 13$ and $\alpha_{zz} = 10$ au were put on the carbon atoms of cyclohexane (The z-axis is parallel to the 3-fold axis.).[53] The isotropic polarizability $\alpha = 17$ au was put on the other carbon atoms.[54]

The multipole expansion of electrostatic interaction converges only if the charge distributions are far enough apart. The multipole approximation can be unreliable if the separation between the two interacting molecules is very small. To avoid this problem we have used distributed multipoles model instead of a conventional single site multipoles model, in which multipoles are given on the center of gravity of a molecule to represent the charge distribution of the whole molecule. In the distributed multipoles model the molecule is divided into regions, each enclosing a single atom. The charges in each region are represented by the multipoles given on the atom in the region. The distributed multipoles model decreases the convergence sphere significantly, which enables us to obtain accurate electrostatic interaction even in short intermolecular separation.[47,48]

Results and Discussion

Basis Set and Electron Correlation. The MP2/6-311G** level optimized geometries of the complexes were used for the calculations of the interaction energies. The calculated M^+-C distances in the M^+/benzene complexes ($M^+ = Li^+$, Na^+, and K^+) were 2.340, 2.803, and 3.137 Å, respectively. These values are close to the M^+-C distances obtained from the MP2/6-311+G* calculations (2.337, 2.804, and 3.217 Å, respectively) reported by Nicholas et al.[34] They have reported that the basis set and electron correlation effects on the optimized geometries are not large.

The interaction energies (E_{HF} and E_{MP2}) of the Li^+/benzene and Na^+/benzene complexes were calculated using several basis sets as summarized in Table 1. The effects of basis set on the calculated interaction energies are small. Nicholas et al. also reported that the basis set effects on the calculated binding energy of the Li^+/benzene complex are very small.[34] They have also reported that the effects of the electron correlation beyond MP2 are very small. The difference between the MP2 and CCSD(T) interaction energies of the Li^+/benzene complex with the 6-311+G* basis set is only 0.22 kcal/mol.[34]

TABLE 1: Calculated Interaction Energies of Li^+/Benzene and Na^+/Benzene Complexes[a]

basis set	Li^+	Na^+
HF/6-31G*	−39.5	−26.2
HF/6-311G*	−39.7	−24.3
HF/6-311G**	−39.4	−24.0
HF/6-311++G**	−38.8	−23.5
HF/6-311G(2d,2p)	−41.1	−25.4
HF/6-311G(3d,3p)	−40.7	−25.3
MP2/6-31G*	−37.4	−24.8
MP2/6-311G*	−37.1	−22.8
MP2/6-311G**	−35.6	−21.6
MP/6-311++G**	−34.8	−21.0
MP/6-311G(2d,2p)	−36.9	−22.8
MP/6-311G(3d,3p)	−36.4	−22.7

[a] Energy in kcal/mol. The geometries optimized at the MP2/6-311G** level were used.

TABLE 2: Calculated Interaction Energies of Cation/π Complexes[a]

complex	E_{HF}[b]	E_{MP2}[b]	E_{def}[c]	E_{total}[d]	E_{es}[e]	E_{ind}[f]	E_{rep}[g]
Li^+/benzene	−39.4	−35.6	0.3	−35.4	−18.7	−46.9	30.1
Li^+/toluene	−42.2	−38.3	0.3	−38.0	−20.3	−50.7	32.7
Li^+/ethylbenzene	−42.5	−38.7	0.4	−38.4	−19.8	−53.9	35.0
Li^+/*t*-butylbenzene	−44.2	−40.2	0.4	−39.7	−20.0	−56.0	35.8
Na^+/benzene	−24.0	−21.6	0.3	−21.3	−14.8	−21.0	14.1
Na^+/toluene	−25.9	−23.4	0.3	−23.1	−16.0	−23.3	15.8
Na^+/ethylbenzene	−26.1	−23.8	0.3	−23.4	−15.4	−25.9	17.5
Na^+/*t*-butylbenzene	−27.2	−24.8	0.4	−24.4	−15.6	−27.4	18.2
K^+/benzene	−15.5	−17.2	0.3	−17.0	−11.9	−12.8	7.4

[a] Energy in kcal/mol. Geometries were optimized at the MP2/6-311G** level. [b] Basis set superposition error (BSSE) corrected interaction energies of complexes calculated with the 6-311G** basis set. BSSE was corrected by the counterpoise method. [c] Increases of the energies of monomer aromatic molecules by the deformation of geometries in complex formation. [d] Total interaction energy of complex. Sum of E_{MP2} and E_{def}. [e] Electrostatic energy. E_{es} was calculated as the interaction between the cation and the distributed multipoles of the π system obtained from MP2/6-311G** wave function. [f] Induction energy. E_{ind} was calculated as the interaction between the distributed polarizable sites of the π system and the electric field produced by the cation. The $\alpha_{xx} = \alpha_{yy} = 14$ and $\alpha_{zz} = 7$ au are used for carbon atoms of benzene ring and $\alpha = 17$ au is used for other carbon atoms. [g] $E_{rep} = E_{total} - (E_{es} + E_{ind})$. E_{rep} is mainly exchange-repulsion energy.

Electrostatic, Induction, and Total Interaction Energies. The calculated interaction energies of the complexes are summarized in Table 2. The complex formation deformed the geometries of the π systems. The E_{HF} and E_{MP2} are the HF and MP2 level intermolecular interaction energies between the cation and the deformed π system, respectively. The E_{def} is the MP2/6-311G** level deformation energy of the π system. The deformation energies of the complexes are not large (less than 0.4 kcal/mol). The E_{total} is the sum of the E_{MP2} and E_{def}. The absolute value of E_{total} corresponds to the binding energy. The E_{es} and E_{ind} are the electrostatic and induction energies, respectively.

The E_{total} values of the M^+/benzene complexes ($M^+ = Li^+$, Na^+, and K^+) are −35.4, −21.3, and −17.0 kcal/mol, respectively. The E_{total} value of the Li^+ complex is 14.1 kcal/mol larger (more negative) than that of the Na^+ complex. The E_{total} value of the K^+ complex is 4.3 kcal/mol smaller than the Na^+ complex. On the other hand the E_{es} values of the M^+/benzene complexes are −18.7, −14.8, and −11.9 kcal/mol, respectively. The E_{es} value of the Li^+ complexes is only 3.9 kcal/mol larger than the Na^+ complex. The difference of the E_{es} values (3.9 kcal/mol) is considerably smaller than the difference of the E_{total} values (14.1 kcal/mol), which indicates that the larger interaction energy (E_{total}) of the Li^+ complex has its origin not only in the electrostatic interaction.

The E_{ind} values of the Li^+ and Na^+ complexes are larger (more negative) than the E_{es} values. Especially the E_{ind} values of Li^+ complexes are considerably larger than the E_{es} values. The E_{ind} values of the Li^+ complexes are 2.5−2.8 times larger than the E_{es} values. The E_{ind} values of the Na^+ complexes are 40−80% larger than the E_{es} values. These results indicate that the induction energy is the major source of the attraction in the

TABLE 3: Calculated Geometries and Energies of Cation/Benzene Complexes[a]

cation	M^+-C	M^+−centroid[b]	E_{total}[c]	E_{es}[d]	E_{ind}[e]
Li^{+f}	2.340	1.869	−35.4	−18.7	−46.9
Na^{+f}	2.803	2.425	−21.3	−14.8	−21.0
K^{+f}	3.137	2.805	−17.0	−11.9	−12.8
Rb^{+g}	3.461	3.165[h]	−13.9[i]	−9.2	−8.4
Cs^{+g}	3.690	3.414[h]	−12.1[i]	−7.9	−6.4

[a] Distance in Å. Energy in kcal/mol. [b] Distance between the cation and the center of benzene carbon atoms. [c] Total interaction energy of the complex calculated at the MP2/6-311G** level. [d] Electrostatic energy. See footnote (e) of Table 2. [e] Induction energy. See footnote (f) of Table 2. [f] Geometries of the complexes were optimized at the MP2/6-311G** level. [g] Monomer benzene geometry optimized at the MP2/6-311G** level was used for the calculations of the E_{es} and E_{ind}. [h] The M^+−centroid distances were taken from ref 34. [i] Ref 34.

Li^+ and Na^+ complexes. The E_{ind} values of the Li^+/π complexes (−47 to −56 kcal/mol) are very large. The induction energy has its origin in the induced polarization of the π system by the electric field produced by the cation. The amount of the induction energy is proportional to the polarizability and the square of the electric field.[48] The magnitude of the electric field produced by a cation is approximately proportional to R^{-2} (R is the distance from the cation.). Therefore the E_{ind} is approximately proportional to R^{-4}. Apparently the short intermolecular distances in the Li^+ complexes are the cause of the large E_{ind} values. The M^+-C distance of the Li^+/benzene complex is only 2.340 Å. The E_{ind} value of the K^+/benzene complex is comparable to the E_{es} value. The E_{ind} decreases more rapidly by the increase of the intermolecular distance compared to the E_{es}. The E_{ind} values of the Rb^+ and Cs^+ complexes are still not negligible, while the E_{ind} values of these complexes are smaller than the E_{es} values as shown in Table 3.

To confirm the reliability of the E_{es} and E_{ind} values derived from distributed multipoles and induced-dipole theory, E_{es} and E_{ind} values obtained by our methods were compared with the E_{es} value derived from molecular electrostatic potential and the perturbational E_{ind} reported by Cubero et al.[32] They reported that the E_{es} and E_{ind} values of the Na^+/benzene complex (Na^+ is 2.47 Å above the benzene ring) derived from the HF/6-31G** wave functions are −15.0 and −9.9 kcal/mol, respectively. The E_{es} value obtained by our method using the same geometry and the same wave functions is −15.2 kcal/mol, which is very close to the value from molecular electrostatic potential. The E_{ind} value obtained from induced-dipole theory using the anisotropic polarizabilities of carbon atoms ($\alpha_{xx} = \alpha_{yy} = 11.4$ and $\alpha_{zz} = 3.5$ au, respectively) from the HF/6-31G** wave functions is −12.4 kcal/mol. The E_{ind} value from induced-dipole theory is not largely different (about 25% larger) from the perturbational E_{ind} value.

Cubero et al. reported that inclusion of the induction energy is important to predict the binding energies.[32] They evaluated the electrostatic and induction energies using the 6-31G** basis set. The calculated E_{es} and E_{ind} values of the Na^+/benzene complex were −15.0 and −9.9 kcal/mol, respectively. The E_{ind} was not negligible, while the E_{ind} was substantially smaller than the E_{es}. They reported that the E_{es} depend strongly on the substituent of the aromatic ring. The E_{es} is very small, if the aromatic ring has electron withdrawing substituents such as fluorine, chlorine, and cyano group. They reported that the E_{ind} is larger than the E_{es} only in such complexes. However, our calculations showed that the E_{ind} values of the Li^+/benzene and Na^+/benzene complexes are larger than the E_{es} values. It is well-known that a large basis set is necessary to evaluate molecular polarizability and small basis sets considerably underestimate it.[38−40] The 6-31G** basis set is too small to evaluate the molecular polarizability of benzene and the induction energy. The calculated α_{zz} of benzene (z axis is parallel to the 6-fold axis) with the 6-31G** basis set (21.24 au) is about the half of the experimental value (42.85 au).[52] Apparently their calculations underestimated the induction energies.

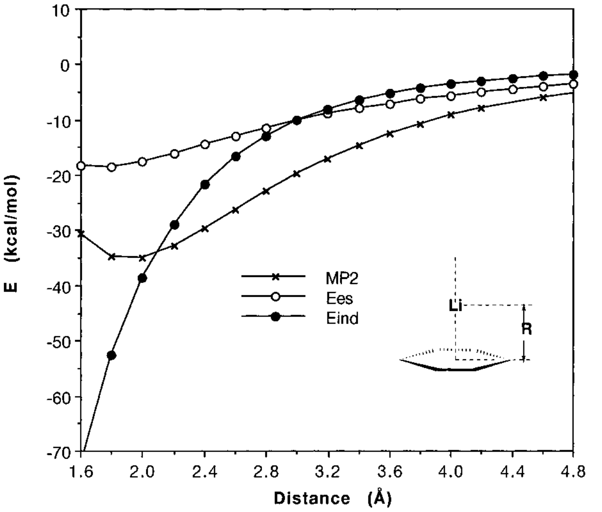

Figure 1. The MP2/6-311G** level interaction energy and electrostatic and induction energies of the Li^+/benzene complex. The Li^+ is on the 6-fold axis of the benzene.

Other Intermolecular Forces. We have discussed the electrostatic and cation → benzene induction terms, while there exist some other terms, such as repulsion, dispersion, charge-transfer, and benzene → cation induction terms. Dispersion, well-known as the attraction between rare gas atoms, has its origin in electron correlation and molecular polarization.[48] The molecular polarizabilities of Li^+, Na^+, and K^+ are very small. The calculated polarizabilities of these cations at the HF/6-311G(3d) level are only 0.14, 0.87, and 5.31 au, respectively. The polarizabilities of these cations are considerably smaller than that of methane (17.28 au).[54] It has been reported that the estimated dispersion energy in the benzene−methane complex is −2.3 kcal/mol when the intermolecular distance R is 3.8 Å.[55] If we assume that the dispersion energy is proportional to the R^{-6}, we can estimate that the dispersion energy in the K^+/benzene complex ($R = 2.805$ Å) is −4.4 kcal/mol from the polarizabilities of methane and K^+ and the dispersion energy in the benzene−methane complex. The estimated dispersion energies of Li^+/benzene and Na^+/benzene complexes are smaller than the K^+/benzene complex, and therefore the contribution of the dispersion is negligible in the Li^+ and Na^+ complexes. The dispersion energy will be larger in more polarizable Rb^+ and Cs^+ complexes. The dispersion energy will be comparable to the electrostatic and induction energies in these complexes.

The calculated intermolecular interaction potential of the Li^+/benzene complex (Figure 1) indicates that substantial attraction still exists, even if the intermolecular distance is larger than 4.0 Å, which suggests that the major source of the attraction is not a short-range interaction (E−$e^{-\alpha R}$) such as charge-transfer, but a long-range interaction (E−R^{-n}) such as electrostatic and induction. Short-range interactions arise at distances where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance.[48]

The small polarizabilities of the cations suggest that the benzene → cation induction energies are negligible. The benzene → K^+ induction energy was calculated as the interaction

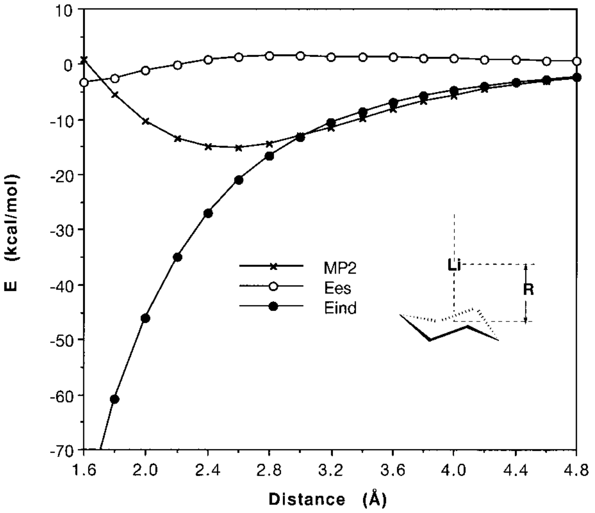

Figure 2. The MP2/6-311G** level interaction energy and electrostatic and induction energies of the Li^+/cyclohexane complex. The Li^+ is on the 3-fold axis of the cyclohexane.

between the K^+ ($\alpha = 5.3$ au) and the electric field produced by the distributed multipoles of the benzene. The calculated benzene → K^+ induction energy is only 0.07 kcal/mol.

The E_{rep} in Table 2 includes a number of intermolecular interaction terms such as dispersion, charge-transfer and benzene → cation induction. However, these terms are not large in these cation/π complexes as we have discussed. Therefore the E_{rep} is mainly the exchange-repulsion energy. The order of the E_{rep} value is $Li^+ > Na^+ > K^+$. The Li^+ complexes have large attractive electrostatic and induction forces. The complexes must have the same amounts of repulsive force at the equilibrium distances. The Li^+ complexes have very short intermolecular distance where the complexes have large repulsive force, and therefore they have large E_{rep}. The large E_{rep} cancels out substantial portion of the attraction by induction and electrostatic interactions. Therefore the sum of the E_{ind} and E_{es} is larger than the total interaction energy (E_{total}).

Li^+/Cyclohexane Interaction. Our calculations indicate that induction is always significantly important for the cation/π interaction. It has been a controversial issue whether polarizability is the defining feature of the cation/π interaction. Ma and Dougherty stated that electrostatic was playing a prominent role in the cation/π interaction and that the polarizability was not the defining feature of the cation/π interaction.[2] If polarizability was the only defining feature of the cation/π interaction substantially more polarizable cyclohexane was a better cation binder than benzene. However, cyclohexane is not a better cation binder than benzene. Meccozi et al. reported that the HF/6-31G** level interaction energy of Na^+/cyclohexane complex (−8.4 kcal/mol) is considerably smaller (less negative) than that of the Na^+/benzene complex (−27.1 kcal/mol).[31]

Our MP2/6-311G** level calculations also indicate that the interaction energy of the Li^+/cyclohexane complex (−15 kcal/mol) is considerably smaller than that of the Li^+/benzene complex (−35 kcal/mol) as shown in Figures 1 and 2. The MP2/6-311G** level optimized geometries of isolated cyclohexane and benzene were used for the calculations of the intermolecular interaction potentials. The calculated intermolecular potentials of the Li^+/cyclohexane and Li^+/benzene complexes have their minima at intermolecular distances of 2.6 and 2.0 Å, respectively. The intermolecular distance of the Li^+/cyclohexane complex is considerably larger than that of the Li^+/benzene complex. The steric repulsion between the cation and the axial hydrogen atoms of the cyclohexane leads to the considerably larger separation. More polarizable cyclohexane has a larger induction energy than benzene at the same intermolecular distance. The E_{ind} values of the Li^+/cyclohexane and Li^+/benzene complexes ($R = 2.6$ Å) are −21.0 and −16.6 kcal/mol, respectively. The induction energy is approximately proportional to R^{-4}. The larger separation in the cyclohexane complex leads to the considerably smaller induction energy. The E_{ind} values of the Li^+/cyclohexane ($R = 2.6$ Å) and Li^+/benzene ($R = 2.0$ Å) complexes are −21.0 and −38.7 kcal/mol, respectively. The Li^+/benzene complex has 17.7 kcal/mol larger (more negative) E_{ind} than the Li^+/cyclohexane complex. Apparently the larger intermolecular distance in the cyclohexane complex is one of the causes of the smaller binding energy of the Li^+/cyclohexane complex. The thin structure of benzene, which enables the cation to have the short contact with carbon atoms, is essential for the large E_{ind}. Although induction is often the most important source of the attraction in the cation/π complexes, the induction energy depends significantly on the intermolecular separation and therefore it is not possible to predict the amount of the induction energy only from molecular polarizability. The E_{es} values of the Li^+/cyclohexane ($R = 2.6$ Å) and Li^+/benzene ($R = 2.0$ Å) complexes are 1.2 and −17.5 kcal/mol, respectively. The Li^+/benzene complex has 18.7 kcal/mol larger (more negative) E_{es} than the Li^+/cyclohexane complex. The Li^+/benzene complex has larger attractive E_{es} and E_{ind} values than the Li^+/cyclohexane complex, which indicates that both electrostatic and induction are important for the larger binding energy of the benzene complex.

Effects of Alkyl Substituents. It is interesting to note that the methyl-, ethyl-, and *tert*-butyl substituents lead to substantial increase of the calculated interaction energy. Especially the *tert*-butyl group leads to increase the calculated interaction energies of the Li^+ and Na^+ complexes as much as 4.3 and 3.1 kcal/mol, respectively. Deakyne and Meot-Ner (Mautner) reported that the methyl groups lead to increase the interaction energy of the NH_4^+/π complex.[17] They reported that the experimental interaction energies of the NH_4^+/benzene and NH_4^+/1,3,5-trimethylbenzene complexes are −19.3 and −21.8 kcal/mol, respectively. The E_{es} values of toluene complexes are larger than those of the benzene complexes as shown in Table 2, which explains the larger interaction energies of the toluene and trimethylbenzene complexes than the benzene complex. On the other hand the E_{es} values of toluene and *tert*-butylbenzene complexes are nearly equal, while the interaction energies of the *tert*-butylbenzene complexes are substantially larger than the toluene complexes. The E_{ind} values of the *tert*-butylbenzene complexes are larger than the benzene and toluene complexes. Apparently the larger induction energies are the cause of the larger interaction energies of the *tert*-butylbenzene complexes. These results indicate that the bulky *tert*-butyl group substantially increases the induction energy and that the larger induction energy is a cause of the larger interaction energy.

Conclusion

Induction (polarization) and electrostatic interactions are the major source of the attraction in the M^+/π ($M^+ = Li^+$, Na^+, and K^+) complexes. Induction is significantly important for the Li^+/π and Na^+/π complexes. The calculated induction energies of the Li^+/π complexes are 2.5−2.8 times larger than the electrostatic energies. The induction energies of Na^+/π complexes are 40−80% larger than the electrostatic energies. The induction and electrostatic energies are comparable in the K^+/benzene complex.

The calculated potential suggests that the major source of the attraction in the cation/π interaction is long-range interactions such as induction and electrostatic. The contributions of dispersion and benzene → cation inductions are negligible in the Li$^+$, Na$^+$, and K$^+$ complexes. The comparison between the Li$^+$/benzene and Li$^+$/cyclohexane complexes indicates that both induction and electrostatic interactions are essential for the larger binding energy of the Li$^+$/benzene complex. The Li$^+$/cyclohexane complex has larger induction energy than the Li$^+$/benzene complex at the same intermolecular separation. However, the cation cannot have short contact with cyclohexane, since the axial hydrogen atoms of cyclohexane have steric repulsion with the cation. The calculated intermolecular interaction potentials of the Li$^+$/cyclohexane and Li$^+$/benzene complexes have their minima at the intermolecular distances of 2.6 and 2.0 Å, respectively. The amount of the induction energy depends greatly on the intermolecular distance (R). The induction energy is approximately proportional to R^{-4}. Therefore the Li$^+$/benzene complex has considerably large induction energy than the Li$^+$/cyclohexane complex. The thin structure of benzene, which enables the cation to have the short contact with carbon atoms of benzene, is essential for the large induction energy. In addition the Li$^+$/benzene complex has larger attractive electrostatic interaction, while the electrostatic interaction in the Li$^+$/cyclohexane complex is negligible. The attractive electrostatic interaction is also one of the causes of the larger binding energy of the benzene complex.

The cation/*tert*-butylbenzene complexes have larger binding energies than the benzene complexes. The bulky *tert*-butyl group increases the attractive induction energy. The larger induction energy is a cause of the larger binding energies of the *tert*-butylbenzene complexes.

Acknowledgment. We thank Prof. K. Hiratani, Dr. Y. Nagawa, and Dr. H. Houjou for helpful discussion. We thank Tsukuba Advanced Computing Center for the provision of the computational facilities.

References and Notes

(1) Dougherty, D. A. *Science* **1996**, *271,* 163.

(2) Ma, J. C.; Dougherty D. A. *Chem. Rev.* **1997**, *97,* 1303.

(3) Dougherty, D. A.; Stauffer, D. A. *Science* **1990**, *250,* 1558.

(4) Sussman, J. L.; Harel, M.; Frolow, F.; Oefner, C.; Goldman, A.; Toker, L.; Silman, I. *Science* **1991**, *253,* 872.

(5) Cervenansky, C.; Engstrom, A.; Karlsoon, E. *Eur. J. Biochem.* **1995**, *229,* 270.

(6) Bellamy, H. D.; Lim, L. W.; Mathews, F. S.; Dunham, W. R. *J. Biol. Chem.* **1989**, *264,* 11887.

(7) Kuusk, V.; McIntire, W. S. *J. Biol. Chem.* **1994**, *269,* 26136.

(8) Heginbotham, L.; MacKinnon, R. *Neuron* **1992**, *8,* 483.

(9) Kumpf, R. A.; Dougherty, D. A. *Science* **1993**, *261,* 1708.

(10) Armstrong, K. M.; Fairman, R.; Baldwin, R. L. *J. Mol. Biol.* **1993**, *230,* 284.

(11) *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Elsevier Science Ltd.: Oxford, 1996.

(12) Forman, J. E.; Barrans, R. E., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.* **1995**, *117,* 9213.

(13) Amabilino, D. B.; Ashton, P. R.; Balzani, V.; Boyd, S. E.; Credi, A.; Lee, J. Y.; Menzer, S.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120,* 4295.

(14) Raymo, F. M.; Houk, K. N.; Stoddart, J. F. *J. Org. Chem.* **1998**, *63,* 6523.

(15) Sunner, J.; Nishizawa, K.; Kebarle, P. *J. Phys. Chem.* **1981**, *85,* 1814.

(16) Meot-Ner (Mautner), M.; Deakyne, C. A. *J. Am. Chem. Soc.* **1985**, *107,* 469.

(17) Deakyne, C. A.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1985**, *107,* 474.

(18) Guo, B. C.; Purnell, J. W.; Castleman, A. W., Jr. *Chem. Phys. Lett.* **1990**, *168,* 155.

(19) Taft, R. W.; Anvia, F.; Gal, J.-F.; Walsh, S.; Capon, M.; Holmes, M. C.; Hosn, K.; Oloumi, G.; Vasanwala, R.; Yazdani, S. *Pure Appl. Chem.* **1990**, *62,* 17.

(20) Kearney, P. C.; Mizoue, L. S.; Kumpf, A.; Forman, J. E.; McCurdy, A.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115,* 9907.

(21) Cabarcos, O. M.; Wenheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1998**, *108,* 5151.

(22) Roelens, S.; Torriti, R. *J. Am. Chem. Soc.* **1998**, *120,* 12443.

(23) Cabarcos, O. M.; Wenheimer, C. J.; Lisy, J. M. *J. Chem. Phys.* **1999**, *110,* 8429.

(24) Bartoli, S.; Roelens, S. *J. Am. Chem. Soc.* **1999**, *121,* 11908.

(25) Gaberscek, M.; Mavri, J. **1999**, *308,* 421.

(26) Duffy, E. M.; Kowalczyk, P. J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1993**, *115,* 9271.

(27) Luhmer, M.; Bartik, K.; Dejaegere, A.; Bovy, P.; Reisse, J. *Bull. Soc. Chim Fr.* **1994**, *131,* 603.

(28) Lee, J. Y.; Lee, S. J.; Choi, H. S.; Ho, S. J.; Kim, K. S.; Ha, T.-K. *Chem. Phys. Lett.* **1995**, *232,* 67.

(29) Caldwell, J. W.; Kollman, P. A. *J. Am. Chem. Soc.* **1995**, *117,* 4177.

(30) Mecozzi, S.; West, P., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118,* 2307.

(31) Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93,* 10566.

(32) Cubero, E.; Luque, F. J.; Orozco, M. *Proc. Natl. Acad. Sci. U.S.A.* **1998**, *95,* 5976.

(33) Chipot, C.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996,** *118,* 2998.

(34) Nicholas, J. B.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **1999**, *103,* 1394.

(35) Nicholas, J. B.; Hay, B. P. *J. Phys. Chem. A* **1999**, *103,* 9815.

(36) Minoux, H.; Chipot, C. *J. Am. Chem. Soc.* **1999**, *121,* 10366.

(37) Gallivan, J. P.; Dougherty, D. A. *J. Am. Chem. Soc.* **2000**, *122,* 870.

(38) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **1994**, *94,* 1723.

(39) Tsuzuki, S.; Uchimaru, T.; Tanabe, K. *J. Mol. Struct. (THEOCHEM)* **1994**, *307,* 107.

(40) Tsuzuki, S.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Phys. Chem. A* **1998**, *102,* 2091.

(41) *Gaussian 98, Revision A.6*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. Jr.; Stratmann, R. E.; Burant, J. C.;Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; C. Peng, Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.;Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(42) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72,* 650.

(43) Mϕller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46,* 618.

(44) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153,* 503.

(45) Ransil, B. J. *J. Chem. Phys.* **1961**, *34,* 2109.

(46) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19,* 553.

(47) Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, *56,* 1047.

(48) Stone, A. J. *The theory of intermolecular forces;* Clarendon Press: Oxford, 1996.

(49) Amos, R. D. *CADPAC: The Cambridge Analytical Derivatives Package, Issue 6,* Technol. rep., University of Cambridge, 1995, A suite of quantum chemistry programs developed by R. D. Amos with contributions from I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, K. E. Laidig, G. Laming, A. M. Lee, P. E. Maslen, C. W. Murray, J. E. Rice, E. D. Simandiras, A. J. Stone, M. D. Su, and D. J. Tozer.

(50) Stone, A. J.; Dullweber, A.; Hodges, M. P.; Popelier, P. L. A.; Wales, D. J. *Orient: a program for studying interactions between molecules version 3.2*; University of Cambridge, 1995.

(51) Stone, A. J. *Mol. Phys.* **1985**, *56,* 1065.

(52) Stuart, H. A.; Volkmann, H. *Z. Phys.* **1933**, *80,* 107.

(53) Stuart, H. A.; Schiebl, U. V. *Ann. Phys.* **1948**, *2,* 321.

(54) Werner, H.-J.; Mayer, W. *Mol. Phys.* **1976**, *31,* 855.

(55) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122,* 3746.