# Origin of the Attraction and Directionality of the NH/π Interaction: Comparison with OH/π and CH/π Interactions

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*Received May 30, 2000. Revised Manuscript Received September 20, 2000*

**Abstract:** High-level ab initio calculations were carried out to evaluate the interaction between the π face of benzene and ammonia as a model of NH/π interaction. The intermolecular interaction energy was calculated from the extrapolated MP2 interaction energy at the basis set limit and a CCSD(T) correction term. The calculated interaction energy (−2.22 kcal/mol) is considerably smaller than that of the hydrogen bond between waters. The monodentate complex is slightly more stable than the bidentate and tridentate complexes. The potential energy surface is very flat near the minimum, which shows that the major source of the attraction is a long-range interaction. The HF interaction energy of the monodentate complex (0.13 kcal/mol) is repulsive. The large gain in the attraction by electron correlation correction (−2.36 kcal/mol) indicates that the dispersion interaction is significantly important for the attraction. The electrostatic energy (−1.01 kcal/mol) is also important for the attraction. The benzene−water (OH/π) interaction energy (−3.17 kcal/mol) is larger than the benzene−ammonia (NH/π) interaction. The dispersion interaction is again important for the attraction in the benzene−water complex. The attraction in the benzene−ammonia complex is stronger than that in the benzene−methane (CH/π) complex (−1.45 kcal/mol). The amount of electrostatic energy is mainly responsible for the magnitude of the attractions in these three complexes. The directionality for the NH/π and OH/π interactions is mainly controlled by the electrostatic interaction.

## Introduction

Hydrogen bonding plays a dominant role in many forefront areas of modern chemistry from molecular biology to material design.[1−6] Hydrogen bonding is the attraction between a proton donor (a proton attached to an electronegative atom; OH, NH, etc.) and a proton acceptor (another electronegative atom or an electronegative group).[7] Aromatic hydrocarbons have proton-accepting ability and can play a role as proton acceptors. Suzuki et al.[8] and Rodham et al.[9] reported spectroscopic measurements of the benzene−water and benzene−ammonia complexes. Their measurements showed that the water and ammonia molecules are positioned above the benzene plane and that the benzene acts as a proton acceptor.

The attraction between an NH bond and a π-system is called an NH/π interaction. This interaction was first reported in 1959 by Oki and Imamura from the measurements of the IR spectra of *N*-benzylaniline and its derivatives.[10] The NH/π interaction was also observed in other systems.[11−16] In 1986 Perutz et al. reported the NH/π interaction in the hemoglobin-drug complex.[17] The short contact was also found in several proteins.[18−28] Fong et al. reported that the NH/π interaction is important for the selective binding of receptor protein with neurotransmitter.[21] Burley and Petsko reported that amino groups prefer to locate above and below the aromatic ring and close to the center.[29]

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10.1021/ja001901a CCC: $19.00

The NH/$\pi$ interaction is believed to be an important interaction for structures of proteins. The close contact was also observed in crystals of small molecules.[30−32] It is believed that the NH/$\pi$ interaction is also important for crystal packing.

Whetsel and Lady reported that the NH/$\pi$ interaction energies in the *N*-methylaniline−benzene and aniline−benzene systems were −1.5 and −1.6 kcal/mol, respectively.[33] Oki and Mutai reported from thermodynamic analysis that the interaction energy in *N*-benzylaniline was smaller (less negative) than −2 kcal/mol.[16,34] Rodham et al. reported that one NH bond pointed toward the benzene ring in the benzene−ammonia complex. They estimated from the experimental centrifugal distortion constant $D_J$ that the interaction energy was −1.4 kcal/mol.[9]

A few theoretical calculations of the benzene−ammonia complex were reported. In early studies the interaction energies were calculated by using Hartree−Fock (HF) level optimized geometries.[31,35−37] But HF calculation cannot evaluate the dispersion interaction, which is a significantly important interaction in the benzene−ammonia complex as we will describe later. Rodham et al. reported[9] the geometry optimization by the second-order Møller−Plesset perturbation method (MP2)[38,39] using the 6-31G** basis set.[40] Inoue et al. reported[41] the geometry obtained by the density functional calculation with Becke's exchange and Lee, Yang, and Parr's correlation functionals (BLYP).[42,43] Both groups obtained monodentate structures. The calculated MP2/6-31G** interaction energy without basis set superposition error (BSSE)[44] correction was −2.4 kcal/mol.[9] The interaction energy from the density functional calculation was −1.4 kcal/mol.[41]

Although these experimental and theoretical studies provided valuable pieces of information on the NH/$\pi$ interaction, there still remain a number of important and fundamental unsettled issues about the NH/$\pi$ interaction. (1) Despite broad interests in the NH/$\pi$ interaction in many area of chemistry and biology, very little is known about the origin of the NH/$\pi$ interaction. (2) Another important issue is the directionality of the NH/$\pi$ interaction. Spectroscopic measurements[9] and recent theoretical calculations[9,41] indicate that the benzene−ammonia complex prefers a monodentate structure, while it is not certain why the monodentate structure is the most stable. A statistical analysis of the crystal structure database showed that different types of orientations also exist in crystals.[31] The energy difference among the monodentate, bidentate, and tridentate structures has not yet been accurately evaluated. (3) The similarity among the NH/$\pi$, OH/$\pi$, and CH/$\pi$ interactions has been pointed out repeatedly,[10,14,16,45] while the difference among these interactions (the origin of the attraction and the magnitude of the attraction) is still not well understood.

In this paper we have provided detailed evaluations of the interaction of the benzene−ammonia complex by high-level ab initio calculations. Absolute values of recently reported experimental interaction energies of the NH/$\pi$ interaction are less than 3 kcal/mol. It is well-known that ab initio calculations using very large basis sets and appropriate electron correlation correction are necessary to accurately evaluate such weak interactions.[46−48] However, such a very accurate calculation has not yet been reported for this system. We have calculated the MP2 interaction energies of a few orientations of benzene−ammonia complexes with Dunning's correlation consistent basis sets and estimated the MP2 interaction energies at the basis set limit. In addition we have carried out the coupled cluster calculations using single and double substitutions with noniterative triple excitations (CCSD(T))[49,50] to include electron correlation beyond MP2. We have discussed the orientation dependence of the stability of the complexes and the role of electrostatic, dispersion, and charge-transfer terms for the attraction. We have also carried out calculations of the benzene−water complexes and have discussed the difference among the NH/$\pi$, OH/$\pi$, and CH/$\pi$ interactions.

## Computational Method

The Gaussian 94 and Gaussian 98 programs[51,52] were used for the ab initio molecular orbital calculations. The 6-311G**[53] and cc-pVXZ (X = **D**, **T**, and **Q**)[54,55] basis sets were used. Electron correlation was corrected by the MP2[38,39] and CCSD(T)[49,50] methods. The geometries of isolated molecules were optimized at the MP2/6-311G** level, and were used for the calculations of complexes. Basis set superposition error (BSSE)[44] was corrected for all calculations using the counterpoise method.[56] MP2 interaction energies at the basis set limit were estimated by the method proposed by Feller.[57] Distributed multipoles[58,59] were

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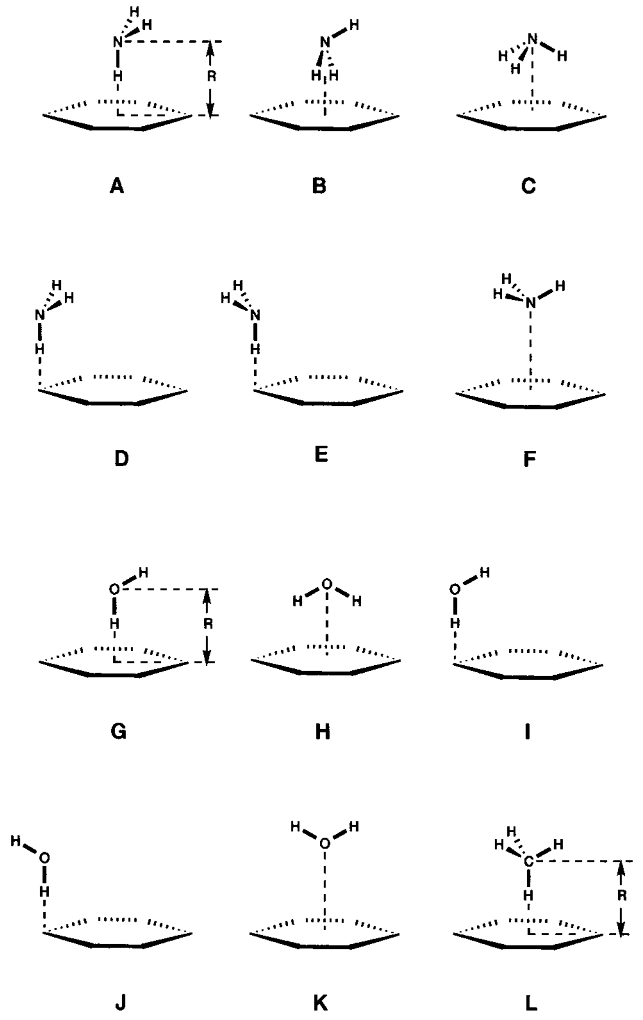

**Figure 1.** The geometries of the benzene−ammonia, benzene−water, and benzene−methane complexes considered in this work. The ammonia, water, and methane are above the center of the benzene ring in the complexes **A**−**C**, **F**−**H**, **K**, and **L**. The ammonia and water are above one of the carbon atoms of the benzene in the complexes **D**, **E**, **I**, and **J**.

obtained from MP2/6-311G** wave functions of isolated molecules using CADPAC version 6.[60] Electrostatic energies of the complexes were calculated as interactions between distributed multipoles using ORIENT version 3.2.[61]

## Results and Discussion

**Basis Set Effects on HF and MP2 Interaction Energies.** The intermolecular interaction potentials of the benzene−ammonia and benzene−water complexes **A** and **G** (Figure 1) were calculated using the 6-311G** and cc-pVXZ (X = **D**, **T**, and **Q**) basis sets as shown in Figures 2 and 3. The basis set dependence of the HF interaction energies is very small. The HF interaction energy is mainly exchange-repulsion and electrostatic energies. On the other hand the depths of the MP2 potentials strongly depend on basis set. The calculated interaction energies of the complexes **A**−**D** and **G**−**J** (Figure 1) are summarized in Table 1. The intermolecular distances (*R*) of the complexes correspond to the MP2/cc-pVTZ potential minima (Figures 4 and 5). The small cc-pVDZ and 6-311G** basis sets (143 and 180 basis functions for the benzene−ammonia complex, respectively) lead to considerable underestimation of the attraction compared to a large cc-pVQZ basis set (655 basis functions). The MP2/cc-pVDZ interaction energies of the complexes **A**−**D** and **G**−**I** are −1.25, −1.13, −0.66, −1.02, −1.88, −2.03, and −1.81 kcal/mol, respectively, while the energies at the MP2/cc-pVQZ level are −2.37, −2.15, −1.70, −1.97, −3.13, −3.17, and −2.90 kcal/mol, respectively. The MP2/cc-pVDZ calculation thus underestimates the interaction energies as much as 36−61%. These results illustrate the well-known fact that very large basis sets are necessary to accurately evaluate the dispersion interaction.[46−48]

Electron correlation leads to considerable increase in the attraction. The HF interaction energies of the complexes **A**−**D** and **G**−**I** calculated with the cc-pVQZ are 0.13, 0.23, 0.62, 0.29, −0.79, −0.92, and −0.79 kcal/mol, respectively. The large gain in the attraction by electron correlation (−2.11 to −2.50 kcal/mol) indicates that the dispersion interaction is significantly important for the attraction in both the benzene−ammonia and benzene−water complexes.

The calculated BSSE values in Table 1 indicate that the MP2 calculations have substantially larger BSSE than the HF calculations. The size of the BSSE depends strongly on the basis set. The MP2 calculations with small 6-311G** and cc-pVDZ basis sets have large BSSE (1.01−2.02 kcal/mol). The magnitude of the BSSE values is close to the size of the calculated interaction energies. The increase in the size of the basis set decreases the BSSE. The BSSE values in the MP2/cc-pVQZ calculations are 0.47−0.81 kcal/mol. The BSSE values in the calculations of the benzene−water complex **G** are larger than those of the benzene−ammonia complex **A**. The shorter intermolecular distance of the benzene−water complex would be the cause of the larger BSSE.

**Effects of Electron Correlation Beyond MP2.** The interaction energies of the benzene−ammonia and benzene−water complexes were calculated by the MP3, CCSD, and CCSD(T) methods with the cc-pVDZ basis set to evaluate the effect of electron correlation beyond MP2 as summarized in Table 2. The MP2 interaction energies are larger (more negative) than the CCSD(T) energies. The MP3 interaction energies are close to the CCSD(T) values. The CCSD calculations substantially underestimate the attraction compared to the CCSD(T) values. Similar underestimation is also observed in the calculations of $CO_2$ clusters,[62,63] hydrogen bonding complexes,[64] and benzene−hydrocarbon systems.[65,66] These results suggest the importance of triple excitations to evaluate the attractive interaction.

The CCSD(T) correction term ($\Delta_{CCSD(T)}$), the difference between the MP2 and CCSD(T) interaction energies using the

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**Table 1.** Calculated Interaction Energies of the Benzene−Ammonia and Benzene−Water Complexes[a]

| | benzene-anmmonia | | | | benzene-water | | |
|---|---|---|---|---|---|---|---|
| method | **A** | **B** | **C** | **D** | **G** | **H** | **I** |
| HF/6-311G** | 0.06 (0.58) | 0.06 (0.64) | 0.45 (0.93) | 0.16 (0.48) | −0.88 (0.87) | −1.23 (1.14) | −0.95 (0.76) |
| HF/cc-pVDZ | 0.10 (0.55) | 0.14 (0.65) | 0.51 (0.98) | 0.25 (0.46) | −0.81 (0.81) | −1.08 (1.06) | −0.80 (0.70) |
| HF/cc-pVTZ | 0.13 (0.35) | 0.22 (0.43) | 0.61 (0.62) | 0.29 (0.33) | −0.79 (0.55) | −0.93 (0.76) | −0.78 (0.51) |
| HF/cc-pVQZ | 0.13 (0.21) | 0.23 (0.23) | 0.62 (0.30) | 0.29 (0.21) | −0.79 (0.32) | −0.92 (0.38) | −0.79 (0.31) |
| MP2/6-311G** | −1.45 (1.40) | −1.37 (1.20) | −0.89 (1.55) | −1.24 (1.04) | −2.11 (1.87) | −2.34 (2.02) | −2.09 (1.52) |
| MP2/cc-pVDZ | −1.25 (1.26) | −1.13 (1.22) | −0.66 (1.61) | −1.02 (1.01) | −1.88 (1.64) | −2.03 (1.87) | −1.81 (1.39) |
| MP2/cc-pVTZ | −2.07 (0.82) | −1.85 (0.87) | −1.38 (1.19) | −1.70 (0.72) | −2.78 (1.19) | −2.81 (1.49) | −2.60 (1.09) |
| MP2/cc-pVQZ | −2.37 (0.47) | −2.15 (0.48) | −1.70 (0.60) | −1.97 (0.47) | −3.13 (0.72) | −3.17 (0.81) | −2.90 (0.69) |
| $E_{MP2}$(limit)[b] | −2.55 | −2.35 | −1.94 | −2.14 | −3.36 | −3.46 | −3.10 |
| ΔCCSD(T)[c] | 0.33 | 0.27 | 0.22 | 0.30 | 0.34 | 0.29 | 0.33 |
| $E_{CCSD(T)}$(limit)[d] | −2.22 | −2.07 | −1.72 | −1.84 | −3.02 | −3.17 | −2.77 |
| $R$[e] | 3.6 | 3.6 | 3.6 | 3.6 | 3.4 | 3.4 | 3.4 |

[a] Energies in kcal/mol. BSSE corrected interaction energies. The values in parentheses are BSSE's. The geometries of the complexes are shown in Figure 1. [b] Estimated MP2 interaction energies at the basis set limit. See text. [c] Difference between the interaction energies calculated with the CCSD(T)/cc-pVDZ and MP2/cc-pVDZ methods. [d] Expected CCSD(T) interaction energies at the basis set limit. Sum of $E_{MP2}$(limit) and ΔCCSD(T). [e] Intermolecular distances in Å. See Figure 1.

**Table 2.** Interaction Energies of the Benzene−Ammonia Complex **A**−**D** and Benzene−Water Complexe **G**−**I** Calculated with Electron Correlation Correction by Several Methods[a]

| | benzene-ammonia complex[b] | | | | benzene-water complex[c] | | |
|---|---|---|---|---|---|---|---|
| | **A** | **B** | **C** | **D** | **G** | **H** | **I** |
| HF | 0.10 | 0.14 | 0.51 | 0.25 | −0.81 | −1.08 | −0.80 |
| MP2 | −1.25 | −1.13 | −0.66 | −1.02 | −1.88 | −2.03 | −1.81 |
| MP3 | −0.88 | −0.82 | −0.41 | −0.69 | −1.52 | −1.73 | −1.47 |
| CCSD | −0.79 | −0.72 | −0.31 | −0.57 | −1.43 | −1.61 | −1.34 |
| CCSD(T) | −0.92 | −0.86 | −0.45 | −0.72 | −1.54 | −1.74 | −1.48 |

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the complexes are shown in Figure 1. The cc-pVDZ basis set was used. [b] Intermolecular distance $R = 3.6$ Å. [c] Intermolecular distance $R = 3.4$ Å.

**Table 3.** Basis Set Effects on the Calculated HF, MP2, MP3, CCSD, and CCSD(T) Interaction Energies of Benzene−Ammonia Complex **A** and Benzene−Water Complex **G**[a]

| basis set | HF | MP2 | MP3 | CCSD | CCSD(T) | ΔCCSD(T)[b] |
|---|---|---|---|---|---|---|
| benzene−ammonia complex **A**[c] | | | | | | |
| 6-311G* | −0.01 | −1.31 | −1.02 | −0.90 | −1.03 | 0.28 |
| 6-311G** | 0.06 | −1.45 | −1.07 | −0.96 | −1.12 | 0.32 |
| cc-pVDZ | 0.10 | −1.25 | −0.88 | −0.79 | −0.92 | 0.33 |
| cc-pVTZ | 0.13 | −2.07 | −1.55 | −1.41 | −1.69 | 0.38 |
| benzene−water complex **G**[d] | | | | | | |
| 6-311G* | −1.13 | −2.15 | −1.89 | −1.75 | −1.85 | 0.30 |
| 6-311G** | −0.88 | −2.11 | −1.74 | −1.63 | −1.77 | 0.33 |
| cc-pVDZ | −0.81 | −1.88 | −1.52 | −1.43 | −1.54 | 0.34 |
| cc-pVTZ | −0.79 | −2.78 | −2.30 | −2.17 | −2.43 | 0.35 |

[a] Energies in kcal/mol. BSSE corrected interaction energies. The geometries of the complexes are shown in Figure 1. [b] Difference between the interaction energies calculated with the CCSD(T) and MP2 methods. [c] Intermolecular distance $R = 3.6$ Å. [d] Intermolecular distance $R = 3.4$ Å.

cc-pVDZ, is not large. The $\Delta_{CCSD(T)}$ values of the complexes **A**−**D** and **G**−**I** are 0.33, 0.27, 0.22, 0.30, 0.34, 0.29, and 0.33 kcal/mol, respectively. The CCSD(T) interaction energies of the complex **A** and **G** were also calculated using the 6-311G*, 6-311G**, and cc-pVTZ basis sets as shown in Table 3. The CCSD(T) interaction energies depend on the basis set, while the basis set dependence of the $\Delta_{CCSD(T)}$ is very small. The $\Delta_{CCSD(T)}$ values of complex **A** calculated with these basis sets (0.28, 0.32, and 0.38 kcal/mol, respectively) are close to that with cc-pVDZ (0.33 kcal/mol). The $\Delta_{CCSD(T)}$ values of complex **G** calculated with these basis sets (0.30, 0.33, and 0.35 kcal/mol, respectively) are also close to that with cc-pVDZ (0.34 kcal/mol).

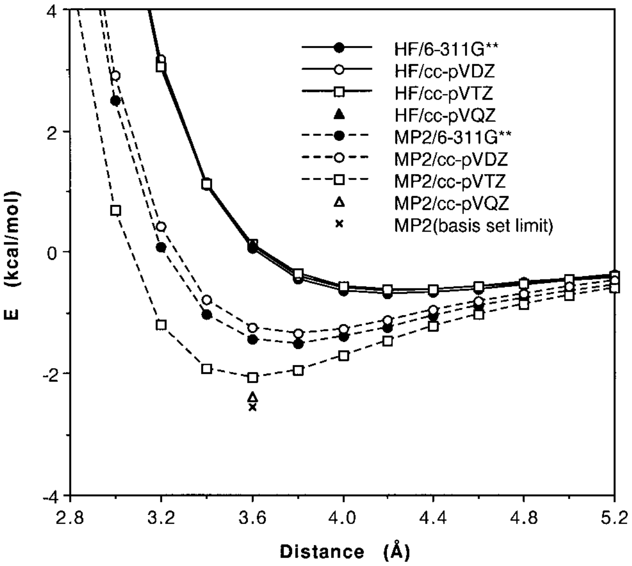

**Figure 2.** The HF and MP2 intermolecular interaction potentials of the benzene−ammonia complex **A** calculated with several basis sets.

**Intermolecular Interaction Potentials of Benzene−Ammonia Complexes.** The intermolecular interaction potentials of the six complexes **A**−**F** (Figure 1) were calculated at the MP2/cc-pVTZ level as shown in Figure 4. Although the complex **F** does not have a hydrogen bond, this complex was added to understand to what extent the hydrogen bond stabilizes the complexes. The potential of complex **A** has the deepest minimum. The calculated potentials of complexes **A**−**E** have their minima at intermolecular distances ($R$) of 3.6, 3.6, 3.6, 3.6, and 3.8 Å, respectively. The potential of complex **F** does not have a minimum. The calculated potentials are very flat near the minima. The calculated potential of complex **A** (Figure 2) shows that substantial attraction still exists, even if the intermolecular distance is larger than 4.0 Å. This suggests that the major source of the attraction is not short-range interactions ($E \sim e^{-\alpha R}$), such as charge transfer, but long-range interactions ($E \sim R^{-n}$), such as electrostatic and dispersion.[67] The calculated interaction energy of complex **A** is substantially larger than those

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(67) Nonbonding interactions can be separated into two main types. One is long-range interactions such as electrostatic and dispersion interactions where the energy of interaction behaves as some inverse power of R. Another is short-range interactions such as exchange-repulsion and charge-transfer interactions. Short-range interactions arise at distances where the molecular wave functions overlap significantly. The energies of short-range interactions decrease exponentially with distance.

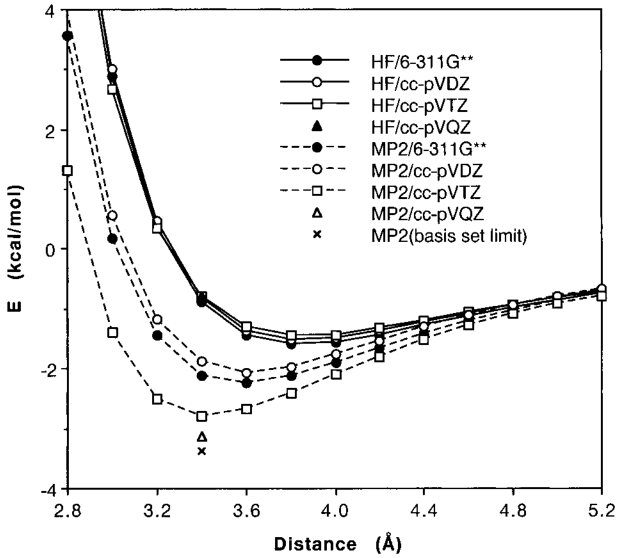

**Figure 3.** The HF and MP2 intermolecular interaction potentials of the benzene−water complex **G** calculated with several basis sets.

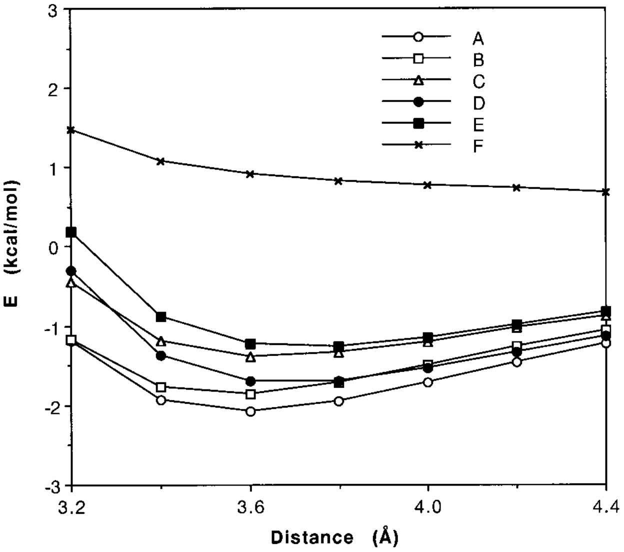

**Figure 4.** The MP2/cc-pVTZ intermolecular interaction potentials of the six benzene−ammonia complexes.

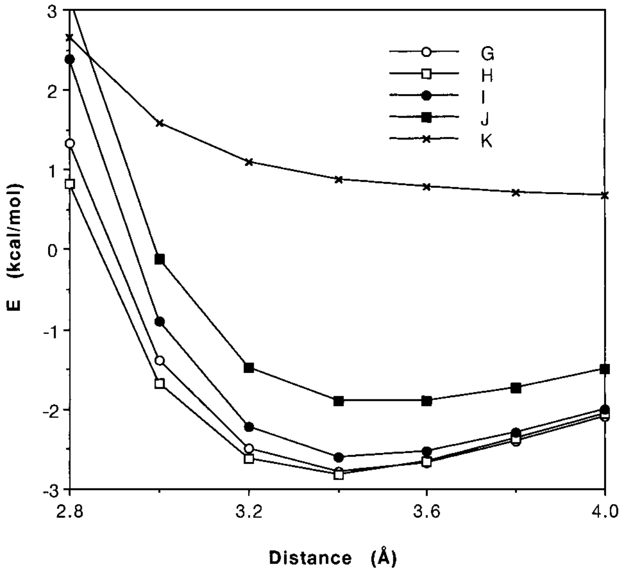

**Figure 5.** The MP2/cc-pVTZ intermolecular interaction potentials of the five benzene−water complexes.

of **D** and **E**, which indicates that the ammonia prefers to locate above the center of the benzene ring. This preference agrees well with the experimental observation. Burley and Petsko have reported that the amino group prefers to locate above the center of the aromatic ring.[29]

The MP2 interaction energies at the basis set limit ($E_{\rm MP2(limit)}$) were estimated by extrapolation of the MP2 interaction energies calculated with Dunning's correlation consistent basis sets using the method proposed by Feller. The form $a + b\ \exp(-cX)$ (where $X$ is 2 for cc-pVDZ, *3* for cc-pVTZ, etc.) was fitted to the calculated interaction energies.[57] The $E_{\rm MP2(limit)}$ of complexes **A**−**D** at their potential minima are −2.55, −2.35, −1.94, and −2.14 kcal/mol, respectively, as summarized in Table 1. These values are not largely different from the values calculated with cc-pVQZ, indicating that cc-pVQZ is close to the saturation. The MP2/cc-pVQZ interaction energies are only 0.17−0.29 kcal/mol smaller (less negative) than the corresponding $E_{\rm MP2(limit)}$. The expected CCSD(T) interaction energies of the complexes at the basis set limit ($E_{\rm CCSD(T)(limit)}$, the sum of the $E_{\rm MP2(limit)}$ and $\Delta C$CSD(T)) are −2.22, −2.07, −1.72, and −1.84 kcal/mol, respectively. This shows that the monodentate complex **A** (one NH bond points toward the benzene) is slightly more stable than the bidentate and tridentate complexes **B** and **C**. Rodham et al. reported from their spectroscopic measurement that the ammonia is above the benzene ring and one N−H bond points toward the benzene ring.[9] Our calculations agree well with their experimental measurement. The calculated interaction energy ($E_e$) of the benzene−ammonia complex **A** (−2.22 kcal/mol) is about 40% of the hydrogen bonding energy of the water dimer.[68,69]

The vibrational zero-point energies (ZPE) of monomers and the energy minimum monodentate complex were calculated at the MP2/cc-pVTZ level. The calculated ZPE values of benzene and ammonia monomers and the benzene−ammonia complex were 0.100713, 0.034813, and 0.136502 hartrees, respectively. The change of the ZPE by the formation of the dimer (ΔZPE) is 0.61 kcal/mol. The calculated $E_e$ value of the benzene−ammonia complex **A** ($E_{\rm CCSD(T)(limit)} = -2.22$ kcal/mol) and the ΔZPE led to the $E_0$ value of −1.61 kcal/mol. This value is very close to the experimental $E_0$ (−1.4 kcal/mol) of the benzene−ammonia complex.[9] Rodham et al. reported that the MP2/6-31G* level interaction energy ($E_e$) was −2.4 kcal/mol.[9] Although they used a considerably smaller 6-31G* basis set, the calculated $E_e$ is slightly larger (more negative) than our value. They did not correct the BSSE in their calculations, which leads to the large interaction energy. Inoue et al. reported that the $E_e$ was −1.4 kcal/mol from their density functional calculations with the BLYP functionals.[41] It has been reported that the BLYP functionals cannot evaluate the attractive dispersion interaction in rare gas dimers and hydrocarbon dimers.[70−73] This deficiency of the BLYP functionals would be the cause of the small $E_e$.

**Intermolecular Interaction Potentials of Benzene−Water Complexes.** The intermolecular interaction potentials of the five complexes **G**−**K** (Figure 1) were calculated at the MP2/cc-pVTZ level as shown in Figure 5. Complex **K** was added for

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**Table 4.** Electrostatic and Dispersion Energies of the Benzene−Ammonia, Benzene−Water, and Benzene−Methane Complexes[a]

| | benzene−anmmonia | | | | benzene−water | | | benzene−methane[b] |
|---|---|---|---|---|---|---|---|---|
| energy | **A** | **B** | **C** | **D** | **G** | **H** | **I** | **L** |
| $E_{\mathrm{total}}$[c] | −2.22 | −2.07 | −1.72 | −1.84 | −3.02 | −3.17 | −2.77 | −1.45 |
| $E_{\mathrm{es}}$[d] | −1.01 | −0.91 | −0.79 | −1.22 | −1.86 | −2.14 | −2.14 | −0.25 |
| $E_{\mathrm{rep}}$[e] | 1.14 | 1.14 | 1.41 | 1.51 | 1.07 | 1.22 | 1.36 | 1.10 |
| $E_{\mathrm{corr}}$[f] | −2.36 | −2.31 | −2.34 | −2.13 | −2.23 | −2.25 | −1.98 | −2.30 |
| $R$[g] | 3.6 | 3.6 | 3.6 | 3.6 | 3.4 | 3.4 | 3.4 | 3.8 |

[a] Energies in kcal/mol. The geometries of the complexes are shown in Figure 1. [b] Reference 65. [c] Expected CCSD(T) interaction energies at the basis set limit ($E_{\mathrm{CCSD(T)(limit)}}$). See text and footnote *d* of Table 1. [d] Electrostatic interaction energy. See text. [e] The difference between the HF/cc-pV5Z interaction energy ($E_{\mathrm{HF}}$) and $E_{\mathrm{es}}$. [f] The difference between the $E_{\mathrm{total}}$ ($E_{\mathrm{CCSD(T)(limit)}}$) and HF/cc-pV5Z interaction energy ($E_{\mathrm{HF}}$). [g] Intermolecular distances in Å.

comparison. The depths of the potentials of complexes **G** and **H** are not largely different. The calculated potentials of complexes **G**−**J** have their minima at intermolecular distances ($R$) of 3.4, 3.4, 3.4, and 3.6 Å, respectively. The potential of complex **K** does not have a minimum. The calculated potentials are very flat near the minima, as in the case of the benzene−ammonia complex. The calculated potential of complex **G** (Figure 3) shows that substantial attraction still exists, even if the intermolecular distance is larger than 4.0 Å.[67] The major source of the attraction in the benzene−water complex is again long-range interactions. The calculated potential depths of complexes **I** and **J** are smaller than those of **G** and **H**, which indicates that the water also prefers to locate above the center of the benzene ring. The $\mathbf{E}_{\mathrm{MP2(limit)}}$ values of complexes **G**−**I** are −3.36, −3.46, and −3.10 kcal/mol, respectively. The $E_{\mathrm{CCSD(T)(limit)}}$ values of the complexes are −3.02, −3.17, and −2.77 kcal/mol, respectively. The interaction energies ($E_{\mathrm{e}}$) of the benzene−water complex **G** and **H** (−3.02 and −3.17 kcal/mol, respectively) are substantially larger than that of the benzene−ammonia complex **A** (−2.22 kcal/mol). The $E_{\mathrm{e}}$ values are about 60% of the hydrogen bonding energy of water dimer.[68,69]

Recently Fredericks and co-workers[74] and Feller[75] reported ab initio calculations of the interaction energy of the benzene−water complex. Fredericks et al. reported that the interaction energy of the monodentate complex was −2.83 kcal/mol from the MP2 calculations using the 6-31+G[2d,p] basis set.[74] Feller reported the calculations using large Dunning's correlation consistent basis sets.[75] The BSSE corrected MP2 interaction energies calculated with the aug-cc-pVDZ, aug-cc-pVTZ, cc-pVQZ ,and cc-pV5Z basis sets were −2.89, −3.31, −3.42, and −3.42 kcal/mol, respectively. The estimated $E_{\mathrm{MP2(limit)}}$ from these values is −3.7 kcal/mol. This value is not largely different from our $E_{\mathrm{MP2(limit)}}$ values of complexes **G** and **I** (−3.36 and −3.46 kcal/mol, respectively). Although Feller obtained the $E_{\mathrm{MP2(limit)}}$ value of −3.7 kcal/mol from the BSSE corrected interaction energies, he proposed the $E_{\mathrm{MP2(limit)}}$ value of −3.9 ± 0.2 kcal/mol from the average of this value and the BSSE not corrected MP2/cc-pVQZ interaction energy of −4.1 kcal/mol.

Feller also reported that the MP2 calculations slightly overestimate the attraction (0.2−0.3 kcal/mol) compared to the CCSD(T) calculations using the aug-cc-pVDZ and aug-cc-pVTZ basis sets.[75] The $E_{\mathrm{MP2(limit)}}$ value of complex **G** (−3.36 kcal/mol) is slightly smaller (less negative) than the $E_{\mathrm{MP2(limit)}}$ of the monodentate complex (−3.7 kcal/mol) obtained from the BSSE corrected MP2 interaction energies by Feller. Feller optimized the geometry of the complex, while the intermolecular geometrical parameters of complex **G** was fixed in our calculations and one N−H bond was on the $C_6$ axis of the benzene. The difference between the two geometries would be the slightly smaller interaction energy of the **G** complex.

Feller reported an MP2/aug-cc-pVDZ vibrational energy calculation of the monodentate benzene−water complex. The change of the ZPE by the formation of the complex (ΔZPE) is 1.0 kcal/mol. The calculated $E_{\mathrm{e}}$ value of the benzene−water complex **G** ($E_{\mathrm{CCSD(T)(limit)}} = -3.02$ kcal/mol) and the ΔZPE lead to the $E_0$ value of −2.0 kcal/mol. The experimental $E_0$ was measured by a few groups.[76−78] Gotch and Zwier reported the $E_0$ value of 1.63−2.78 kcal/mol.[76] Cheng et al. reported 2.25 ± 0.28 kcal/mol.[77] Recently Courty et al. reported that the $E_0$ value is 2.44 ± 0.09 kcal/mol.[78] The calculated $E_0$ value is close to these experimental $E_0$ values.

**Roles of Electrostatic and Dispersion Interactions.** Electrostatic and correlation interaction energies of the benzene−ammonia and benzene−water complexes were analyzed to understand the details of the interactions as summarized in Table 4. The electrostatic energy ($E_{\mathrm{es}}$) was calculated as an interaction between the distributed multipoles of isolated molecules. The HF interaction energy ($E_{\mathrm{HF}}$) was the interaction energy calculated at the HF/cc-pVQZ level, which is mainly the exchange-repulsion and electrostatic energies. The $E_{\mathrm{rep}}$ was the difference between $E_{\mathrm{HF}}$ and $E_{\mathrm{es}}$. Although the $E_{\mathrm{rep}}$ is mainly the exchange-repulsion energy, it may also contain some other energy components. The correlation interaction energy ($E_{\mathrm{corr}}$) is the difference between the $E_{\mathrm{total}}$ ($E_{\mathrm{CCSD(T)(limit)}}$) and $E_{\mathrm{HF}}$. The $E_{\mathrm{corr}}$ is mainly attractive dispersion energy.

The $E_{\mathrm{corr}}$ values of complexes **A**−**D** and **G**−**I** are −1.98 to −2.36 kcal/mol. The large $E_{\mathrm{corr}}$ values indicate that the dispersion interaction is significantly important for the attraction in the benzene−ammonia and benzene−water complexes as in the case of the benzene−methane complex.[65] The $E_{\mathrm{corr}}$ value of the benzene−ammonia complex **A** is about 2.3 times as large as the $E_{\mathrm{es}}$ value. The $E_{\mathrm{corr}}$ values are still comparable to the $E_{\mathrm{es}}$ values even in the benzene−water complexes **G** and **H**, which have the stronger electrostatic interaction.

The electrostatic energies ($E_{\mathrm{es}}$) of the six benzene−ammonia complexes are shown in Figure 6. The $E_{\mathrm{es}}$ values strongly depend on the orientation of the complexes. The complex **F** has very large repulsive $E_{\mathrm{es}}$. Apparently this large repulsive $E_{\mathrm{es}}$ is responsible for the calculated repulsive intermolecular interaction potential of complex **F** shown in Figure 4. The intermolecular interaction potential of complex **D** has a deeper minimum than complex **E**. The larger attractive $E_{\mathrm{es}}$ of complex **D** is responsible for this. These results indicate that the electrostatic interaction is highly orientation dependent and is important in determining the relative stability of these complexes. Bucking-

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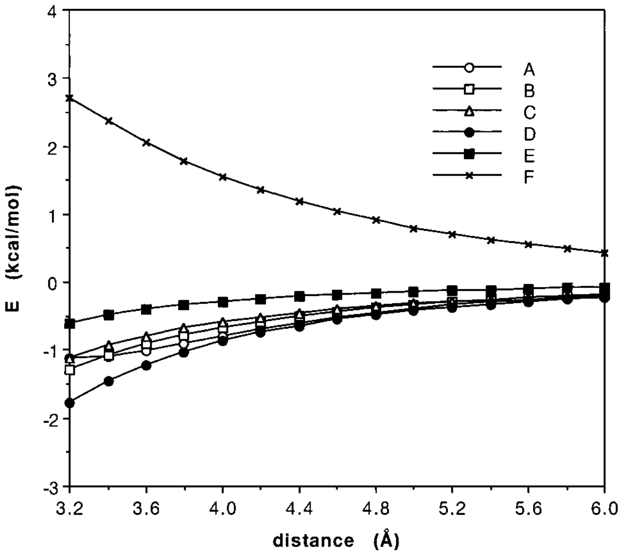

**Figure 6.** The electrostatic energies ($E_{es}$) of the six benzene−ammonia complexes.

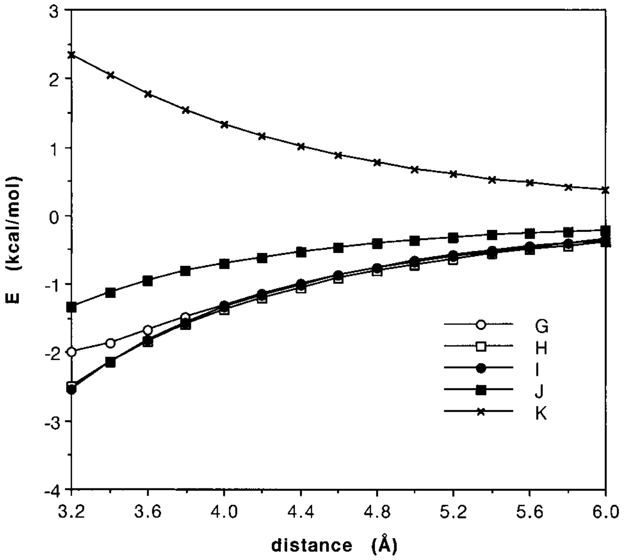

**Figure 7.** The electrostatic energies ($E_{es}$) of the five benzene−water complexes.

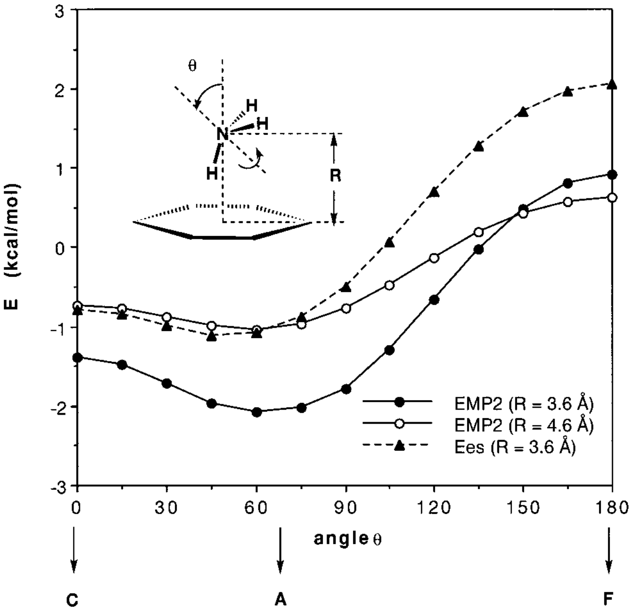

**Figure 8.** The orientation dependence of the MP2/cc-pVTZ interaction energies ($E_{MP2}$) and the electrostatic energies ($E_{es}$) of benzene−ammonia complexes.

ham and Fowler pointed out from simple model calculations that structures of molecular clusters are mainly determined by the exchange-repulsion and electrostatic interactions.[79,80]

Complex **A** ($E_{total} = -2.22$ kcal/mol), in which one N−H bond points toward the benzene ring, is more stable than complexes **B** and **C** (−2.07 and −1.72 kcal/mol, respectively). The structure of complex **A** is close to the observed monodentate structure in the gas phase.[9] Although the monodentate complex **A** is more stable than the bidentate and tridentate complexes **B** and **C**, the energy difference among the three complexes is only 0.5 kcal/mol. The small energy difference explains the different types of orientations found in crystals.[31] The $E_{corr}$ values of complexes **A**−**C** are nearly equal (−2.31 to −2.34 kcal/mol) as shown in Table 4. The $E_{es}$ values of complexes **A**−**C** are −1.01, −0.91, and −0.79 kcal/mol, respectively. Complex **A** has slightly stronger electrostatic attraction than complexes **B** and **C**. The $E_{rep}$ values of the three complexes are 1.14, 1.14, and 1.41 kcal/mol, respectively. Complex **C** has stronger repulsion than complexes **A** and **B**. The small difference of the $E_{es}$ and $E_{rep}$ values controls the relative stability of complexes **A**−**C**.

The calculated $E_{es}$ values of the benzene−water complexes (Figure 7) show that the electrostatic interaction is again important in determining the relative stability of the complexes. The repulsive $E_{es}$ of complex **K** is responsible for the repulsive intermolecular interaction potential of this complex shown in Figure 5. The $E_{corr}$ values of complexes **G** and **H** are again nearly equal (−2.23 and −2.25 kcal/mol). Although the benzene−water complex **H** has a larger attractive $E_{es}$ (−2.14 kcal/mol) value than **G** (−1.86 kcal/mol), complex **H** has a larger $E_{rep}$ (1.22 kcal/mol) value than **G** (1.07 kcal/mol). As a result the $E_{total}$ values of the two complexes are not largely different.

The directionality of hydrogen bonding was sometimes explained by the interactions between orbitals such as charge transfer.[81] Oki and Mutai also tried to explain the NH/$\pi$ interaction as the interaction between orbitals.[13] The orientation dependence of the MP2/cc-pVTZ interaction energy of the benzene−ammonia complexes is shown in Figure 8. The calculated interaction energy of the complex has strong orientation dependence even in a long intermolecular separation ($R = 4.6$ Å). The orientation dependence is the same as that in a short separation ($R = 3.6$ Å). The same orientation dependence suggests that the directionality is controlled mainly by the electrostatic interaction, which is a long-range interaction.[67] If short-range interactions such as charge transfer are the major source of the directionality, the directionality should disappear in a long separation. The orientation dependence of the $E_{es}$ of the complex ($R = 3.6$ Å) is also shown in Figure 8. The orientation dependence of the MP2/cc-pVTZ interaction energy is close to that of the $E_{es}$, which indicates that the directionality of the interaction is mainly controlled by the electrostatic interaction. The orientation dependence of the calculated interaction energy of the benzene−water complex in a long separation ($R = 4.4$ Å) is again the same as that in a short separation ($R = 3.4$ Å) and the dependence of the MP2/cc-pVTZ interaction energy is again close to that of the $E_{es}$ of the

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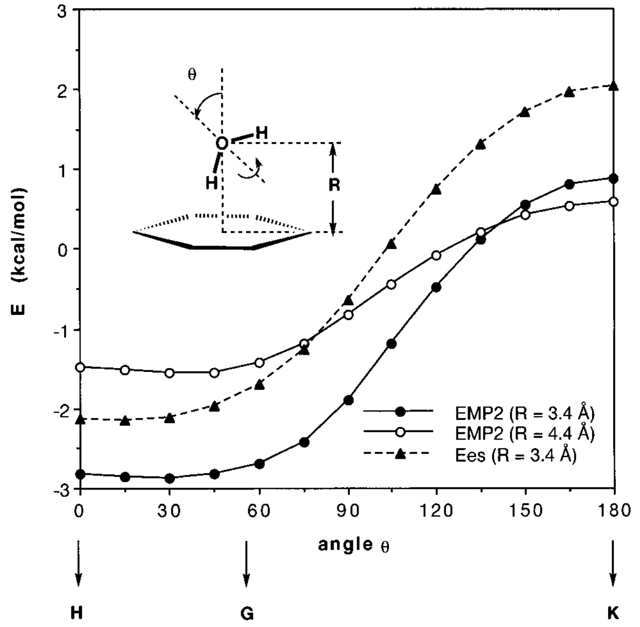

**Figure 9.** The orientation dependence of the MP2/cc-pVTZ interaction energies ($E_{MP2}$) and the electrostatic energies ($E_{es}$) of benzene−water complexes.

complex ($R$ = 3.4 Å) as shown in Figure 9. These results indicate that the directionality of the NH/π (benzene−ammonia) and OH/π (benzene−water) interactions are determined mainly by the electrostatic interaction.

Atomic charge distributions of complexes **A** ($R$ = 3.6 Å) and **G** ($R$ = 3.4 Å) were obtained by the electrostatic potential fitting with the Merz−Singh−Kollman scheme[82,83] using the MP2/cc-pVTZ wave functions to evaluate the amount of charge transfer from the benzene to the water or to the ammonia. The calculated charges on ammonia and water (sum of the atomic charges) are −0.022 e and −0.042 e (1 e = 1.602 × $10^{-19}$ C), respectively. Calculated negative charges on the ammonia and water, which correspond to the charge transfer from benzene, are larger than the calculated charge on the methane in the benzene−methane complex (−0.002 e).[65] The calculations suggest that the amounts of charge transfer in the benzene−ammonia and benzene−water complexes are larger than that in the benzene−methane complex. However, the calculated intermolecular interaction potentials of the benzene−ammonia and benzene−water complexes (Figures 2 and 3) indicate that substantial attraction still exists even if the intermolecular distance is larger than 4.0 Å. This shows that the major source of the attraction is not short-range interactions such as charge transfer, but long-range interactions such as electrostatic and dispersion. In addition the directionality of the benzene−ammonia and benzene−water complexes is mainly determined by the electrostatic interaction. These results show that the charge transfer is not essential for the attraction and directionality of the NH/π and OH/π interactions.

**Comparison of NH/π, OH/π, and CH/π Interactions.** The MP2/cc-pVTZ level interaction potentials of the benzene−ammonia complex **A**, the benzene−water complex **G**, and the benzene−methane complex **L**[65] are compared in Figure 10. The C−H bond of methane points toward the benzene ring in the most stable benzene−methane complex.[65] The benzene−water complex has stronger attraction than the benzene−ammonia complex. The attraction in the benzene−methane complex is weaker than that in the benzene−ammonia complex. The intermolecular potentials of the benzene−water, benzene−ammonia, and benzene−methane complexes have their minima at intermolecular distances of 3.4, 3.6, and 3.8 Å, respectively. The size of the van der Waals radii of the proton-donating atoms (C, 1.75 Å; N, 1.55 Å; and O, 1.40 Å) would be one of the causes of the different intermolecular distances at the potential minima. However, the size of the attraction is also a cause of the difference of the intermolecular distance. The stronger attraction leads the smaller equilibrium intermolecular distance.

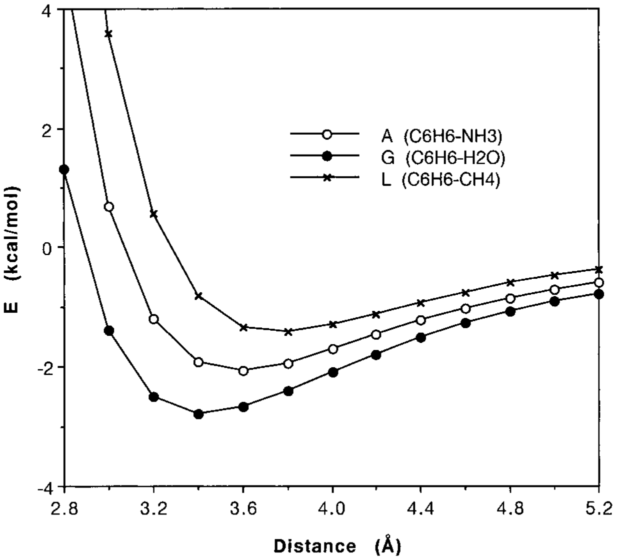

**Figure 10.** The MP2/cc-pVTZ intermolecular interaction potentials of the benzene−ammonia, benzene−water, and benzene−methane complexes **A**, **G**, and **L**.

The order of the size of the interaction energies ($E_{total}$) of the benzene−water (**G**), benzene−ammonia (**A**), and benzene−methane (**L**) complexes is water > ammonia > methane. The $E_{total}$ values of these complexes are −3.17, −2.22, and −1.45 kcal/mol, respectively, as shown in Table 4. The $E_{corr}$ values of the three complexes (−2.25 to −2.31 kcal/mol) are not largely different, while the $E_{es}$ values of the three complexes are considerably different. The $E_{es}$ values of the benzene−water (**G**), benzene−ammonia (**A**), and benzene−methane (**L**) complexes are −2.64, −1.08, and −0.25 kcal/mol, respectively. Apparently the amount of $E_{es}$ is mainly responsible for the magnitude of the interaction energies ($E_{total}$) of the three complexes. The order of the $E_{total}$ values agrees with the electronegativity order of the proton-donating atoms (C < N < O). This agreement also indicates that the size of the interactions is mainly governed by the electrostatic interaction.

Our calculations of the XH/π (X = O, N, and C) interactions indicate that there are some similarities between the XH/π interactions and the cation/π interaction, which is the strong noncovalent attractive interaction between the cation and the π system.[84−88] The cation/π interaction has been studied extensively in these two decades. Electrostatic energy is important in the cation/π interaction. Although the electrostatic energy is not large and dispersion is important for the attraction in the

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XH/$\pi$ interactions, the electrostatic interaction plays an important role in determining the magnitude and the directionality of the XH/$\pi$ interactions.

## Conclusion

Attraction between benzene and ammonia is weaker than the hydrogen bond between waters. The calculated interaction energy of the benzene–ammonia complex (−2.22 kcal/mol) is about 40% of the hydrogen bonding energy of the water dimer. Electron correlation greatly increases calculated interaction energies of the benzene–ammonia and benzene–water complexes, which indicates that the dispersion interaction is important for the attraction in these complexes as in the case of the benzene–methane complex. The electrostatic interaction is also important for the attraction in the benzene–ammonia and benzene–water complexes.

The calculated potentials of the benzene–ammonia and benzene–water complexes indicate that substantial attraction still exists in a long intermolecular separation ($R > 4.0$ Å), which indicates that the major source of the attraction is not the short-range interactions such as charge transfer, but the long-rang interactions such as electrostatic and dispersion.

The electrostatic interaction is mainly responsible for the directionality of the NH/$\pi$ (benzene–ammonia) and OH/$\pi$ (benzene–water) interactions. The directionality observed in a long intermolecular separation is the same as that in a short separation, which suggests that the origin of the directionality of these interactions is not short-range interactions.

The monodentate benzene–ammonia complex is slightly more stable than the bidentate and tridentate complexes. The calculated energy differences among these three complexes are only 0.5 kcal/mol. The correlation interaction energies of the three complexes are nearly equal. The small difference of the repulsive and electrostatic energies is mainly responsible for the relative stability of the three complexes.

The attraction in the benzene–water complex (OH/$\pi$) is stronger than that in the benzene–ammonia complex (NH/$\pi$). The benzene–ammonia complex (NH/$\pi$) has stronger attraction than the benzene–methane complex (CH/$\pi$). The amount of attractive electrostatic energy is mainly responsible for the magnitude of the attractions of these complexes.

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

**Supporting Information Available:** Tables of geometries and energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001901A