

# Molecular orbital calculations of the substituent effect on intermolecular CH/ $\pi$ interaction in C<sub>2</sub>H<sub>3</sub>X-C<sub>6</sub>H<sub>6</sub> complexes (X=H, F, Cl, Br, and OH)

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## Abstract

The effect of a substituent group in dimeric complexes of benzene with ethylene and its four derivatives on the intermolecular CH/ $\pi$  interaction was studied theoretically. The hydrogen-bonding nature of the CH/ $\pi$  interaction is confirmed by the bond critical point analysis within the atoms-in-molecules (AIM) theory. It has been found that the CH  $\cdots$   $\pi$  access angle depends on the exchange repulsion and the induction effect from the substituent group. The effect of the CT interaction by the substituent group is energetically insignificant. However, the charge density can be varied by substitution, and this contribution cannot be ignored.

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## 1 Introduction

The weak molecular interaction between a nonpolar CH bond and an electron-rich aromatic moiety has been recognized to be important in various fields of chemistry and biochemistry. This attractive force, termed the CH/ $\pi$  interaction, has been reviewed in a recent monograph [1]. As in the ordinary case of hydrogen bonding, the concept of the CH/ $\pi$  interaction is useful for understanding the basis of many chemical and biological phenomena such as chiral recognition, self-assembly [2], and the structures of proteins [3] and nucleic

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acids. Despite the general acceptance in various fields of chemistry, the nature of the CH/ $\pi$  interaction still remains controversial, because this interaction is too weak to be distinguished from the trivial van der Waals attractive force.

The mechanism of the CH/ $\pi$  interaction have widely been studied to date by experiment [4–6] and theory [7–17], but the directionality of this interaction, especially that caused by the substituent group, has scarcely been reported. In our previous study of the orientation dependence of the CH/ $\pi$  interaction by a crystallographic database analysis [12], the non-bonded distance between a CH hydrogen atom and a C<sub>6</sub> aromatic  $\pi$  plane ( $D$ , see Fig. 1) and the CH  $\cdots$   $\pi$  access angle ( $\alpha$ ) were found to depend on the acidity of the hydrogen atom; our conclusions were also supported by ab initio calculations. For the methane/benzene complex, the stabilization energy was shown to become maximal when the CH group approaches coaxially from the direction perpendicular to the  $\pi$ -molecular plane [1]. On the other hand, the access angle was found to deviate from 180° in the ethylene/benzene system. There we argued that the CH  $\cdots$   $\pi$  access angle in the ethylene (or ethylene derivative)/benzene system was sensitive, on steric grounds, to the substituent group at the  $\alpha$  position. In this study [12], however, the geometry of the interacting molecules was not optimized, nor was the substituent effect studied systematically. With regard to the role of the charge transfer (CT) in the CH/ $\pi$  hydrogen bond, different opinions have been presented to date. Tsuzuki et al. studied, by high-level ab initio calculations, the distance dependence of the CH/ $\pi$  interaction in complexes of benzene with methane and its halogen derivatives [7–9,14]. There they concluded that the contribution of the CT interaction was insignificant in the CH/ $\pi$  interaction. On the other hand, a possible contribution from the CT interaction has been pointed out by a number of other workers, although this interaction was not the main contribution [6,10,11,18]. Ugozzoli et al., in particular, made DFT calculations of CH<sub>3</sub>X/benzene complexes (X=F, Cl, Br, I, CN, and NO<sub>2</sub>) to study the effect of substituent to the CH/ $\pi$  interaction [15], and concluded that a non-negligible contribution comes from the CT interaction in the substituent group effect, but the amounts of the interaction were not discussed explicitly.

To elucidate the points discussed above and to investigate the nature of the CH/ $\pi$  interaction, we have here made systematic calculations on model complexes of benzene with five ethylene derivatives C<sub>2</sub>H<sub>3</sub>X (X=H, F, Cl, Br, and OH).

## 2 Computational Method

Calculations were carried out using the Gaussian 98 program [19]. The basis sets implemented in the program were employed without modification. The

electron correlation energies were calculated by applying the second order Møller-Plesset perturbation theory (MP2). Each geometry of the complexes was optimized at the MP2/6-311++G(2d,p) level. The 6-311++G(2d,p) basis sets were utilized to estimate the interaction energy as precisely as possible: Two diffuse functions were augmented for incorporating long-range interactions.

The basis set superposition error (BSSE) was corrected by the counterpoise method. The process to assign the components of the intermolecular interactions (electrostatic, repulsion, and correlation energies) was the same as that employed by Tsuzuki et al. [7–9,14] The distributed multipoles [20] were obtained from the MP2/6-311++G(2d,p) densities using GDMA coded by Stone. The electrostatic interaction and induction energies of the complexes were calculated as the interactions between the distributed multipoles by the use of ORIENT version 3.2. To estimate the induction effect, anisotropic polarizabilities  $\alpha_{xx} = \alpha_{yy} = 123.1$  and  $\alpha_{zz} = 63.5 \times 10^{-25} \text{ cm}^3$  [21] were placed in the center of the benzene ring. The atomic charge distributions of the complexes were estimated by the electrostatic potential fitting with the Merz-Singh-Kollman scheme [22] to evaluate the amount of CT from benzene to each ethylene derivative.

A topological analysis of the electron density was performed using Bader’s theory of atoms in molecules (AIM) [23]. The AIM analysis has been applied to studies of properties of a variety of hydrogen-bonded systems exhibiting both conventional and nonconventional hydrogen bonds [11,24–28]. Specifically, the topology of the electron density was analyzed for complexes of the  $\pi$  systems with CH donors (methane, chloroform, and HCN) [11,26]. The bond critical points (BCPs),  $\rho(r_c)$ , and the eigenvalues of the Hessian of the charge density at the critical point,  $\lambda_1 < \lambda_2 < \lambda_3$ , were obtained using the AIM2000 [29]. The derived measures were the Laplacian of the charge density at that point,  $\nabla^2\rho(r_c) = \sum_{i=1}^3 \lambda_i$ , and the ratio,  $|\lambda_1|/\lambda_3$ . These measures are used in the following for the description of hydrogen bonding.

### 3 Results and discussion

#### 3.1 Optimized geometries of the complexes

The optimized geometries of  $\text{C}_2\text{H}_4\text{-C}_6\text{H}_6$  **1**,  $\text{C}_2\text{H}_3\text{F-C}_6\text{H}_6$  **2**,  $\text{C}_2\text{H}_3\text{Cl-C}_6\text{H}_6$  **3**,  $\text{C}_2\text{H}_3\text{Br-C}_6\text{H}_6$  **4**, and  $\text{C}_2\text{H}_3\text{OH-C}_6\text{H}_6$  **5** are shown in Fig. 2. Variables  $D$ ,  $x$ , and  $\alpha$  are summarized in Table 1. The hydrogen atom is located in the range of  $D < 2.9 \text{ \AA}$  (sum of the van der Waals radii), suggesting the existence of a specific CH/ $\pi$  interaction between the two components.

We first discuss the substituent effect. The interaction energy  $E_{\text{total}}$  is smaller than "strong hydrogen bonds", such as the OH/O bond, and increases with the decreasing equilibrium distance  $D$ . In complexes **1**, **3**, and **4**, the hydrogen atom interacting with the benzene molecule is located almost exactly above the center of the aromatic ring. In complexes **2** and **5**, on the other hand, the interacting points are shifted a little from the center of the ring. In our previous study [12], where the geometry of the isolated molecule was not optimized, the offset distance  $x$  was estimated to be  $\approx 0.1$  Å from the ring center. In the present study, where the geometry is fully optimized, this offset is nearly removed in complexes **2** and **5**. The offset may be caused by the steric effect between the other parts of the ethylene molecule and the benzene ring. The potential energy profile vs. the offset distance from the ring center is found to be rather flat.

### 3.2 Topological parameters of CH/ $\pi$ interaction at BCP

The bond critical point properties,  $\rho(r_c)$ ,  $\nabla^2\rho(r_c)$ , and  $|\lambda_1|/\lambda_3$  associated with the CH/ $\pi$  interactions at the MP2/6-311++G(2d,p) level are shown in Table 2. The BCPs between two molecules are also shown in Fig. 2. Only one intermolecular BCP is found for complexes **2**, **3**, and **4**. These values satisfy the characteristics of the hydrogen bonding, i.e.,  $0.002 < \rho(r_c) < 0.0034$  a.u.,  $0.02 < \nabla^2\rho(r_c) < 0.14$  a.u., and  $|\lambda_1|/\lambda_3 < 1$  [24]. This reflects the dominant contraction of the electron density toward the atomic basins found in closed-shell interactions. We note that  $\rho(r_c)$  corresponds well to the total energy in Table 1. In comparison with **1**, the  $\rho(r_c)$  values for all the other systems are larger. This suggests that the CH/ $\pi$  interaction is induced by the substituent group. For complexes **1** and **5**,  $\nabla^2\rho(r_c)$  is smaller than 0.02, and two intermolecular BCPs are found; this indicates that these bonds are looser than the others, and  $\rho(r_c)$  of **1** is the smallest of the other systems.

The total charges on ethylene derivatives are summarized in Table 3. The atomic charge is known to depend on the basis sets when inadequate basis sets are used. In the present study, where large enough basis sets have been used, the results are essentially independent of basis sets. The estimated fractions of the transferred electrons listed in this table are only a few percent, but these values are not negligible. As pointed out by Tsuzuki et al. [7–9,14], the CT interaction is indeed a minor element as the energy component. The charge density, however, can be varied by substitution, and this contribution cannot be ignored. It can influence various molecular properties, e.g., those related to NMR and IR spectra [1,11,15].

The orientation dependence is one of the most important properties for the hydrogen-bonding system. The access angle  $\alpha$  tends to approach  $180^\circ$  with increasing total interaction energy. Earlier papers [12] suggested the directionality of the CH/ $\pi$  interaction originating from the electrostatic interaction but not from the correlation interaction (mainly the van der Waals interaction). It is natural to consider that the electrostatic interaction is reflected in the CH proton acidity, which has been shown to increase in the following order:  $\text{C}_2\text{H}_3\text{F} > \text{C}_2\text{H}_3\text{Cl} > \text{C}_2\text{H}_3\text{Br} > \text{C}_2\text{H}_3\text{H} > \text{C}_2\text{H}_3\text{OH}$  [1,12]. However, the  $\alpha$  angle does not approach  $180^\circ$  in the same order. Besides, the number of electrons in the substituent group seems to influence the access angle. What is the origin of the orientation dependence of the CH/ $\pi$  interaction?

To investigate this issue in more detail, the energetic components of the interaction energy for various benzene complexes have been examined. Table 4 summarizes the results. We note that the total energy depends on the correlation energy, but not on the electrostatic energy, being consistent with the reported conclusions of ours and other workers [8,9,12,14]; the CH/ $\pi$  interaction largely arises from the dispersion force. We note that the CH/ $\pi$  distance  $D$  is shortened upon substitution of a functional group; this shortening depends on the correlation energy. In addition, the CH/ $\pi$  distance  $D$  is correlated with the induction energy. The induction energy originates from the interaction between polar and non-polar molecules and is approximately proportional to  $r^{-6}$ , where  $r$  is the intermolecular distance between the permanent and induced dipole moments [30]. Furthermore, we also find from this table that the induction energy, which does not work as a main contributor, increases as the  $\alpha$  angle approaches  $180^\circ$ . Although the atomic polarizability of the substituent group X is not included in our calculations, a large polarizability is expected to influence the benzene ring. For a closer examination, the angular dependence of the energy components for the  $\text{C}_2\text{H}_3\text{Cl}-\text{C}_6\text{H}_6$  complex are shown in Fig. 3 as a typical example. In this calculation the geometry of each isolated molecule is fixed and only the molecular orientation is varied. This figure shows that the induction energy, as well as the total energy, is stabilized when the access angle approaches  $180^\circ$  similarly to the total energy and that this tendency is independent of the offset distance  $x$ . However, the variance in the total energy with the access angle is  $1.5 - 2.8 \text{ kcal mol}^{-1}$ , whereas the variance in the induction energy is only  $0.04 \text{ kcal mol}^{-1}$ . The main component of this energy seems to be the exchange-repulsion (data are not shown here). The electrostatic energy has a different tendency, however, because a significant interaction is possible between the benzene edge and a CH bond depending on the access angle. In this case, the electrostatic energy is not necessarily an important factor for determining the orientation.

As discussed above, the decisive term for the orientation of the CH/ $\pi$  interaction is the exchange repulsion. The induction energy has the same tendency as the total energy, but its contribution is much smaller. As for the OH/ $\pi$  and NH/ $\pi$  interaction, the electrostatic interactions are in general stronger than that of the CH/ $\pi$  interaction but depend on the situation. As suggested earlier [12], the directionality of the CH/ $\pi$  interaction originates from the electrostatic interaction, but not from the correlation interaction (mainly the van der Waals interaction). Note, however, that the induction effect was disregarded in this reference, because the target systems were hydrocarbons, CH<sub>4</sub>-C<sub>6</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>2</sub>-C<sub>6</sub>H<sub>6</sub>, and C<sub>2</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>6</sub>, where this effect seemed trivial. Thus, the molecular orientation of the CH/ $\pi$  interaction by a substituent group is expected to depend largely on the exchange repulsion (so-called steric hindrance) and to be closely related to the induction effect at the same time, rather than the increase in the CH proton acidity. The substituent effect of the CH/ $\pi$  interaction depends on the correlation energy (mainly the dispersion force), which determines the amount of the interaction energy.

## 4 Conclusions

Our bond critical point analysis has shown that the CH/ $\pi$  interaction is a kind of hydrogen bonding; the orientation dependence of the CH/ $\pi$  interaction is similar to that of the conventional hydrogen bonds. Most of the interaction energy of the CH/ $\pi$  bonding originates from the correlation energy (essentially the van der Waals force). The directionality of the CH/ $\pi$  interaction by the substituent group is suggested to depend on mainly on the exchange repulsion and the induction effect from the substituent group, which is a small amount of contribution. The effect of CT interaction by the substituent group is energetically insignificant but influences molecular properties such as those related to NMR and IR spectra.

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Table 1

Total energies and geometric parameters of the CH/ $\pi$  interactions for ethylene derivative/benzene complexes

complex	$E_{\text{total}}^{\text{a}}$	$D^{\text{b}}$	$x^{\text{b}}$	$\alpha^{\text{c}}$
C <sub>2</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>6</sub> <b>1</b>	-2.14	2.516	0.078	156.5
C <sub>2</sub> H <sub>3</sub> F-C <sub>6</sub> H <sub>6</sub> <b>2</b>	-2.86	2.420	0.151	160.2
C <sub>2</sub> H <sub>3</sub> Cl-C <sub>6</sub> H <sub>6</sub> <b>3</b>	-3.41	2.298	0.070	186.0
C <sub>2</sub> H <sub>3</sub> Br-C <sub>6</sub> H <sub>6</sub> <b>4</b>	-3.68	2.298	0.020	188.7
C <sub>2</sub> H <sub>3</sub> OH-C <sub>6</sub> H <sub>6</sub> <b>5</b>	-2.53	2.428	0.131	160.7

<sup>a</sup> Total MP2 interaction energies corrected for BSSE in kcal mol<sup>-1</sup>.

<sup>b</sup> Distances in Å.

<sup>c</sup> Angles in degrees.

Table 2

Topological parameters associated with the CH/ $\pi$  interactions<sup>a</sup>

complex	BCP(1) <sup>b</sup>			BCP(2) <sup>b</sup>		
	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$ \lambda_1 /\lambda_3$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$ \lambda_1 /\lambda_3$
C <sub>2</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>6</sub> <b>1</b>	0.0063	0.021	0.150	0.0040	0.012	0.116
C <sub>2</sub> H <sub>3</sub> F-C <sub>6</sub> H <sub>6</sub> <b>2</b>	0.0076	0.025	0.169			
C <sub>2</sub> H <sub>3</sub> Cl-C <sub>6</sub> H <sub>6</sub> <b>3</b>	0.0090	0.032	0.161			
C <sub>2</sub> H <sub>3</sub> Br-C <sub>6</sub> H <sub>6</sub> <b>4</b>	0.0086	0.030	0.150			
C <sub>2</sub> H <sub>3</sub> OH-C <sub>6</sub> H <sub>6</sub> <b>5</b>	0.0074	0.025	0.164	0.0036	0.011	0.081

<sup>a</sup> At the MP2/6-311++G(2df,2p) level.<sup>b</sup> For **1** and **5**, two bond critical points are shown. BCP1 is located above the center of the benzene ring and BCP2 above the edge of the benzene ring.

Table 3

Total charge on each ethylene derivative consisting of complexes<sup>a</sup>

complex	6-311++G(2d,p)	6-311++G(2df,2p)	6-311++G(3df,3pd)	cc-pVTZ
C <sub>2</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>6</sub> <b>1</b>	0.022	0.022	0.023	0.024
C <sub>2</sub> H <sub>3</sub> F-C <sub>6</sub> H <sub>6</sub> <b>2</b>	0.039	0.038	0.040	0.039
C <sub>2</sub> H <sub>3</sub> Cl-C <sub>6</sub> H <sub>6</sub> <b>3</b>	0.034	0.034	0.037	0.034
C <sub>2</sub> H <sub>3</sub> Br-C <sub>6</sub> H <sub>6</sub> <b>4</b>	0.025	0.026	0.029	0.026
C <sub>2</sub> H <sub>3</sub> OH-C <sub>6</sub> H <sub>6</sub> <b>5</b>	0.013	0.013	0.014	0.015

<sup>a</sup> The Merz-Singh-Kollman scheme at the MP2 level. Each geometry was optimized by the MP2/6-311++G(2d,p) level.

Table 4

Calculated energies of the CH/ $\pi$  interactions for ethylene derivative/benzene complexes<sup>a</sup>

complex	$E_{\text{total}}^{\text{b}}$	$E_{\text{es}}^{\text{c}}$	$E_{\text{rep}}^{\text{d}}$	$E_{\text{corr}}^{\text{e}}$	$E_{\text{ind}}^{\text{f}}$
C <sub>2</sub> H <sub>4</sub> -C <sub>6</sub> H <sub>6</sub> <b>1</b>	-2.14	-1.26	3.19	-3.97	-0.10
C <sub>2</sub> H <sub>3</sub> F-C <sub>6</sub> H <sub>6</sub> <b>2</b>	-2.86	-2.57	4.02	-3.73	-0.58
C <sub>2</sub> H <sub>3</sub> Cl-C <sub>6</sub> H <sub>6</sub> <b>3</b>	-3.41	-1.81	4.00	-4.94	-0.75
C <sub>2</sub> H <sub>3</sub> Br-C <sub>6</sub> H <sub>6</sub> <b>4</b>	-3.68	-1.84	4.10	-5.25	-0.69
C <sub>2</sub> H <sub>3</sub> OH-C <sub>6</sub> H <sub>6</sub> <b>5</b>	-2.53	-1.91	3.78	-4.09	-0.31

<sup>a</sup> Energies in kcal mol<sup>-1</sup>.

<sup>b</sup> Total MP2 interaction energies corrected for BSSE.

<sup>c</sup> Electrostatic interaction energy.

<sup>d</sup> Exchange repulsion energy.

<sup>e</sup> Electron correlation (dispersion) energy.

<sup>f</sup> Induction energy.

Figure captions.

Fig. 1. Geometry of ethylene derivative/benzene complexes.  $D$  : distance from an H atom to the aromatic  $\pi$  plane,  $x$  : horizontal distance of an H atom from the center of the aromatic ring, and  $\alpha$  : CH  $\cdots$   $\pi$  access angles.

Fig. 2. Optimized structures of complexes. Intermolecular bond critical points (BCPs) from AIM analysis are also shown: (a) C<sub>2</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>6</sub> **1**, (b) C<sub>2</sub>H<sub>3</sub>F-C<sub>6</sub>H<sub>6</sub> **2**, (c) C<sub>2</sub>H<sub>3</sub>Cl-C<sub>6</sub>H<sub>6</sub> **3**, (d) C<sub>2</sub>H<sub>3</sub>Br-C<sub>6</sub>H<sub>6</sub> **4**, and (e) C<sub>2</sub>H<sub>3</sub>OH-C<sub>6</sub>H<sub>6</sub> **5**.

Fig. 3. Interaction energies of C<sub>2</sub>H<sub>3</sub>Cl-C<sub>6</sub>H<sub>6</sub> system on the CH  $\cdots$   $\pi$  access angle  $\alpha$  (see Fig. 1) at various offset distances,  $x = -0.2 - +0.2$  Å. Intermolecular distance  $D$  is fixed at 2.4 Å.

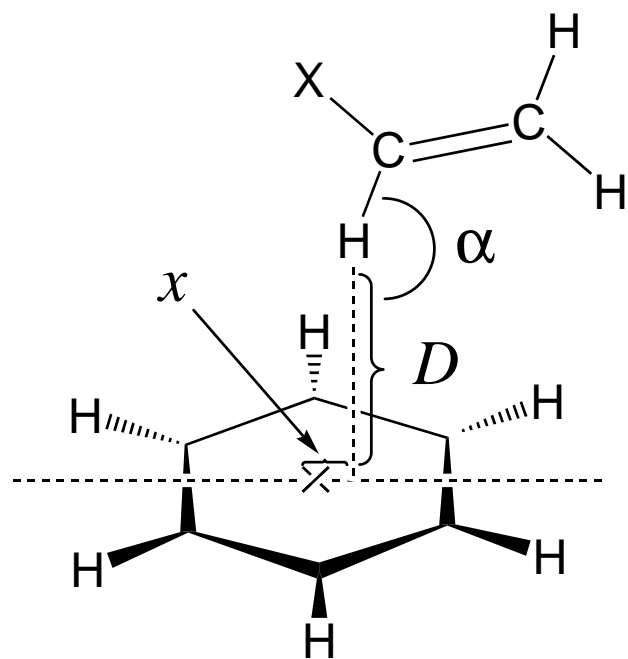


Fig.1 Takahashi et al.

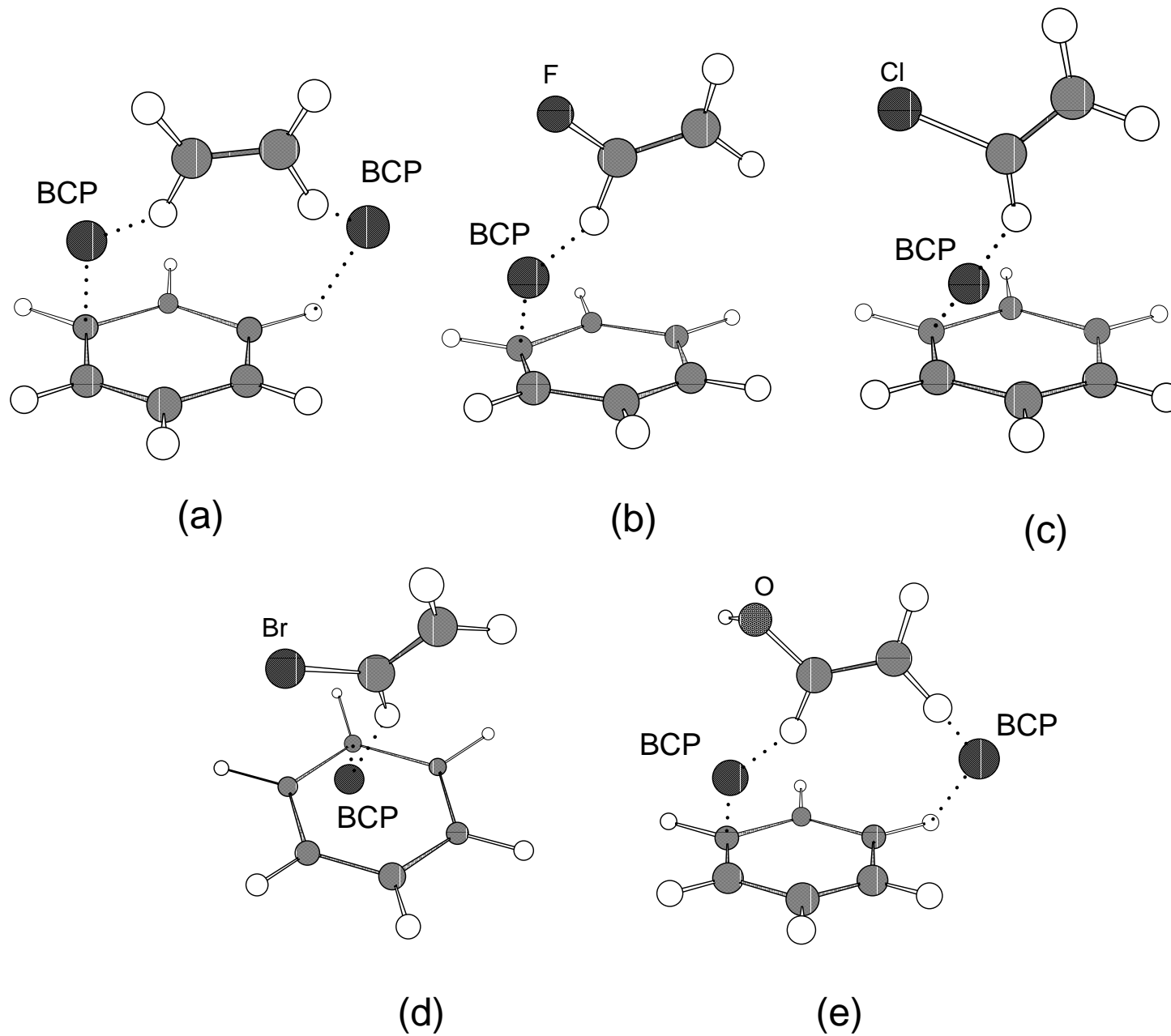


Fig. 2 Takahashi et al.

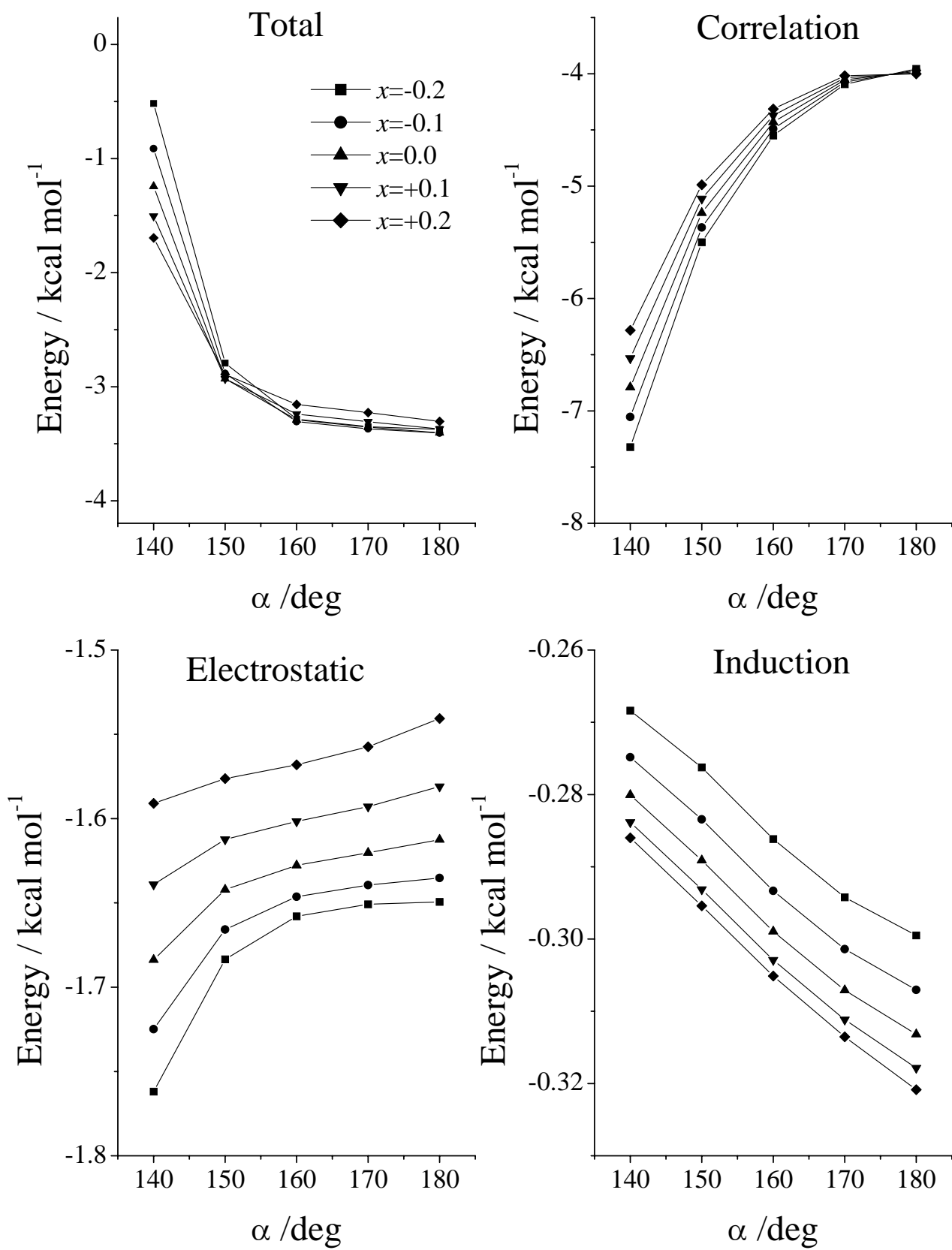


Fig.3 Takahashi et al.