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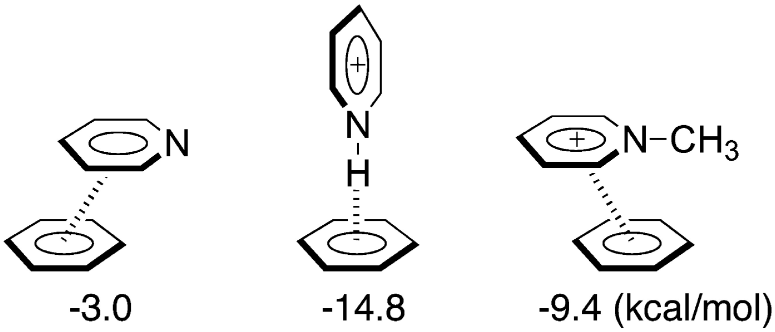

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# Origin of Attraction, Magnitude, and Directionality of Interactions in Benzene Complexes with Pyridinium Cations

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***Abstract:*** Geometries and interaction energies of benzene complexes with pyridine, pyridinium, *N*-methylpyridinium were studied by ab initio molecular orbital calculations. Estimated CCSD(T) interaction energies of the complexes at the basis set limit were −3.04, −14.77, and −9.36 kcal/mol, respectively. The interactions in the pyridinium and *N*-methylpyridinium complexes should be categorized into a cation/$\pi$ interaction, because the electrostatic and induction interactions greatly contribute to the attraction. On the other hand, the interaction in the pyridine complex is a $\pi/\pi$ interaction. The dispersion interaction is mainly responsible for the attraction in the benzene−pyridine complex. Short-range interactions including charge-transfer interactions are not important for the attraction in the three complexes. The most stable pyridinium complex has a T-shaped structure, in which the N−H bond points toward the benzene, while the *N*-methylpyridinium complex prefers a slipped-parallel structure. The benzene−pyridine complex has two nearly isoenergetic (Slipped-parallel and T-shaped) structures.

## Introduction

Nonbonding interactions involving aromatic rings play important roles in various fields in chemistry and biochemistry. They control the three-dimensional structures of proteins, molecular recognitions processes and the packing of molecules in the crystals.[1−6] Crystal structures of organic molecules and biological molecules suggest the existence of $\pi/\pi$, OH/$\pi$, NH/$\pi$, CH/$\pi$, and cation/$\pi$ interactions.[4] During past two decades, the interactions have been studied extensively both by experimental[7−15] and theoretical methods.[16−26]

A strong attraction between a nitrogen-containing aromatic cation and a neutral $\pi$ system has been reported (Figure 1). Dougherty et al. reported the strong attraction between a quinolinium cation and a $\pi$ system.[27] They also reported that this interaction is stronger than that between a neutral quinoline and the $\pi$ system. This interaction has been widely used for controlling self-organization processes, catalytic reactions and crystal engineering. Stoddart et al. reported the formation of donor−acceptor complexes of pyridinium derivatives with cyclophanes.[28] They used this interaction for the synthesis of rotaxanes and catenanes by self-organization.[28−34] Recently, this

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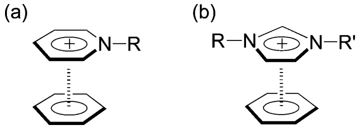

**Figure 1.**

interaction was used for controlling crystal packing,[35−37] molecular conformation,[38−40] and folding of oligomers.[41−43]

This interaction is also important in other fields. For example, the interaction between a protonated histidine and a $\pi$ system plays important roles in the stabilization of protein structures and ligand binding.[44−46] Nitrogen-containing aromatic cations (imidazolium and pyridinium) are commonly used for room-temperature ionic liquids (RTILs). Due to low-flammability and low-volatility, many applications of RTILs as green solvents for reaction and separation processes are expected.[47−50] The interactions of the aromatic cations with a $\pi$ system are important for understanding the solvation of an aromatic molecule in the RTILs.

This interaction has often been explained as a cation/$\pi$ interaction,[6] while the same interaction has sometimes been called a donor−acceptor, charge-transfer, $\pi/\pi$, or CH/$\pi$ interaction.[28,31,51] The interaction energies for various pyridinium-$\pi$ systems were experimentally estimated; −0.5 to −2.6 kcal/mol[14,52−54] and −0.6 kcal/mol[55] were obtained in water and in chloroform, respectively. These energies consist of the sum of various attractive and repulsive forces arising from the inherent property of each system; therefore, they do not represent the straight attractive interaction energy between a pyridinium cation and a phenyl ring.

Recently, high-level ab initio calculation is becoming a powerful tool for studying nonbonding interactions.[56,57] Several ab initio calculations on $\pi/\pi$ interactions[16−20] and cation/$\pi$ interactions of alkali metal cations have been reported.[23−26] These calculations show that a very large basis set near saturation and a CCSD(T) level electron correlation correction are necessary for an accurate evaluation of the interaction energies of aromatic molecules.[16−20] Small basis sets underestimate the attraction considerably. MP2 level calculations overestimate the attraction compared with more reliable CCSD(T) level calculations. Although MP2 calculations of the neutral benzene−pyridine complex were reported,[58] high-level ab initio calculations of the benzene complexes with pyridinium cations have not been reported.

Despite the broad interests in the interactions in benzene complexes with pyridinium cations, many unsettled fundamental issues on the interactions still remain. (1) The origin of the attraction is not well understood. It is not certain whether the electrostatic interaction is the major source of attraction or orbital−orbital interactions such as the charge-transfer interactions are mainly responsible for the attraction. (2) The size of the interaction energy is not clear. (3) Directionality of the interaction is still unclear. The slipped-parallel (offset face-to-face) and T-shaped (edge-to-face) structures are nearly isoenergetic in the benzene dimer. Polycyclic aromatic hydrocarbon dimers prefer slipped-parallel structures. On the other hand, the stable structures of the benzene complexes with pyridinium cations were not known. (4) The difference between the interaction in the benzene−pyridinium complex and that in the benzene−*N*-alkylpyridinium complex was not clear. Detailed information on the difference is important for using these interactions for molecular recognition and self-organization. (5) The difference between the interaction in the neutral benzene−pyridine complex and that in the benzene−pyridinium cation complex was not clear. Therefore, we studied the interactions of the benzene complexes with pyridine, pyridinium and *N*-methylpyridinium by high-level ab initio calculations.

## Computational Method

The Gaussian 03 program[59] was used for the ab initio molecular orbital calculations. The 6-31G*, 6-311G**, and Dunning's correlation consistent basis sets[60−62] were used. Electron correlation was accounted for by the second-order Mφller−Plesset perturbation (MP2) method[63,64] and by coupled cluster calculations with single and double substitutions with noniterative triple excitations [CCSD(T)].[65] The basis set superposition error (BSSE)[66] was corrected for all calculations using the counterpoise method.[67] Geometries of the complexes were optimized by the counterpoise corrected MP2/6-311G* level calculations. Basis set and electron correlation effects on the calculated interaction energy of the cluster are discussed in the Supporting Information. Calculated interaction energy depends considerably on the basis set. MP2 calculations overestimate the attraction compared to more reliable CCSD(T) calculations. Therefore, an estimation of the CCSD(T) interaction energy at the basis set limit is necessary to obtain an accurate interaction energy for a complex. The MP2 interaction energy at the basis set limit [$E_{\mathrm{MP2(limit)}}$] for the complex was estimated by

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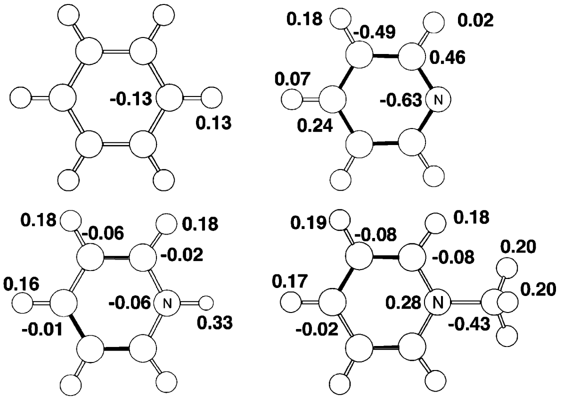

***Figure 2.*** Atomic charges obtained by electrostatic potential fitting using the Merz−Singh−Kollman scheme from the MP2/cc-pVTZ level wave functions. The MP2/6-311G** level optimized geometries were used for the calculations.

Helgaker's method[68] from the calculated MP2 interaction energies ($E_{\mathrm{MP2}}$) using the aug-cc-pVDZ and aug-cc-pVTZ basis sets. The CCSD(T) interaction energy at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] was estimated as the sum of the $E_{\mathrm{MP2(limit)}}$ and the CCSD(T) correction term [$\Delta$CCSD(T) $= E_{\mathrm{CCSD(T)}} - E_{\mathrm{MP2}}$] at the basis set limit. The $\Delta$CCSD(T) at the basis set limit was estimated from the $\Delta$CCSD(T) calculated using the 6-31G* basis set. Details of the estimation procedure[69,70] are described in Supporting Information. Electrostatic energy was calculated as the interactions between distributed multipoles[71,72] of interacting molecules using the ORIENT version 3.2.[73] Distributed multipoles up to hexadecapole on all atoms were obtained from MP2/cc-pVTZ wave functions of isolated molecules using the GDMA program.[74] Induction energy was calculated as the interactions of polarizable sites with the electric field produced by the distributed multipoles of monomers. The atomic polarizabilities of carbon ($\alpha = 10$ au) and nitrogen ($\alpha = 8$ au) were used for the calculations.[75] The distributed multipoles were used only to estimate the electrostatic and induction energies. Atomic charge distributions were calculated by electrostatic potential fitting using the Merz−Singh−Kollman scheme[76,77] from the MP2/cc-pVTZ wave functions of isolated molecules.[78] The MP2/6-311G** level optimized geometries of isolated molecules were used for calculations of the intermolecular interaction energy potentials. The interaction energy potentials were calculated at the MP2/cc-pVTZ level.

## Results and Discussion

**Charge Distributions.** Calculated atomic charge distributions of benzene, pyridine, pyridinium, and *N*-methylpyridinium are shown in Figure 2. Benzene has a negative charge on the center of ring and a positive charge at the periphery. The nitrogen atom and 3- and 5-carbon atoms in pyridine have large negative charges. On the other hand, 2-, 4-, and 6-carbon atoms have substantial positive charges. The charges on the hydrogen atoms of pyridine are not large. The hydrogen atom of the N−H bond in pyridinium has a large positive charge. Other hydrogen atoms in pyridinium also have positive charges. Charges on the nitrogen and carbon atoms are small. The nitrogen atom in *N*-methylpyridinium has a large positive charge in contrast to the small charge on the nitrogen atom in pyridinium. The methyl group and aromatic hydrogen atoms also have positive charges.

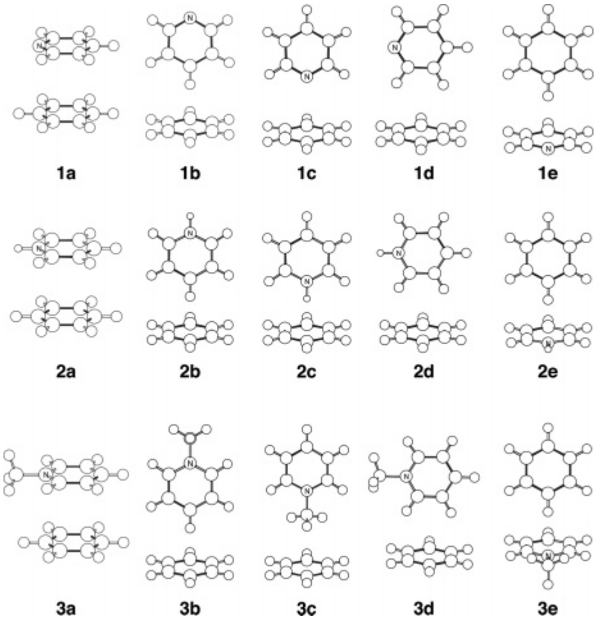

***Figure 3.*** Geometries of benzene−pyridine, benzene−pyridinium and benzene−*N*-methylpyridinium complexes used for calculations of interaction energy potentials.

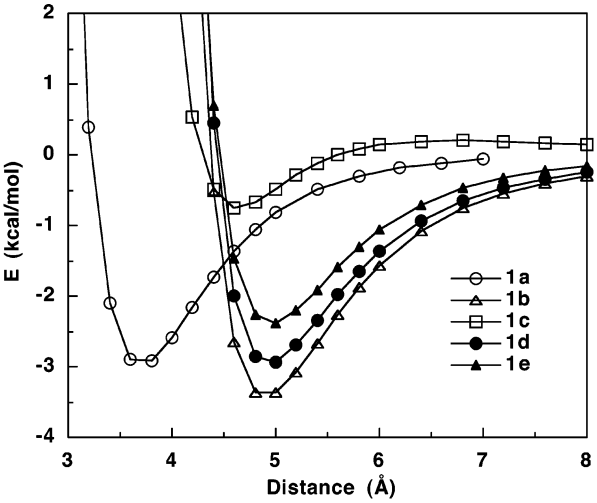

***Figure 4.*** MP2/cc-pVTZ interaction energy potentials for benzene−pyridine complexes. Geometries of the complexes are shown in Figure 3. Intermolecular distance is the distance between the center of benzene and the midpoint of the nitrogen atom and 4-carbon atom of pyridine.

**Interaction Energy in Benzene−Pyridine Complexes.** Calculated interaction energy potentials for five-orientation benzene−pyridine complexes (Figure 3, **1a**−**1e**) are shown in Figure 4. Interaction energy in the benzene−pyridine complex has a strong orientation dependence. The interaction energy in **1c**, in which the nitrogen atom of pyridine points toward the

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(78) The basis set effects on the calculated atomic charge distributions are discussed in the supporting information. The basis set effects are small, if the basis sets including polarization functions (6-31G* or larger) are used.

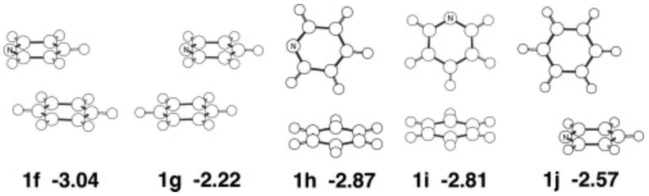

***Figure 5.*** Optimized geometry and estimated CCSD(T) interaction energy (kcal/mol) at the basis set limit for benzene−pyridine complexes.

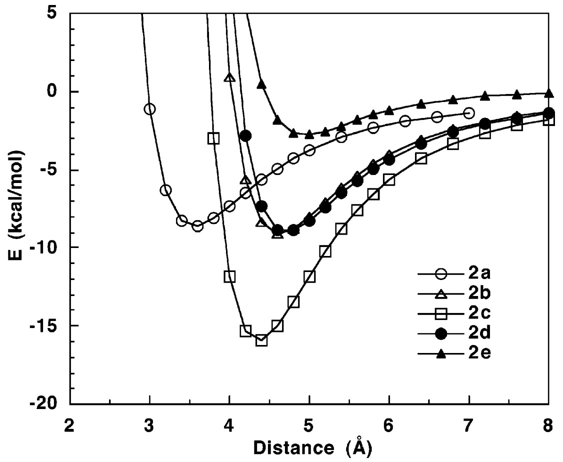

***Figure 6.*** MP2/cc-pVTZ interaction energy potentials for benzene−pyridinium complexes. Geometries of the complexes are shown in Figure 3. Intermolecular distance is the distance between the center of benzene and the midpoint of the nitrogen atom and 4-carbon atom of pyridinium.

center of benzene, is considerably smaller (less negative) than those of other structures.

Five optimized structures for the benzene−pyridine complex (**1f**−**1j**) are shown in Figure 5. Estimated CCSD(T) interaction energies at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] for the five structures are also shown. A slipped-parallel structure **1f** (−3.04 kcal/mol) is the most stable among the five structures. The energy difference between the most stable T-shaped structure **1h** and the most stable slipped-parallel structure **1f** is very small (0.17 kcal/mol).

Mignon et al. reported an MP2 calculation for the slipped-parallel benzene−pyridine complex using a medium size 6-31G*(0.25) basis set.[58] The calculated interaction energy (−2.78 kcal/mol) is not greatly different from the estimated $E_{\mathrm{CCSD(T)(limit)}}$ for **1f** in this work. Apparently, an error cancellation is the cause of the good performance of the MP2 calculation. The MP2 calculation overestimated the attraction, and the medium size basis set underestimated the attraction.

**Interaction Energy in Benzene−Pyridinium Complexes.** Interaction energy potentials for five orientations of benzene−pyridinium complexes (**2a**−**2e**) are shown in Figure 6. The T-shaped structure **2c**, in which the N−H bond of pyridinium points toward the benzene, has a very large interaction energy compared with those of the other structures. The interaction energy for T-shaped structure **2e**, where a C−H bond of the benzene points toward the center of pyridinium, is very small.

Four optimized structures for the benzene−pyridinium complex and their $E_{\mathrm{CCSD(T)(limit)}}$ values are shown in Figure 7. The most stable **2g** (−14.77 kcal/mol) has a T-shaped structure in which the N−H bond of pyridinium points toward the center of benzene. Slipped-parallel structure **2f** and T-shaped structure **2h** are nearly isoenergetic.[79] Interaction energy in the T-shaped structure **2i** is very small.

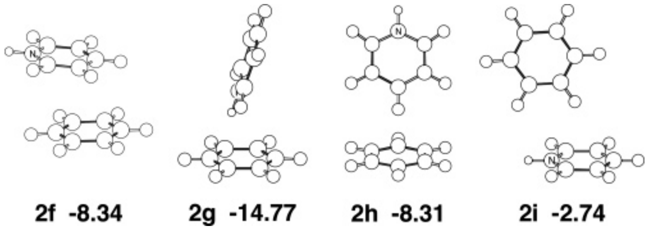

***Figure 7.*** Optimized geometry and estimated CCSD(T) interaction energy at the basis set limit (kcal/mol) for benzene−pyridinium complexes.

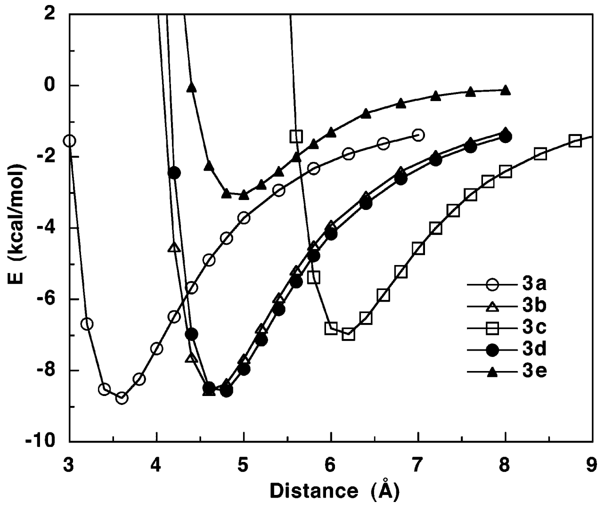

***Figure 8.*** MP2/cc-pVTZ interaction energy potentials for benzene−*N*-methylpyridinium complexes. Geometries of the complexes are shown in Figure 3. Intermolecular distance is the distance between the center of benzene and the midpoint of the nitrogen atom and 4-carbon atom of pyridinium ring.

**Interaction Energy in Benzene−*N*-Methylpyridinium Complex.** Interaction energy potentials for five orientation benzene−*N*-methylpyridinium complexes (**3a**−**3e**) are shown in Figure 8. The interaction energy for T-shaped structure **3e**, where a C−H bond of the benzene has a close contact with the center of the pyridinium ring, is very small.

Six optimized structures for the benzene−*N*-methylpyridinium complex and their $E_{\mathrm{CCSD(T)(limit)}}$ values are shown in Figure 9. Slipped-parallel structure **3f** (−9.36 kcal/mol) is the most stable among the six structures. The most stable T-shaped structure **3h** is 1.36 kcal/mol less stable. The interaction energy of **3k** is very small compared to those of the other five structures. The observed stacked orientation in the reported crystal structures for *N*-methylpyridinium complexes are almost in agreement with these results.[35,38−40]

The benzene−*N*-methylpyridinium complex is a model of the interaction between a nitrogen-containing aromatic cation in the RTILs and a dissolved neutral aromatic solute. The calculations show that the cation binds with a neutral aromatic molecule strongly in the RTILs. The calculated interaction energy for the benzene−*N*-methylpyridinium complex depends greatly on the orientation of benzene. T-shaped structure **3k** is 6.54 kcal/mol less stable than the most stable structure **3f**. The large energy

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(79) Another slipped-parallel structure, in which the nitrogen atom of pyridinium is at the center of benzene as in **1g**, was not a local minimum. This structure turned into a T-shaped structure **2g** after geometry optimization.

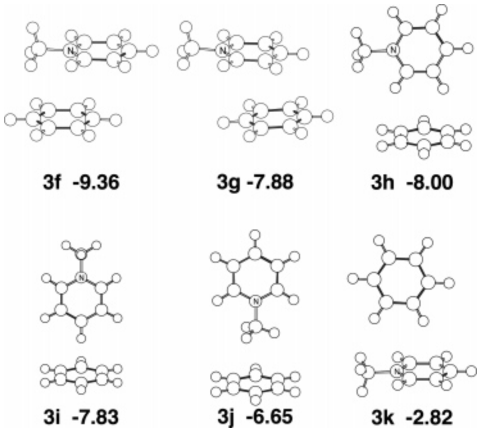

***Figure 9.*** Optimized geometry and estimated CCSD(T) interaction energy at the basis set limit (kcal/mol) for benzene−*N*-methylpyridinium complexes.

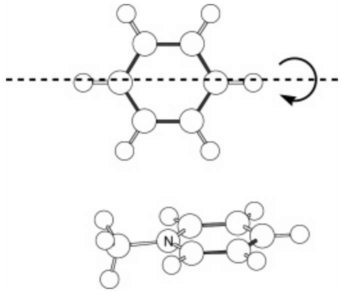

***Figure 10.*** Rotation of benzene interacting with *N*-methylpyridinium.

difference suggests that the rotation of a benzene in pyridinium- or imidazolium-based RTILs (Figure 10) has a large activation energy.[80]

**Origin of Attraction.** Calculated interaction energies for the complexes are summarized in Table 1. The $E_{\text{total}}$ (total interaction energy) is $E_{\text{CCSD(T)(limit)}}$. $E_{\text{es}}$ is the electrostatic energy. $E_{\text{ind}}$ is the induction energy. $E_{\text{corr}}$ ($=E_{\text{total}} - E_{\text{HF}}$) is the electron correlation contribution to the total interaction energy. $E_{\text{corr}}$ is mainly dispersion energy. $E_{\text{rep}}$ ($=E_{\text{HF}} - E_{\text{es}} - E_{\text{ind}}$) is mainly exchange-repulsion energy. However, it also includes some other terms.

The interaction in the pyridine-benzene complex is a $\pi/\pi$ interaction. The dispersion interaction is the major source of the attraction as in the case of the benzene dimer. $E_{\text{corr}}$ is always considerably larger (more negative) than $E_{\text{es}}$ and $E_{\text{ind}}$. Contributions of the electrostatic and induction interactions to the attraction are small. The dispersion interaction enhances the stability of slipped-parallel orientation benzene−pyridine complexes (**1f** and **1g**), while the electrostatic interaction stabilizes the T-shaped orientation (**1h**−**1j**) as in the case of the benzene dimer.[17] The slipped-parallel structure **1g** is less stable than **1f** due to the repulsion between a negative charge on the nitrogen atom of pyridine and a negative charge on the center of benzene. The structure **1j** is slightly less stable than **1h** and **1i** due to the smaller attractive $E_{\text{es}}$ in **1j**.

***Table 1.*** Electrostatic, Induction, and Dispersion Energies of Benzene Complexes with Pyridine, Pyridinium, and *N*-Methylpyridinium[a]

| | $E_{\text{total}}$[b] | $E_{\text{es}}$[c] | $E_{\text{ind}}$[d] | $E_{\text{rep}}$[e] | $E_{\text{corr}}$[f] |
|---|---|---|---|---|---|
| | Benzene−Pyridine | | | | |
| **1f** | −3.04 | 0.39 | −0.22 | 3.27 | −6.48 |
| **1g** | −2.22 | 0.99 | −0.21 | 2.85 | −5.84 |
| **1h** | −2.87 | −0.96 | −0.19 | 1.60 | −3.31 |
| **1i** | −2.81 | −1.01 | −0.20 | 1.26 | −2.86 |
| **1j** | −2.57 | −0.57 | −0.08 | 0.88 | −2.80 |
| | Benzene−Pyridinium | | | | |
| **2f** | −8.34 | −3.50 | −3.15 | 6.02 | −7.71 |
| **2g** | −14.77 | −8.12 | −9.13 | 8.12 | −5.63 |
| **2h** | −8.31 | −4.55 | −3.49 | 3.28 | −3.55 |
| **2i** | −2.74 | 1.29 | −1.57 | 0.88 | −3.34 |
| | Benzene−*N*-Methylpyridinium | | | | |
| **3f** | −9.36 | −4.05 | −3.52 | 5.79 | −7.58 |
| **3g** | −7.88 | −3.05 | −2.77 | 5.79 | −7.86 |
| **3h** | −8.00 | −4.50 | −3.32 | 3.82 | −3.99 |
| **3i** | −7.83 | −4.27 | −3.12 | 3.07 | −3.51 |
| **3j** | −6.65 | −3.73 | −2.58 | 2.95 | −3.29 |
| **3k** | −2.82 | 1.06 | −1.30 | 1.12 | −3.70 |
| | Benzene−Benzene[g] | | | | |
| slipped−parallel | −2.48 | 0.90 | −0.25 | 3.01 | −6.14 |
| T−shape | −2.46 | −0.55 | −0.17 | 1.74 | −3.48 |
| benzene−$K^+$[h] | −17.2 | −11.9 | −12.8 | 11.8[i] | −4.4[j] |

[a] Energy in kcal/mol. The geometries of the clusters are shown in Figures 5, 7, and 9. [b] Estimated CCSD(T) interaction energy at the basis set limit. See text. [c] Electrostatic energy. See text. [d] Induction energy. See text. [e] Repulsion energy ($= E_{\text{HF}} - E_{\text{es}}$). HF/cc-pVQZ interaction energy is used as the $E_{\text{HF}}$. See text. [f] Correlation interaction energy ($= E_{\text{total}} - E_{\text{HF}}$). $E_{\text{corr}}$ is mainly dispersion energy. See text. [g] Refs 17 and 19. [h] Ref 26. [i] Estimated from the sum of $E_{\text{rep}}$ and $E_{\text{corr}}$ (7.4 kcal/mol) and estimated dispersion energy (−4.4 kcal/mol) in ref 26. [j] Estimated dispersion energy in ref 26.

The interactions in the benzene complexes with pyridinium and *N*-methylpyridinium should be categorized into a cation/$\pi$ interaction. The electrostatic and induction interactions contribute largely to the attraction in these complexes as in the cases of the benzene complexes with alkali metal cations.[25,26] The dispersion interaction also contributes substantially to the attraction in the pyridinium and *N*-pyridinium complexes.

The benzene−pyridinium complex **2g** is favored by the strong attraction between the positively charged N−H hydrogen atom and the negative charge on the center of benzene. Induction also stabilizes this structure. A large part of the $E_{\text{ind}}$ in **2g** has its origin in the polarization of benzene by the electric field produced by the pyridinium. The calculated induction energy by polarization of the benzene is −8.71 kcal/mol, while that of the pyridinium is only −0.42 kcal/mol. $E_{\text{es}}$ and $E_{\text{ind}}$ in **2f** are considerably smaller than those in **2g**, while $E_{\text{corr}}$ in **2f** is larger than that in **2g**. The $E_{\text{corr}}$ in **2f** is larger than the sum of $E_{\text{es}}$ and $E_{\text{ind}}$. The $E_{\text{total}}$ for **2i** is small due to the repulsive electrostatic interaction between the positively charged hydrogen atom of the benzene and the pyridinium cation.

Although the interaction in the benzene−pyridinium complex **2g** can be considered as a hydrogen bond, the origin of the attraction in **2g** is considerably different from that in conventional hydrogen bonds, in which the electrostatic interaction is mainly responsible for the attraction and the induction contribution is small.[81] The stable geometry of the benzene−pyridinium complex **2g** is similar to those of neutral NH/$\pi$ complexes such as the benzene−ammonia complex,[21] while the nature of the attraction in **2g** is completely different from that in the neutral NH/$\pi$ complex. The electrostatic and induction interactions are the major source of the attraction in **2g**, while the dispersion and weak electrostatic interactions are responsible for the

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(80) The calculated energy difference between **3f** and **3k** does not directly correspond to the activation energy for the rotation of benzene in pyridinium-based RTILs, because the interaction of benzene with other neighboring ions would affect the activation energy.

(81) Stone, A. J. *Chem. Phys. Lett.* **1993**, *211*, 101−109.

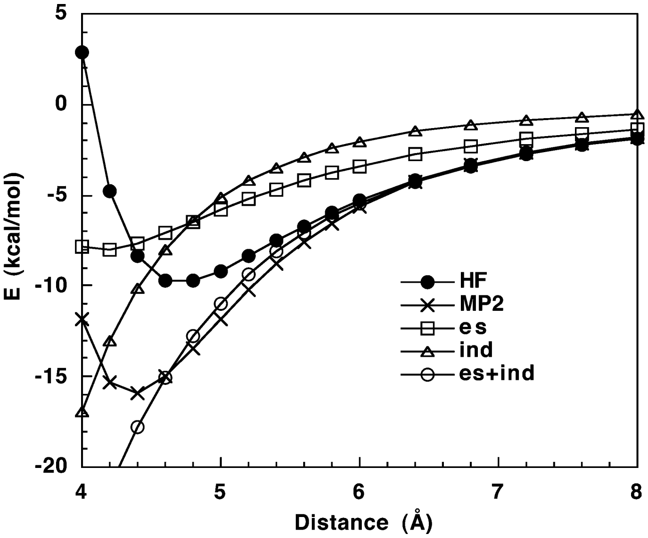

***Figure 11.*** HF and MP2 interaction energies ($E_{\mathrm{HF}}$ and $E_{\mathrm{MP2}}$) and electrostatic and induction energies ($E_{\mathrm{es}}$ and $E_{\mathrm{ind}}$) in benzene−pyridinium complex **2c**.

attraction in the benzene−ammonia complex. The interaction energy in the benzene−ammonia complex (−2.22 kcal/mol) is considerably smaller than that in **2g**.[21]

The slipped-parallel benzene−*N*-methylpyridinium complexes are favored by the strong dispersion interaction. The complex **3f** is more stable than **3g** due to the attraction between the positively charged nitrogen atom and the negative charge on the center of benzene. $E_{\mathrm{total}}$'s for the three T-shaped complexes (**3h**−**3j**) are not largely different due to the small differences in $E_{\mathrm{es}}$, in contrast to a large difference in the $E_{\mathrm{total}}$'s for **2g** and **2h**. $E_{\mathrm{total}}$ for **3k** is small due to the repulsive electrostatic interaction as in the case of **2i**.

The calculated potentials for the three complexes (Figures 4, 6 and 8) show that substantial attraction still exists even when the molecules are well separated, which shows that long-range interactions ($E \sim R^{-n}$) (electrostatic, induction and dispersion interactions) contribute greatly to the attractions in the complexes. The energies of long-range interactions behave as some inverse power of the distance. On the other hand short-range interactions ($E \sim e^{-\alpha R}$) (charge-transfer and orbital−orbital interactions) arise at the distance where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance.[82]

$E_{\mathrm{es}}$ and $E_{\mathrm{ind}}$ in **2c** were calculated by changing the intermolecular distance. The calculated $E_{\mathrm{es}}$ and $E_{\mathrm{ind}}$ are compared with the $E_{\mathrm{HF}}$ and $E_{\mathrm{MP2}}$ to confirm the contributions of the electrostatic and induction interactions to the attraction as shown in Figure 11. The sum of $E_{\mathrm{es}}$ and $E_{\mathrm{ind}}$ are very close to $E_{\mathrm{HF}}$ when the intermolecular distance ($R$) is larger than 5.4 Å, which indicates that the electrostatic and induction interactions are the main components of $E_{\mathrm{HF}}$ and that the contributions of other terms are not large when $R > 5.4$ Å. $E_{\mathrm{HF}}$ is always smaller (less negative) than the sum of $E_{\mathrm{es}}$ and $E_{\mathrm{ind}}$ when $R < 5.4$ Å. The exchange-repulsion, which arises at a short intermolecular separation, is the cause of the smaller $E_{\mathrm{HF}}$. The comparison of $E_{\mathrm{HF}}$ and the sum of $E_{\mathrm{es}}$ and $E_{\mathrm{ind}}$ does not suggest the existence of any specific attraction due to short-range interactions in **2c**. The $E_{\mathrm{MP2}}$ is larger (more attractive) than $E_{\mathrm{HF}}$ due to the dispersion contribution. These results suggest that the short-range interactions are not very important for the attraction in the complexes.

**Comparison with Benzene Dimer and Benzene−Alkali Metal Cation Complexes.** The interaction energies in the benzene complex with pyridinium and *N*-methylpyridinium are significantly larger than those in the benzene−pyridine complex and benzene dimer. The $E_{\mathrm{total}}$ for the most stable benzene−pyridinium complex **2g** (−14.77 kcal/mol) is about 5 times that for the most stable benzene−pyridine complex **1f** (−3.04 kcal/mol). The $E_{\mathrm{total}}$ for the most stable *N*-methylpyridinium complex **3f** (−9.36 kcal/mol) is 3 times that for **1f**. **2g** and **3f** are stabilized by the much larger electrostatic and induction interaction, which is a characteristic feature of the cation/$\pi$ interaction. The size of the $E_{\mathrm{total}}$ for the most stable benzene−pyridinium complex **2g** is close to those for the benzene complexes with $K^+$ and $Rb^+$ (−17.0 and −13.9 kcal/mol, respectively). The size of the $E_{\mathrm{total}}$ for the benzene−*N*-methylpyridinium complex **3f** is smaller than that for the benzene−$Cs^+$ complex (−12.1 kcal/mol).[26] The dispersion interaction also contributes substantially to the attraction in the benzene complexes with pyridinium and *N*-methylpyridinium, while the dispersion energy in the benzene−$K^+$ complex is substantially smaller than the electrostatic and induction energies in the complex as shown in Table 1. The benzene−pyridine complex **1f** (−3.04 kcal/mol) is slightly more stable than the benzene dimer (−2.48 kcal/mol) due to smaller repulsive $E_{\mathrm{es}}$ in **1f**.

## Conclusion

Intermolecular interaction energies for the benzene complexes with pyridine, pyridinium, and *N*-methylpyridinium were evaluated by high-level ab initio calculations. The calculations show that the interactions in the pyridinium and *N*-methylpyridinium complexes are significantly larger than those in the benzene−pyridine complex and the benzene dimer. The pyridinium and *N*-methylpyridinium complexes are stabilized by large electrostatic and induction interactions. The interaction in the pyridinium and *N*-methylpyridinium complexes should be categorized as a cation/$\pi$ interaction. On the other hand, the interaction in the benzene−pyridine complex is a $\pi/\pi$ interaction. The dispersion interaction is mainly responsible for the attraction in the benzene−pyridine complex as in the case of the benzene dimer. Short-range interactions (charge-transfer or orbital−orbital interactions) are not important for the attraction in the complexes.

The benzene−*N*-methylpyridinium complex prefers a slipped-parallel structure. The size of the interaction energy depends strongly on the orientation of benzene, which suggests that the rotation of benzene dissolved in pyridinium- or imidazolium-based RTILs has a large activation energy. The most stable benzene−pyridinium complex has a T-shaped structure, where the N−H bond of pyridinium points toward the benzene. This structure is favored by the strong attraction between the positively charged N−H hydrogen atom and the negatively

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(82) The intermolecular interactions can be separated into two main types. One is long-range interactions where the energy of interaction behaves as some inverse power of $R$. The electrostatic, induction, and dispersion interactions are long-range interactions. Another is short-range interactions where the energy decreases exponentially with distance. The short-range interactions arise at distances where the molecular wavefunctions overlap significantly. The exchange-repulsion and charge-transfer interactions are short-range interactions.

charge on the center of benzene. Although the stable structure of the benzene−pyridinium complex is similar to that of neutral NH/$\pi$ complexes, the nature of the attraction in the pyridinium complex is completely different from that in the neutral NH/$\pi$ complexes. The most stable slipped-parallel structure is about 6 kcal/mol less stable than the T-shaped one. The energy difference between the T-shaped and slipped-parallel benzene−pyridine complexes is very small.

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**Supporting Information Available:** Discussion on basis set and electron correlation effects, estimation procedure for MP2 and CCSD(T) interaction energies at the basis set limit, complete ref 59, Cartesian coordinates and calculated energies of optimized geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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