

# Lewis Acidity/Basicity of $\pi$ -Electron Systems: Theoretical Study of a Molecular Interaction between a $\pi$ System and a Lewis Acid/Base

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**Abstract:** Molecular interactions between  $\pi$  systems having different  $\pi$ -electron character (benzene, hexafluorobenzene, and borazine), and a Lewis acid/base (borane and ammonia) were theoretically studied. An attractive interaction between benzene, the electron-rich  $\pi$  system, and borane was observed. On the other hand, repulsive interactions between benzene and am-

monia was observed when the lone pair of nitrogen points toward the benzene ring. In contrast, an attractive interaction between hexafluorobenzene, an electron-deficient  $\pi$  system, and am-

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monia was observed. Unexpectedly, a weak attractive interaction between hexafluorobenzene and borane was also observed. Borazine shows an interaction both to borane and ammonia. The attraction between the nitrogen atom of borazine and borane was larger than that between the boron atom of borazine and ammonia.

## Introduction

The classic definition of a Lewis acid–base interaction is the interaction between electron donor and electron acceptor.<sup>[1]</sup> The interaction between a  $\pi$  system and electron acceptor and the interaction between an electron-deficient  $\pi$  system and electron donor can be considered as Lewis acid–base interactions, since the Lewis acid–base interaction is generalized as the interaction between an occupied molecular orbital and an unoccupied molecular orbital.<sup>[2]</sup>

The attractive interaction, between an electron-rich  $\pi$  system and a positively charged proton of alkane, is known as CH/ $\pi$  interaction.<sup>[3]</sup> The interaction between a  $\pi$  system and proton donor (electron acceptor), such as the interaction between benzene and water, has been considered as a new type of hydrogen bond.<sup>[4]</sup> Moreover, strong interaction between cation and benzene was reported.<sup>[5]</sup> These interactions suggest that benzene acts as electron donor. On the other hand, recently Gallivan and Dougherty, and Danten et al. independently reported theoretical studies on the water/hexafluorobenzene interaction.<sup>[6a]</sup> They suggested the existence of attractive interaction between the lone pair of the oxygen atom and hexafluorobenzene. Besnard et al. reported remarkable difference between the dynamics of solitary water in benzene and that in hexafluorobenzene based on IR and Raman measurements. They concluded that a proton of the water can form a weak hydrogen bond with benzene but not with hexafluorobenzene.<sup>[6b]</sup> The hydrogen bond between a proton of water and the  $\pi$  system of hexafluorobenzene was not observed experimentally, which agrees well with the theoretically predicted structure. Alkorta et al. reported that the fluorine atom in hydrogen fluoride attracts hexafluorobenzene very weakly.<sup>[6c]</sup> They also reported the interaction between some electron donors,<sup>[6d]</sup> including anions,<sup>[6e]</sup> and electrondeficient  $\pi$  systems. The interaction between an anion and a  $\pi$  system was reported by Quiñero et al.<sup>[6g–k]</sup> and Mascal et al.<sup>[6l]</sup> independently. Recently, we found attractive interaction between an electron-deficient  $\pi$  system and an electron-rich fluorine atom in fluo-

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roalkane.<sup>[6m]</sup> These studies suggest that hexafluorobenzenes act as electron acceptor.

We report herein *ab initio* calculations of the molecular interactions of electron-rich and electron-deficient  $\pi$  systems with Lewis acid and base. Borane and ammonia were used as models of Lewis acid and base, respectively. It has been reported that ammonia acts as proton donor in the benzene–ammonia complex.<sup>[4c,7]</sup> The measurement of R2PI spectroscopy shows that the N–H bond of ammonia points towards the benzene ring.<sup>[7a,b]</sup> However, we focused on the interaction of ammonia with  $\pi$  systems as an electron donor in this study. Benzene ( $\pi_{\text{H}}$ ) and hexafluorobenzene ( $\pi_{\text{F}}$ ) were used as the models of electron-rich and electron-deficient  $\pi$  systems, respectively. Borazine ( $\pi_{\text{BN}}$ ) was used as the model of localized  $\pi$ -electron system (Figure 1), additionally. Fowler et al. reported that borazine's ring current is strongly localized on the nitrogen atoms, in contrast to the flat ring current of benzene and hexafluorobenzene,<sup>[8a,b]</sup> which suggests that borazine has unique molecular interaction. Recently, we have reported remarkable molecular interaction of the borazine dimer.<sup>[8c]</sup>

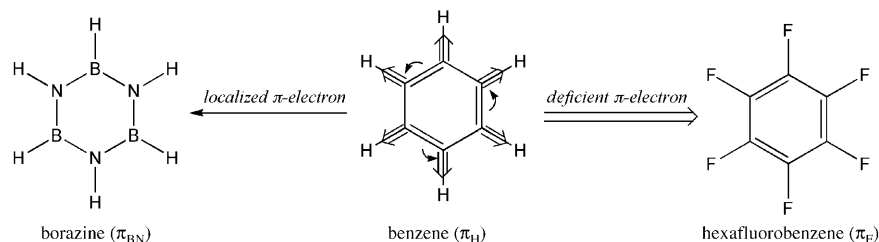


Figure 1. Three types of  $\pi$  systems.

## Calculation Methods

Structure optimization and interaction energy calculations were both carried out using the Gaussian 98 program.<sup>[9]</sup> The structures of borane, ammonia, benzene, hexafluorobenzene and borazine were optimized at the B3LYP/6-311G(d) level of calculation. The molecular interaction energy was calculated at the MP2/aug-cc-pVDZ//B3LYP/6-311G(d) level. The

### Abstract in Japanese:

異なる性質の $\pi$ -電子系(ベンゼン、ヘキサフルオロベンゼン、ボラジン)とルイス酸・塩基(ボラン、アンモニア)の分子間相互作用を分子軌道法により検討した。B3LYP/6-311G(d)にて構造最適化し、MP2/aug-cc-pVDZにて相互作用エネルギーを求めた。ベンゼンとボランの間には引力(-3.22 kcal mol<sup>-1</sup>)、ベンゼンとアンモニアの孤立電子対の間には斥力(+1.25 kcal mol<sup>-1</sup>)が各々働く。反対にヘキサフルオロベンゼンとアンモニアの孤立電子対の間には引力(-3.16 kcal mol<sup>-1</sup>)が働くが、意外にもヘキサフルオロベンゼンとボランの間にも引力(-2.01 kcal mol<sup>-1</sup>)が働く。ボラジンの $\pi$ -電子系は両性であり、その窒素原子とボラン(-3.68 kcal mol<sup>-1</sup>)、ホウ素原子とアンモニアの孤立電子対の間には引力(-0.45 kcal mol<sup>-1</sup>)が働く。これらの相互作用には分散力が最も大きな寄与を持つが、静電力もまた重要な役割を持つ。

molecular interaction energies were evaluated by the supermolecular method. The basis set superposition error (BSSE) was corrected by using the counterpoise method.<sup>[10]</sup> The interaction energy was calculated with changing horizontal ( $X$ , Figure 2) and vertical ( $R$ , Figure 2) displacements. The electrostatic energy ( $E_{\text{ES}}$ ) was calculated as interaction be-

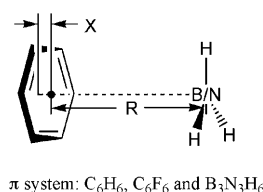


Figure 2. Arrangement of  $\pi$  system and borane/ammonia for the potential energy calculations.  $X$  is horizontal displacement [ $\text{\AA}$ ] and  $R$  is vertical displacement [ $\text{\AA}$ ].

tween distributed multipoles of monomers using ORIENT.<sup>[11]</sup> Distributed multipoles were obtained from MP2/ccpVTZ wave functions of the isolated monomers. GDMA<sup>[12]</sup> was used for obtaining distributed multipoles from the wavefunctions calculated using the Gaussian program. The difference between the Hartree–Fock interaction energy ( $\Delta E_{\text{HF}}$ ) and the

$E_{\text{ES}}$  can be considered mainly as the exchange-repulsion energy. We thus, denote this term as  $E_{\text{rep}}$ , that is,  $E_{\text{rep}} = \Delta E_{\text{HF}} - E_{\text{ES}}$ , but the  $E_{\text{rep}}$  term also includes other energy components, such as the induction energy and the charge transfer attractive interaction ( $E_{\text{CT}}$ ). The electron correlation energy ( $E_{\text{corr}}$ ) was calculated as the difference between the calculated MP2 interaction energy ( $\Delta E_{\text{MP2}}$ ) and the  $\Delta E_{\text{HF}}$  at the aug-cc-pVDZ basis set. The major part of  $E_{\text{corr}}$  is the dispersion energy.

## Results and Discussion

Table 1 shows the effects of basis set and electron correlation on the benzene–borane ( $\text{H}_3\text{B}/\pi_{\text{H}}$ ) and benzene–ammonia ( $\text{H}_3\text{N}/\pi_{\text{H}}$ ) interaction energies in the structures with  $C_3$  symmetry ( $X = 0$ ). In both complexes, the HF level interaction energies ( $\Delta E_{\text{H}_3\text{B}/\pi_{\text{H}}} = +3.55 \text{ kcal mol}^{-1}$  and  $\Delta E_{\text{H}_3\text{N}/\pi_{\text{H}}} = +3.35 \text{ kcal mol}^{-1}$ ) were much more positive than MP2 and CCSD(T) ones ( $\Delta \text{MP2} < -1.0 \text{ kcal mol}^{-1}$ ). Though the MP2 level interaction energies ( $\Delta E_{\text{H}_3\text{B}/\pi_{\text{H}}} = -0.37 \text{ kcal mol}^{-1}$  and  $\Delta E_{\text{H}_3\text{N}/\pi_{\text{H}}} = +1.91 \text{ kcal mol}^{-1}$ ) were more negative than the CCSD(T) level interaction energies ( $\Delta E_{\text{H}_3\text{B}/\pi_{\text{H}}} = +0.29 \text{ kcal mol}^{-1}$  and  $\Delta E_{\text{H}_3\text{N}/\pi_{\text{H}}} = +1.96 \text{ kcal mol}^{-1}$ ), the differences were quite small ( $\Delta \text{CCSD(T)} = +0.66 \text{ kcal mol}^{-1}$  for  $\text{H}_3\text{B}/\pi_{\text{H}}$  and  $+0.05 \text{ kcal mol}^{-1}$  for  $\text{H}_3\text{N}/\pi_{\text{H}}$ ).

The cc-pVDZ basis set underestimates the attraction and overestimates the repulsion compared to the aug-cc-pVDZ ( $\Delta E_{\text{H}_3\text{B}/\pi_{\text{H}}} = -1.38 \text{ kcal mol}^{-1}$  and  $\Delta E_{\text{H}_3\text{N}/\pi_{\text{H}}} = +0.51 \text{ kcal mol}^{-1}$ ) and aug-cc-pVTZ ( $\Delta E_{\text{H}_3\text{B}/\pi_{\text{H}}} = -1.98 \text{ kcal mol}^{-1}$  and  $\Delta E_{\text{H}_3\text{N}/\pi_{\text{H}}} = +0.28 \text{ kcal mol}^{-1}$ ) basis sets ( $\Delta_{\text{Aug}} < -1.0 \text{ kcal mol}^{-1}$ ). Although the interaction energies calculated with the aug-cc-pVDZ basis set were slightly less negative than those calculated with the aug-cc-pVTZ basis set, the

Table 1. Basis set dependence and electron correlation dependence of the calculated interaction energies ( $\Delta E$ , BSSE corrected, kcal mol<sup>-1</sup>) and BSSE (kcal mol<sup>-1</sup>).

Interaction Model	HF	cc-pVDZ		aug-cc-pVDZ	aug-cc-pVTZ
	$\Delta E$ (BSSE)	MP2 $\Delta E$ (BSSE)	CCSD(T) $\Delta E$ (BSSE)	MP2 $\Delta E$ (BSSE)	MP2 $\Delta E$ (BSSE)
BH <sub>3</sub> /π <sub>H</sub> ( $R=3.0$ Å)	+3.55 (+0.61)	-0.37 (+1.66) Δ <sub>MP2</sub> <sup>[a]</sup> -3.92	+0.29 (+1.70) ΔCCSD(T) <sup>[b]</sup> +0.66	-1.38 (+2.23) Δ <sub>Aug</sub> <sup>[c]</sup> -1.01	-1.98 (+0.81) Δ <sub>TZ</sub> <sup>[d]</sup> -0.59
NH <sub>3</sub> /π <sub>H</sub> ( $R=3.5$ Å)	+3.35 (+1.06)	+1.91 (+1.47) Δ <sub>MP2</sub> <sup>[a]</sup> -1.44	+1.96 (+1.39) ΔCCSD(T) <sup>[b]</sup> +0.05	+0.51 (+0.75) Δ <sub>Aug</sub> <sup>[c]</sup> -1.40	+0.28 (+0.41) Δ <sub>TZ</sub> <sup>[d]</sup> -0.23

[a]  $\Delta_{MP2} = \Delta E_{MP2} - \Delta E_{HF}$ . [b]  $\Delta_{CCSD(T)} = \Delta E_{CCSD(T)} - \Delta E_{MP2}$ . [c]  $\Delta_{Aug} = \Delta E_{aug-cc-pVDZ} - \Delta E_{cc-pVDZ}$ . [d]  $\Delta_{TZ} = \Delta E_{aug-cc-pVTZ} - \Delta E_{aug-cc-pVDZ}$ .

differences in the calculated interaction energies were small ( $\Delta_{TZ} = -0.59$  kcal mol<sup>-1</sup> for H<sub>3</sub>B/π<sub>H</sub> and  $-0.23$  kcal mol<sup>-1</sup> for H<sub>3</sub>N/π<sub>H</sub>). Table 1 shows that the magnitude of the basis set effect between aug-cc-pVDZ and aug-cc-pVTZ basis sets ( $\Delta_{TZ}$ ), and the magnitude of electron correlation effect between the MP2 and CCSD(T) levels of theory ( $\Delta_{CCSD(T)}$ ), were close although the signs are different, which suggests that the MP2/aug-cc-pVDZ level interaction energy is not largely different from the CCSD(T)/aug-cc-pVTZ level interaction energy. Therefore, we can expect that the MP2/aug-cc-pVDZ level interaction energies between π systems and Lewis acids/bases are sufficiently accurate.

Trends in the change of the interaction energy and its components were studied with changing horizontal displacement ( $X$ , Å), whose the vertical displacement was fixed ( $R = 3.5$  Å). Figure 3a–f shows the change of each energy component with changing horizontal displacement. In all cases,  $E_{corr}$  had the largest contribution for the stabilization of the complexes. Thus, the dispersion energy is the major factor for the attractive interactions. The  $E_{corr}$  value became the most negative when the borane or ammonia molecule located on the center of the π systems ( $X = 0$ ). The electrostatic interaction ( $E_{ES}$ ) between ammonia and the π systems was much larger than that between borane and the π systems.

Attractive interaction was observed for H<sub>3</sub>B/π<sub>H</sub> (Figure 3a); however, the C<sub>3</sub> structure ( $X = 0$ ) was not potential energy minimum. The potential minimum was observed ( $\Delta E_{MP2}^{X=1.0} = -2.43$  kcal mol<sup>-1</sup>) when the borane was located at the point of  $X = 1.0$  Å. The  $E_{corr}^{X=1.0}$  ( $-2.11$  kcal mol<sup>-1</sup>) had an important contribution to the attractive interaction. In contrast to total interaction energy ( $\Delta E_{MP2}$ ), the potential energy minimum was observed in the C<sub>3</sub> structure for both  $E_{ES}$  and  $E_{corr}$ . Although the electrostatic interaction was also attractive ( $E_{ES}^{X=0.0} = -0.50$  kcal mol<sup>-1</sup>), the contribution was much less than the  $E_{corr}^{X=0.0}$  ( $-2.29$  kcal mol<sup>-1</sup>). On the other hand, the potential energy maximum was observed for  $E_{rep}$  when the borane was located at the point of the center ( $E_{rep}^{X=0.0} = +0.59$  kcal mol<sup>-1</sup>). Thus, the exchange–repulsion is the major reason why the total H<sub>3</sub>B–π<sub>H</sub> interaction in the C<sub>3</sub> structure is not potential energy minimum.

Contrary to the H<sub>3</sub>B/π<sub>H</sub> interaction, total H<sub>3</sub>N/π<sub>H</sub> interaction (Figure 3b) was repulsive, but the C<sub>3</sub> structure was a po-

tential energy minimum ( $\Delta E_{MP2}^{X=0.0} = +0.51$  kcal mol<sup>-1</sup>), and a potential maximum was observed ( $\Delta E_{MP2}^{X=1.0} = +0.59$  kcal mol<sup>-1</sup>) when the ammonia was located at the point of  $X = 1.0$  Å. The size of  $E_{corr}$  in the H<sub>3</sub>N/π<sub>H</sub> interaction  $E_{corr}^{X=0.0}$  ( $-2.43$  kcal mol<sup>-1</sup>) was almost the same as that of the H<sub>3</sub>B/π<sub>H</sub> interaction. The potential energy maximum was observed in the C<sub>3</sub> structure for  $E_{ES}$ .

Since the electrostatic interaction was strongly repulsive ( $E_{ES}^{X=0.0} = +2.03$  kcal mol<sup>-1</sup>), it had the largest contribution for the repulsive interaction. The value of  $E_{rep}$  became maximum when the nitrogen atom was located near a carbon atom of benzene. The repulsion between the lone pair of ammonia and the occupied π orbital of the benzene would be the cause of the large  $E_{rep}$ .  $E_{rep}^{X=0.0}$  ( $+0.91$  kcal mol<sup>-1</sup>) was about a half of  $E_{ES}^{X=0.0}$ .

Attractive interaction was observed for H<sub>3</sub>B/π<sub>F</sub> interaction (Figure 3c); however, the C<sub>3</sub> structure ( $X = 0$ ) was potential energy maximum (not the least negative), similar to the H<sub>3</sub>B/π<sub>H</sub> interaction. The potential minimum was observed ( $\Delta E_{MP2}^{X=0.8} = -1.43$  kcal mol<sup>-1</sup>) when  $X = 0.8$  Å. The  $E_{corr}^{X=1.0}$  ( $-2.44$  kcal mol<sup>-1</sup>) had an important contribution to the attractive interaction. The size of the  $E_{corr}^{X=1.0}$  for the H<sub>3</sub>B/π<sub>F</sub> interaction was comparable to the  $E_{corr}^{X=1.0}$  for H<sub>3</sub>B/π<sub>H</sub> interaction. Weakly repulsive electrostatic interaction was observed ( $E_{ES}^{X=0.0} = +0.41$  kcal mol<sup>-1</sup>) and the potential energy was very flat. The electrostatic interaction is the main reason why the total interaction energy for the H<sub>3</sub>B/π<sub>F</sub> interaction was about 1 kcal mol<sup>-1</sup> less negative than the H<sub>3</sub>B/π<sub>H</sub> interaction. The potential energy maximum was observed for  $E_{rep}$  when the borane was located at the point of the center ( $E_{rep}^{X=0.0} = +0.65$  kcal mol<sup>-1</sup>), and the size of the  $E_{rep}^{X=0.0}$  for the H<sub>3</sub>B/π<sub>F</sub> interaction was comparable to the  $E_{corr}^{X=1.0}$  for H<sub>3</sub>B/π<sub>H</sub> interaction.

Relatively strong interaction ( $\Delta E_{MP2}^{X=0.0} = -3.16$  kcal mol<sup>-1</sup>) was observed for H<sub>3</sub>N/π<sub>F</sub> interaction (Figure 3d). The C<sub>3</sub> structure was potential energy minimum. The value of  $E_{corr}$  was less negative than that of H<sub>3</sub>N/π<sub>H</sub> interaction. The contribution of  $E_{ES}^{X=0.0}$  in H<sub>3</sub>N/π<sub>F</sub> was comparable to the  $E_{corr}$ . The potential energy minimum was observed in the C<sub>3</sub> structure for both  $E_{ES}$  and  $E_{corr}$ . The value of  $E_{rep}^{X=0.0}$  ( $+0.14$  kcal mol<sup>-1</sup>) was smaller than H<sub>3</sub>N/π<sub>H</sub> interaction.

Figure 3e and f show the potential energy of H<sub>3</sub>B/π<sub>BN</sub> interaction and H<sub>3</sub>N/π<sub>BN</sub> interaction, respectively. Considering the asymmetry of the borazine for the horizontal displacements, the interaction energies were calculated for both complexes in the range of  $X = -2.5$  to  $+2.5$  Å. A negative value of  $X$  shows that BH<sub>3</sub> or NH<sub>3</sub> located near a boron atom of the borazine, and the positive value of  $X$  shows BH<sub>3</sub> or NH<sub>3</sub> located near a nitrogen atom of the borazine.

For H<sub>3</sub>B/π<sub>BN</sub> interaction, the potential minimum was observed when  $X = 1.4$  ( $\Delta E_{MP2}^{X=1.4} = -1.86$  kcal mol<sup>-1</sup>). Another

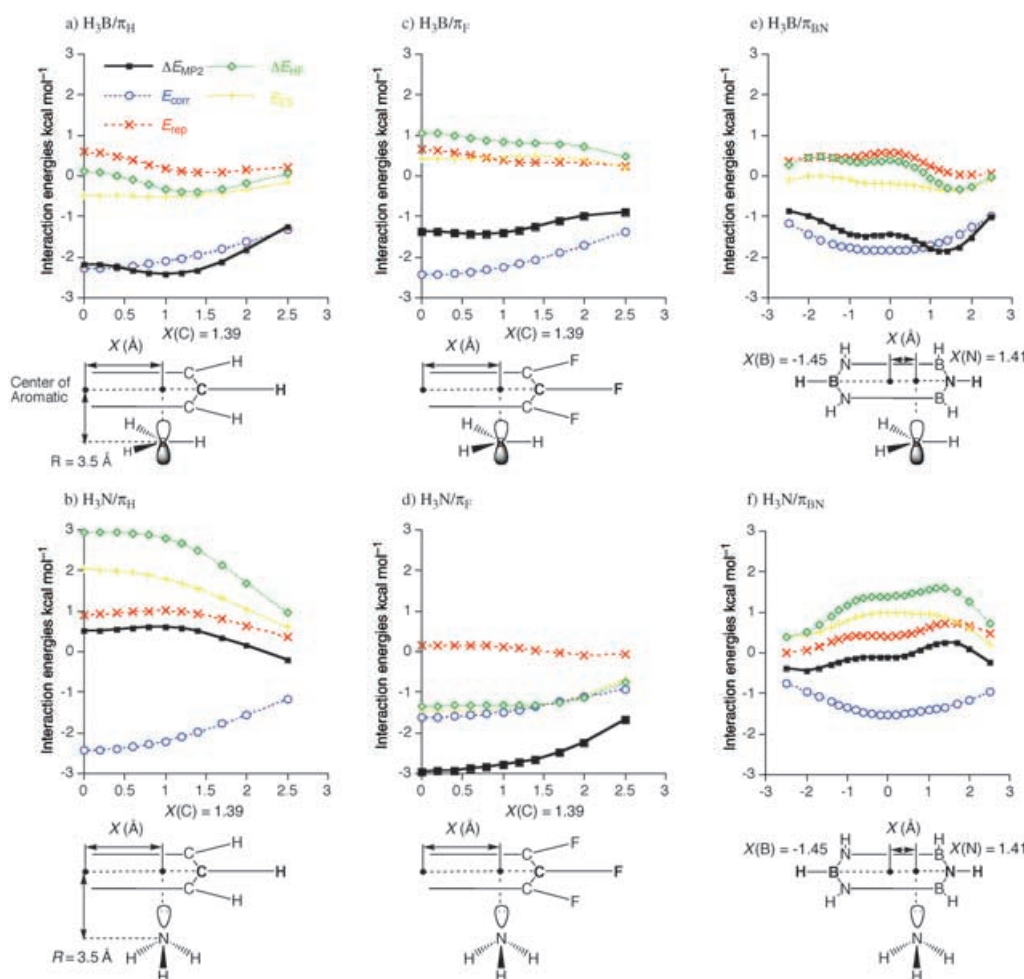


Figure 3. Calculated total interaction energies and energy components with changing the horizontal displacements ( $X$ , Å). The vertical displacement ( $R$ ) was fixed at 3.5 Å.

er potential minimum was observed ( $\Delta E_{\text{MP2}}^{X=-0.6} = -1.49 \text{ kcal mol}^{-1}$ ) when  $X = -0.6 \text{ Å}$ . The  $C_3$  structure was potential energy maximum ( $\Delta E_{\text{MP2}}^{X=0.0} = -1.45 \text{ kcal mol}^{-1}$ ). The potential energy of  $E_{\text{corr}}$  for the  $\text{H}_3\text{B}/\pi_{\text{BN}}$  interaction was almost symmetrical for  $X$ , and the potential minimum was observed when the borane was located at the point of  $X = 0.0$ . The  $E_{\text{corr}}$  had the greatest contribution to the attractive interaction. The  $E_{\text{ES}}$  was negative except at the point of  $X = -1.7 \text{ Å}$ , and the fluctuation of the electrostatic potential energy was small.

The potential minima of the  $\text{H}_3\text{N}/\pi_{\text{BN}}$  interaction were observed when  $X = 0.0 \text{ Å}$  ( $\Delta E_{\text{MP2}}^{X=0.0} = -0.13 \text{ kcal mol}^{-1}$ ) and  $X = -2.0 \text{ Å}$  ( $\Delta E_{\text{MP2}}^{X=-2.0} = -0.45 \text{ kcal mol}^{-1}$ ). On the other hand, the potential maximum was observed when  $X = -0.4 \text{ Å}$  ( $\Delta E_{\text{MP2}}^{X=-0.4} = -0.12 \text{ kcal mol}^{-1}$ ) and  $X = +1.4 \text{ Å}$  ( $\Delta E_{\text{MP2}}^{X=1.4} = +0.25 \text{ kcal mol}^{-1}$ ). The  $E_{\text{corr}}$  ( $E_{\text{corr}}^{X=0.0} = -1.52 \text{ kcal mol}^{-1}$ ) had an important contribution to the attractive interaction. The potential energy minimum was observed in the  $C_3$  structure for  $E_{\text{corr}}$ . The  $E_{\text{ES}}^{0.4}$  was positive in the range of  $X (-2.5 \text{ Å} \leq X \leq +2.5 \text{ Å})$ . The trend in the potential energy of  $E_{\text{rep}}$  was similar to that of  $\Delta E_{\text{MP2}}$ . The trend in the total interaction

potential energy for  $\text{H}_3\text{N}/\pi_{\text{BN}}$  interaction was opposite to the  $\text{H}_3\text{B}/\pi_{\text{BN}}$  interaction. For both  $\text{H}_3\text{B}/\pi_{\text{BN}}$  and  $\text{H}_3\text{N}/\pi_{\text{BN}}$  interactions, the  $E_{\text{ES}}$  was not the main reason for the characteristic potential energy.

Figure 4a–e shows charges of interaction energies by the charge of horizontal displacements ( $R$ , Å), and Table 2 summarizes the total interaction energies and each energy component at the potential minima. The interaction between benzene and borane ( $-3.22 \text{ kcal mol}^{-1}$ ,  $R = 3.0$ ,  $X = 0.0$ , see also Figure 5a), and that between hexafluorobenzene and ammonia ( $-3.16 \text{ kcal mol}^{-1}$ ,  $R = 3.2$ ,  $X = 0.0$ , see also Figure 5d) were attractive. Trends in the contribution of each component at the potential minima (Table 2) were close to that shown in Figure 3 where  $X$  was changed with fixed  $R$  value. The interaction between hexafluorobenzene and borane ( $-2.01 \text{ kcal mol}^{-1}$ ,  $X = 0.8$ , see also Figure 5c) was also attractive. The potential energy minimum was observed at  $R = 3.0$  and  $X = 0.8 \text{ Å}$ . On the other hand, the interaction between benzene and ammonia was repulsive. Table 3 shows the atomic charges of  $\pi$  systems obtained by electrostatic potential fitting according to the scheme by Besler

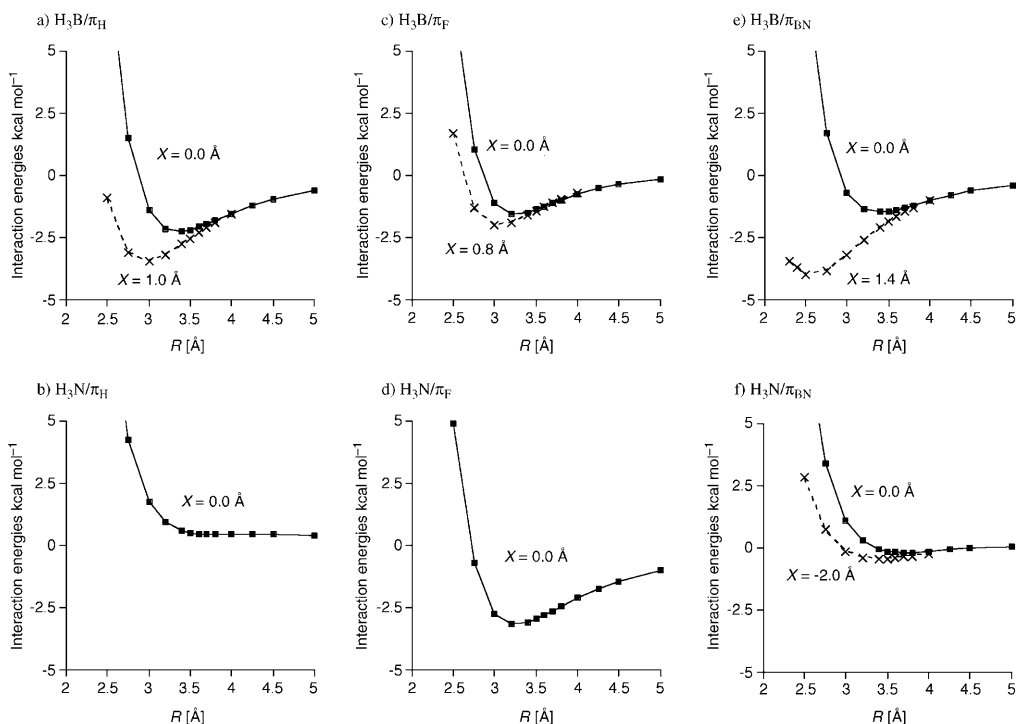


Figure 4. Calculated interaction energies with changing vertical displacement ( $R$ , Å). The horizontal displacement ( $X = 0$  Å and potential minimum shown in Figure 2) was fixed in the calculations.

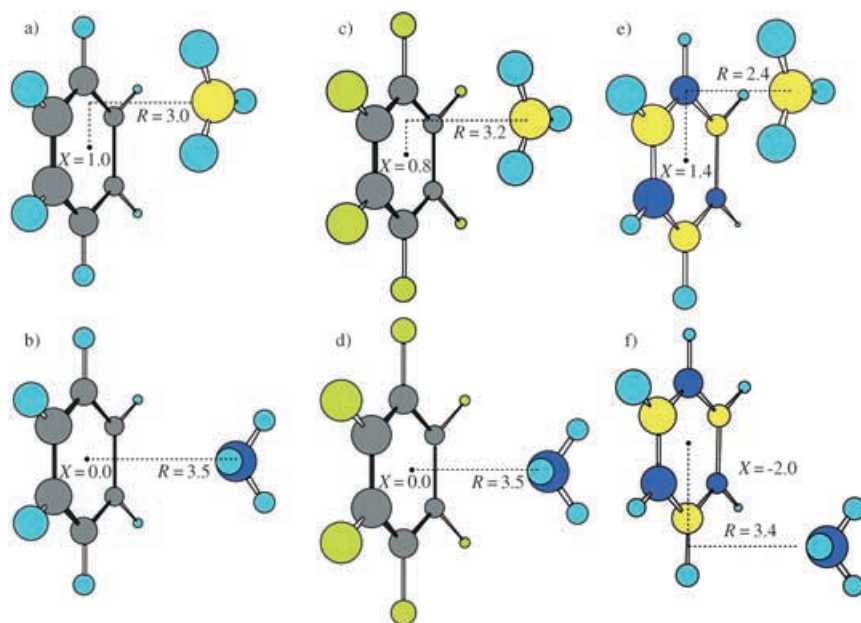


Figure 5. Structures of the complexes in Table 1. H: light blue, B: yellow, C: gray, N: dark blue and F: light green.

et al.<sup>[14]</sup> The total atomic charges of the heavy atoms of benzene and borazine were negative and that of hexafluorobenzene was positive.

For the interaction between benzene and borane ( $R = 3.0$ ,  $X = 1.0$  Å, see also Figure 5a), the electron correlation con-

tribution ( $E_{\text{corr}} = -4.61$  kcal mol<sup>-1</sup>) was the major factor for the attractive interaction. The electrostatic interaction ( $E_{\text{ES}} = -0.71$  kcal mol<sup>-1</sup>) was much less negative than the  $E_{\text{corr}}$ . The value of  $E_{\text{corr}}$  in the interaction between benzene and ammonia ( $-1.68$  kcal mol<sup>-1</sup>, see also Figure 5b) was less negative than that in the interaction between benzene and borane. The  $E_{\text{ES}}$  in the interaction between benzene and ammonia was largely repulsive ( $+2.03$  kcal mol<sup>-1</sup>). As the result, total interaction energy in the interaction between benzene and ammonia became positive. The  $E_{\text{ES}}$  ( $+0.53$  kcal mol<sup>-1</sup>) and  $E_{\text{rep}}$  ( $+2.42$  kcal mol<sup>-1</sup>) were repulsive. On the other hand, the value of  $E_{\text{corr}}$  ( $-4.96$  kcal mol<sup>-1</sup>) in the interaction between hexafluorobenzene and borane (Figure 5c) was largely negative and comparable to that of the interaction between benzene and borane ( $-4.61$  kcal mol<sup>-1</sup>). As a result, attractive  $E_{\text{corr}}$  in hexafluorobenzene and borane interaction overcame the repulsive effect of  $E_{\text{ES}}$  and  $E_{\text{rep}}$ . The intermolecular distances at the potential minima in the



Table 2. BSSE corrected interaction energy ( $\Delta E_{\text{HF}}$  and  $\Delta E_{\text{MP2}}$ , kcal mol<sup>-1</sup>), the contribution of each interaction term (kcal mol<sup>-1</sup>) in MP2/aug-cc-pVDZ potential energy.

	BH <sub>3</sub> / $\pi_{\text{H}}$	NH <sub>3</sub> / $\pi_{\text{H}}$	BH <sub>3</sub> / $\pi_{\text{F}}$	NH <sub>3</sub> / $\pi_{\text{F}}$	BH <sub>3</sub> / $\pi_{\text{BN}}$	NH <sub>3</sub> / $\pi_{\text{BN}}$
$\Delta E_{\text{HF}}$	+1.39	+2.94	+2.95	-1.39	+0.93	+0.62
BSSE <sub>HF</sub>	+0.73	+0.30	+1.30	+0.81	+0.64	+0.32
$\Delta E_{\text{MP2}}$	-3.22	+1.25	-2.01	-3.16	-3.68	-0.45
BSSE <sub>MP2</sub>	+2.06	+0.75	+2.84	+1.62	+2.69	+0.89
$E_{\text{corr}}$	-4.61	-1.68	-4.96	-2.58	-4.61	-1.07
$E_{\text{ES}}$	-0.71	+2.03	+0.53	-1.72	-3.70	+0.44
$E_{\text{rep}}$	+2.10	+0.91	+2.42	+1.14	+4.63	+0.18
$R$ [Å]	3.0	3.5 <sup>[a]</sup>	3.0	3.2	2.4	3.4
$X$ [Å]	1.0	0.0	0.8	0.0	1.4	-2.0
structure	Figure 5a	Figure 5b	Figure 5c	Figure 5d	Figure 5e	Figure 5f

[a] No potential energy minimum was observed for various  $R$ .

Table 3. Local charge of atoms and  $\pi$  system [au] in the Merz–Singh–Kollman scheme<sup>[a]</sup> by using MP2/aug-cc-pVDZ density.

	C	H	F	$\pi$ system	
C <sub>6</sub> H <sub>6</sub>	-0.13	+0.13		-0.76	
C <sub>6</sub> F <sub>6</sub>	+0.11		-0.11	+0.68	
	B	N	H(-B)	H(-N)	$\pi$ system
B <sub>3</sub> N <sub>3</sub> H <sub>6</sub>	+0.62	-0.76	-0.18	+0.32	-0.41

[a] See ref. [14].

H<sub>3</sub>B/ $\pi_{\text{H,F,BN}}$  complexes were remarkably shorter than those in the H<sub>3</sub>N/ $\pi_{\text{H,F,BN}}$  complexes. Therefore,  $E_{\text{corr}}$  had larger contribution in the H<sub>3</sub>B/ $\pi_{\text{H,F,BN}}$  complexes. As shown in Figure 2a and b, the values  $E_{\text{corr}}$  in the H<sub>3</sub>B/ $\pi_{\text{H}}$  complex and that in the H<sub>3</sub>B/ $\pi_{\text{F}}$  complex were comparable, when  $R$  had the same value. Thus, the difference in  $R$  values is the main reason for the difference of  $E_{\text{corr}}$  in these complexes at the potential minima.

Benzene has an attraction to Lewis acids but has repulsion to Lewis bases. In contrast to benzene, hexafluorobenzene has an attraction to both Lewis bases and acids. Because of the amphoteric  $\pi$ -electron system in the borazine, attractive interaction between borane and borazine was observed when the borane located close to the nitrogen atom ( $X=1.4$  Å, see also Figure 5e). On the other hand, attractive interaction between ammonia and borazine was observed when the nitrogen atom is close to the hydrogen attached to a boron atom of borazine ( $X = -2.0$  Å, see also Figure 5f). In borazine, nitrogen and proton, bonded with boron (H(-B) in Table 2), were negatively charged and boron and proton, bonded with nitrogen (H(-N) in Table 2), were positively charged. Total atomic charge of the heavy atoms was negative; thus, the interaction between the borazine and boron ( $-3.68$  kcal mol<sup>-1</sup>) was more attractive than the interaction between the borazine and ammonia ( $-0.45$  kcal mol<sup>-1</sup>).

## Conclusion

The electron correlation effect, the main component of which should be the dispersion energy, had the largest contribution for the attractive interaction between a  $\pi$  system (benzene, hexafluorobenzene and borazine) and a Lewis

acid/base (borane and ammonia). The electrostatic interaction also had an important role. Benzene, an electron-rich  $\pi$  system, has an attraction to borane, and it has repulsion with ammonia when lone pair of ammonia points toward the benzene ring (ammonia acts as a Lewis base). Hexafluorobenzene, an electron-deficient  $\pi$  system, and borazine, an amphoteric  $\pi$ -electron system, have attraction to both borane and ammonia.

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