Magnitude and Directionality of the Interaction Energy of the Aliphatic CH/*π* Interaction: Significant Difference from Hydrogen Bond

Seiji Tsuzuki,*,[†] Kazumasa Honda,[†] Tadafumi Uchimaru,[†] Masuhiro Mikami,[†] and Asuka Fujii[‡]

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan, and Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, Miyagi 980-8578, Japan

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The CCSD(T) level interaction energies of CH/π complexes at the basis set limit were estimated. The estimated interaction energies of the benzene complexes with CH_4, CH_3CH_3, CH_2CH_2, CHCH, CH_3NH_2, CH_3OH, CH_3OCH_3, CH_3F, CH_3Cl, CH_3ClNH_2, CH_3ClOH, CH_2Cl_2, CH_2FCl, CH_2F_2, $CHCl_3$, and CH_3F_3 are −1.45, −1.82, −2.06, −2.83, −1.94, −1.98, −2.06, −2.31, −2.99, −3.57, −3.71, −4.54, −3.88, −3.22, −5.64, and −4.18 kcal/mol, respectively. Dispersion is the major source of attraction, even if substituents are attached to the carbon atom of the C−H bond. The dispersion interaction between benzene and chlorine atoms, which is not the CH/π interaction, is the cause of the very large interaction energy of the $CHCl_3$ complex. Activated CH/π interaction (acetylene and substituted methanes with two or three electron-withdrawing groups) is not very weak. The nature of the activated CH/π interaction may be similar to the hydrogen bond. On the other hand, the nature of other typical (nonactivated) CH/π interactions is completely different from that of the hydrogen bond. The typical CH/π interaction is significantly weaker than the hydrogen bond. Dispersion interaction is mainly responsible for the attraction in the CH/π interaction, whereas electrostatic interaction is the major source of attraction in the hydrogen bond. The orientation dependence of the interaction energy of the typical CH/π interaction energy is very small, whereas the hydrogen bond has strong directionality. The weak directionality suggests that the hydrogen atom of the interacting C−H bond is not essential for the attraction and that the typical CH/π interaction does not play critical roles in determining the molecular orientation in molecular assemblies.

Introduction

Recently, weak intermolecular interactions have attracted much interest, as the weak interactions sometimes play crucial roles in determining the structures and properties of molecular assemblies such as molecular crystals, host−guest complexes, and proteins.[1] The weak attraction between the C−H bond and the π system is called the CH/π interaction.[1,2] The CH/π interaction is a very weak interaction compared with the conventional hydrogen bond. High-level ab initio calculations predicted that the intermolecular interaction energy of the benzene−methane cluster is −1.45 kcal/mol.[3] The calculated interaction energy agrees well with the recently reported experimental bonding energy of the cluster in the gas phase.[4] Ab initio calculations show that the dispersion interaction is mainly responsible for the attraction in the CH/π interaction.[3]

Sometimes, the CH/π interaction was regarded as a weak hydrogen bond. Probably structural analogy between the CH/π interaction and the π-hydrogen bond would be the cause of this claim. The interacting C−H bond prefers to point toward the benzene ring as for the π-hydrogen bond (Figure 1).[5] Crystal structure analysis shows that CH/π contacts are observed in many systems. It was often claimed that the sum of the many CH/π interactions may not be negligible and that the very weak CH/π interactions might play crucial roles in controlling the structures of molecular assemblies as for the conventional hydrogen bond.

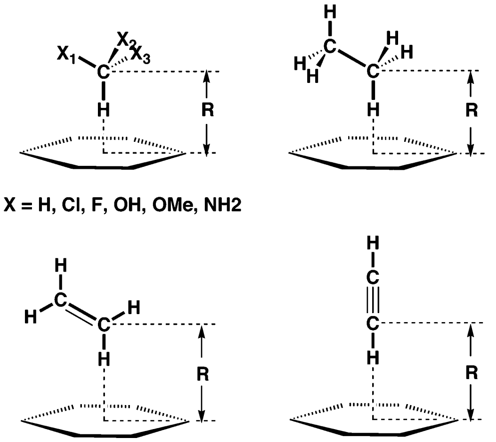

Figure 1. Structures of model CH/π complexes.

Desiraju and Steiner reported that the hydrogen bond plays critical roles in determining the structures of molecular assemblies, as the hydrogen bond is sufficiently strong and sufficiently directional.[1] The interaction energy of the hydrogen bond has strong orientation dependence, as the highly orientation dependent electrostatic interaction is the major source of the attraction in the hydrogen bond.[6] On the other hand, an

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* To whom correspondence should be addressed. E-mail: s.tsuzuki@aist.go.jp.

[†] AIST.

[‡] Tohoku University.

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electrostatic interaction is not the major source of the attraction in the CH/π interaction,[3,7] which suggests the weak orientation dependence of the CH/π interaction energy.

Detailed information on the magnitude and orientation dependence of the CH/π interaction "energy" is necessary to confirm its role in controlling structures of molecular assemblies, as the intermolecular forces control the structures. The size of the electrostatic interaction is important for understanding the orientation dependence of the interaction energy, as the electrostatic interaction mainly determines the orientation dependence of the interaction energy.[8−10] The directionality of the CH/π interaction has been studied extensively by statistical analysis of crystal structures, which shows that the C−H bond prefers to point toward the benzene ring.[5] Although the crystal structure analysis provides detailed information on structures, it does not provide any direct information on the orientation dependence of the interaction energy.

The nature of the CH/π interaction will depend on the acidity of the interacting C−H bond. The acidity of a C−H bond depends strongly on its hybridization type and substituents. The acidity of methane is extremely low (pK_a = 49), whereas it is remarkably enhanced in acetylene (pK_a = 25).[11] Ab initio calculations of the benzene−acetylene complex show that the electrostatic interaction is also important for the attraction in an "activated" CH/π interaction in this complex.[3] The CH/π interaction energy of the activated C−H bond (acetylene) has a weak orientation dependence.[12−14] The activated CH/π interaction has a little similarity with the π-hydrogen bond[15] and that it may possibly play little roles in controlling molecular orientation in molecular assemblies as for the hydrogen bond. On the other hand, the electrostatic interaction is very weak in a "typical" (nonactivated) CH/π interaction (C−H bonds of alkanes). This difference suggests that the nature of the CH/π interaction (magnitude of the interaction energy and its directionality) depends strongly on the hybridization type and substituents.

From the above discussion, it becomes clear that the nature of the CH/π interaction of typical C−H bonds and its roles in controlling the structures of molecular assemblies should be discussed separately from those of activated C−H bonds. Many CH/π interactions were found in crystals, although it is unclear whether the interacting C−H bonds are activated or not. Most of C−H bonds in nature are typical (low-acidic) C−H bonds. Therefore, detailed information on the magnitude and directionality of the interaction energy of the typical CH/π interaction is essential for understanding the roles of the CH/π interaction in controlling the structures of molecular assemblies.

Several theoretical calculations of model systems of the CH/π interaction were reported[3,7,16−32] Electron correlation was accounted for at the MP2 level in most of the calculations. However, recent high-level ab initio calculations of aromatic molecules show that a very large basis set and CCSD(T) level electron correlation correction are necessary for quantitative evaluation of the CH/π interaction energies.[3,7,19,33−36] The size of the total interaction energy and electrostatic energy of the activated CH/π interaction (benzene complexes with acetylene and chloroform) were reported from high-level ab initio calculations.[3,7] However, the effects of other substituents were not well understood. The orientation dependence of the interaction energy of the typical CH/π interaction was unclear.

In this paper, we have calculated the interaction energies of benzene complexes with several substituted methanes to evaluate the effects of substituents on the total interaction energy and electrostatic contribution. We have discussed which substituents "activate" the C−H bond. We have analyzed the orientation dependence of the typical CH/π interactions and have discussed the roles of the typical CH/π interaction for controlling the structures of molecular assemblies. We have also discussed the roles of the hydrogen atom for the attraction in the typical CH/π interaction and the cause of very large attraction in the benzene−chloroform complex.

Computational Method

The Gaussian 98 and 03 programs[37,38] were used for the ab initio molecular orbital calculations to evaluate total interaction energies. The basis sets implemented in the Gaussian programs were used. Electron correlation was accounted for at the MP2[39,40] and CCSD(T) levels.[41] Geometries of isolated molecules were optimized at the MP2/6-31G* level and were used for calculations of complexes. The basis set superposition error (BSSE)[42] was corrected for all calculations using the counterpoise method.[43] The MP2 level interaction energies (E_{MP2}) were calculated using Dunning's cc-pVXZ (X = D, T, and Q) basis sets.[44,45] The MP2 interaction energies at the basis set limit [$E_{\mathrm{MP2(limit)}}$] were estimated by the method of Feller[46] from the calculated E_{MP2} values using the Dunning's basis sets. The CCSD(T) level interaction energies at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] were estimated as the sum of the estimated $E_{\mathrm{MP2(limit)}}$ and CCSD(T) correction term (the difference between the calculated CCSD(T) and MP2 level interaction energies using cc-pVDZ basis set).[3,7] The details of the estimation procedure are described in the Supporting Information. The electrostatic energy of the complex was calculated using the ORIENT version 3.2.[47] The electrostatic energy of the dimer was calculated as interactions between distributed multipoles of monomers.[10,48] Distributed multipoles up to hexadecapole on all atoms were obtained from the MP2/6-311G** wave functions of an isolated molecule using CADPAC version 6.[49] Distributed multipoles were used only to estimate the electrostatic energy.

Results and Discussion

Magnitude of the CH/π Interaction and Electrostatic and Dispersion Contributions. The interaction energy potentials of benzene clusters with substituted methanes (Figure 1) calculated at the MP2/cc-pVTZ level are shown in Figure 2. The estimated $E_{\mathrm{CCSD(T)(limit)}}$ values (E_{total}, total interaction energy) of the complexes at the potential minima are summarized in Table 1. The estimated E_{total} of the benzene−methane complex, which corresponds to $-D_e$, is −1.45 kcal/mol. The vibrational zero-point energy contribution (ΔZPE) reported from ab initio calculations is 0.30 kcal/mol.[4] The calculated D_0 (= D_e − ΔZPE) is 1.15 kcal/mol, which is very close to the recently reported experimental D_0 (1.03−1.13 kcal/mol) in the gas phase.[4] The good agreement suggests that the estimated E_{total} values of the complexes are sufficiently accurate. Detailed evaluation of the effects of basis set and electron correlation is described in the Supporting Information.

E_{es} is the electrostatic energy. E_{corr} is the effect of electron correlation on the calculated total interaction energy, which is the difference between E_{total} and E_{HF} (HF level interaction energy using the cc-pVQZ basis set). The dispersion interaction is the major contributor to E_{corr}. E_{rep} (= $E_{\mathrm{HF}} - E_{\mathrm{es}}$) is mainly the exchange-repulsion energy, but it also includes some other terms. The calculated potentials (Figure 2) show that substantial attraction still exists in these complexes even when molecules are well separated, which shows that the major source of attraction in the CH/π interaction is not short-range interactions

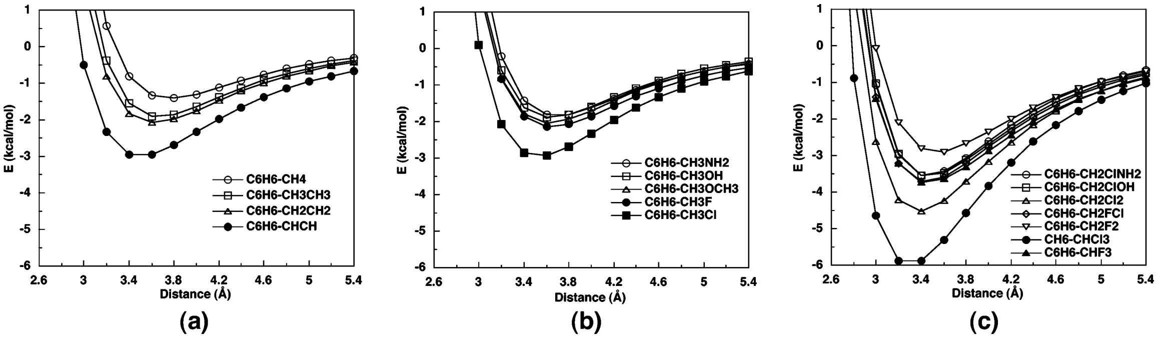

Figure 2. Calculated interaction energies of model CH/π complexes at the MP2/cc-pVTZ level. Geometries of complexes are shown in Figure 1.

TABLE 1: Electrostatic and Dispersion Energies of CH/π Complexes[a]

	E_{total}[b]	E_{es}[c]	E_{rep}[d]	E_{corr}[e]
$C_6H_6-CH_4$[f]	−1.45	−0.25	1.10	−2.30
$C_6H_6-CH_3CH_3$[f]	−1.82	−0.17	1.97	−3.62
$C_6H_6-CH_2CH_2$[f]	−2.06	−0.65	1.82	−3.23
C_6H_6-CHCH[f]	−2.83	−2.01	1.44	−2.26
monosubstituted				
$C_6H_6-CH_3NH_2$	−1.94	−0.28	1.92	−3.58
$C_6H_6-CH_3OH$	−1.98	−0.37	1.63	−3.24
$C_6H_6-CH_3OCH_3$	−2.06	−0.44	1.73	−3.35
$C_6H_6-CH_3F$	−2.31	−0.93	1.48	−2.86
$C_6H_6-CH_3Cl$[g]	−2.99	−1.06	1.44	−3.37
disubstituted				
$C_6H_6-CH_2ClNH_2$	−3.57	−1.09	2.68	−5.16
$C_6H_6-CH_2ClOH$	−3.71	−1.48	2.67	−4.90
$C_6H_6-CH_2Cl_2$[g]	−4.54	−1.81	2.41	−5.14
$C_6H_6-CH_2FCl$	−3.88	−1.93	2.44	−4.39
$C_6H_6-CH_2F_2$	−3.22	−1.55	1.01	−2.68
trisubstituted				
$C_6H_6-CHCl_3$[g]	−5.64	−2.42	4.63	−7.85
$C_6H_6-CHF_3$[g]	−4.18	−2.43	1.67	−3.42
hydrogen bond				
$C_6H_6-H_2O$[h]	−3.02	−1.86	1.07	−2.23
H_2O-H_2O[i]	−4.80	−6.65	3.20	−1.35

[a] Energies in kcal/mol. The geometries of complexes are shown in Figure 1. [b] Estimated CCSD(T) level interaction energy at the basis set limit. See text. [c] Electrostatic energy. See text. [d] Repulsion energy [$= E_{\mathrm{HF}} - E_{\mathrm{es}}$]. E_{HF} was calculated at the HF/cc-pVQZ level. See text. [e] Correlation interaction energy [$= E_{\mathrm{total}} - E_{\mathrm{HF}}$]. E_{corr} is mainly dispersion energy. See text. [f] Reference 3. [g] Reference 7. [h] Reference 62. [i] E_{total} and E_{corr} were taken from ref 69. E_{es} was calculated using the same geometry.

($E \sim e^{-\alpha R}$) such as charge transfer, but long-range interactions ($E \sim R^{-n}$) such as electrostatic and dispersion.[51] Calculated atomic charge distributions of the benzene-methane cluster also show that the charge-transfer is negligible.[3]

The E_{total} of the benzene−acetylene complex (−2.83 kcal/mol) is substantially larger (more negative) than those of the benzene complexes with methane and ethane (−1.45 and −1.82 kcal/mol, respectively). The large E_{es} in the benzene−acetylene complex (−2.01 kcal/mol) shows that electrostatic interaction is responsible for the large attraction in the activated CH/π interaction in the complex. The E_{total} of the benzene−ethylene complex (−2.06 kcal/mol) is close to that of the benzene−ethane complex. The E_{es} values of methane, ethane, and ethylene complexes (−0.25, −0.17, and −0.65 kcal/mol, respectively) are small. These results show that the sp2 C−H bond of ethylene is not activated.

The attraction in the benzene complexes with monosubstituted methanes is only slightly larger than that in the benzene−methane complex, which shows that the activation of the C−H bonds in the monosubstituted methanes is very weak. The E_{total} of the benzene complexes with monosubstituted methanes are −1.45 to −2.31 kcal/mol with one exception of the chloromethane complexes (−2.99 kcal/mol). (The origin of the large attraction in the benzene-chloromethane complex will be discussed later.) The E_{es} values of monosubstituted methane complexes (−0.28 to −1.06 kcal/mol) are only slightly larger (more negative) than that of the methane complex. The small electrostatic contributions show that the nature of the CH/π interactions of the monosubstituted complexes is close to that of the methane complex (nonactivated CH/π interaction).

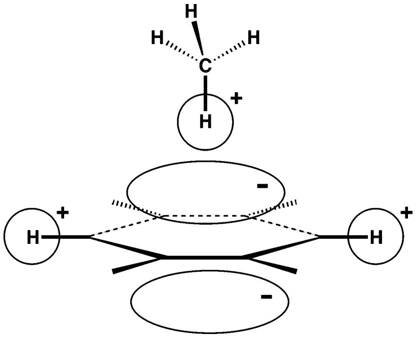

Figure 3. Electrostatic interaction between benzene and methane.

The benzene complexes with di- or tri-sbustituted methanes have large interaction energies (−3.22 to −5.64 kcal/mol). The interaction energy of the benzene−chloroform complex (−5.64 kcal/mol) is larger than that of the water dimer (about −5 kcal/mol).[51,52] The large E_{es} of the complexes (−1.29 to −2.43 kcal/mol) is a cause of the large E_{total} of the di- or trisubstituted methane complexes. The electron withdrawing groups increase the positive charge on the hydrogen atom of the interacting C−H bond, which increases the attractive electrostatic interaction with the benzene, as benzene has quadrupole moment as shown in Figure 3. The large electrostatic contributions suggest that the C−H bonds of the di- or trisubstituted methanes are substantially activated. The nature of these activated CH/π interaction may be similar to that of the π-hydrogen bond.

The E_{corr} values are always considerably larger than E_{es}, which shows that dispersion is mainly responsible for the attraction in the CH/π complexes, even if the C−H bond is activated by electron-withdrowing substituents. Electrostatic interaction is not the major source of attraction in the benzene complexes with substituted methanes. The substituents increase the E_{corr}. The E_{corr} values of the complexes (−2.86 to −7.85 kcal/mol) are larger than that of the benzene−methane complex (−2.30 kcal/mol). Especially the E_{corr} values of chlorinated methane complexes (−3.37 to −7.85 kcal/mol) are very large.

The different origins of the typical and activated CH/π interactions are evidenced by electronic spectroscopy of gas-

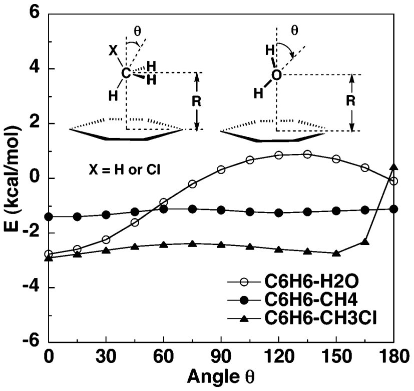

Figure 4. Orientation dependence of calculated interaction energies of CH/π and OH/ π complexes at the MP2/cc-pVTZ level with BSSE correction. The distances between the centroid of benzene and the carbon atoms of methane and chloromethane were fixed at 3.8 and 3.6 Å, respectively, in the calculations. The distance between the centroid of benzene and the oxygen atom of water was fixed at 3.4 Å.

phase complexes. In aromatic complexes of the van der Waals type, such as benzene−rare gas and benzene−tetrachrolomethane complexes,[53,54] the S_1-S_0 electronic transition is generally low-frequency shifted in comparison with that of the bare molecule. The low-frequency shift of the electronic transition means the enhancement of the binding (interaction) energy of the complex, and it is caused by the larger polarizability of the aromatic moiety in the electronic excited state. On the other hand, a high-frequency shift is generally seen in π-hydrogen-bonded complexes such as benzene−water.[55] The electronic transition of these complexes is localized in the aromatic moiety, and the enhancement of the dispersion interaction is expected also for the π-hydrogen-bonded complexes. The high-frequency shift of the π-hydrogen-bonded complexes means a decrease of the binding energy in the electronic excited state. Therefore, it indicates that the contribution of the electrostatic interaction is more important in the π-hydrogen-bonded complexes, and the reduction of the electrostatic interaction upon the electronic excitation is dominant over the enhancement of the dispersion interaction. Electronic transition of the benzene−methane and benzene−ethane complexes shows low-frequency shifts,[56] suggesting the major contribution of the dispersion force in these complexes. This is in contrast with the trend of the “activated” CH/π interaction type complexes, benzene−acetylene and benzene−chloroform, which are known to show the high-frequency shifts in the S_1-S_0 transition,[15,57−60] and it reflects the importance of the electrostatic interaction in the total intermolecular interactions.

Directionality of CH/π Interaction. The details of the orientation dependence of the interaction energy of the typical CH/π interaction were not well understood. The orientation dependence of the interaction energies of the benzene complexes with methane and chloromethane was calculated at the MP2/cc-pVTZ level, as the MP2/cc-pVTZ level interaction energies are always very close to the estimated $E_{CCSD(T)(limit)}$ as shown in Table 1S. The distance between the centroid of benzene and the carbon atom of the interacting C−H bond was fixed. The methane and chloromethane were rotated to evaluate the orientation dependence of the interaction energies of the typical CH/π interaction. The interaction energy of the benzene-water complex (π-hydrogen bond) was also calculated for comparison.

The orientation dependence of the calculated interaction energies of the CH/π complexes is very small as shown in Figure 4. The calculated interaction energies of the benzene−methane complex are −1.12 to −1.42 kcal/mol. The change of the interaction energy by the rotation (ΔE) is only 0.30 kcal/mol. The calculated interaction energies of the benzene-chloromethane complex are −2.39 to −2.93 kcal/mol (ΔE = 0.54 kcal/mol) when θ are 0° to 150°.[61] The calculated interaction energy potentials of the two CH/π complexes have their minima when $\theta = 0°$. The calculations show that the C−H bond prefers to point toward the benzene ring, which agrees well with the crystal structure databese analysis.

The directionality of the interaction energy of the typical CH/π interaction is very weak compared with the π-hydrogen bond (ΔE = 3.64 kcal/mol). Highly orientation dependent electrostatic interaction is mainly responsible to the directionality of the π-hydrogen bond (OH/π interaction).[62] On the other hand, the electrostatic contribution is small in typical CH/π interaction.[63]

Roles of Hydrogen Atom for Attraction in Typical CH/π Interaction. The comparison of E_{es} and E_{corr} shows that dispersion is the major source of attraction in the CH/π complexes, which suggests that the hydrogen atom of the C−H bond is not essential for the attraction. Dispersion has its origin in molecular polarization. Polarizability of a hydrogen atom is considerably smaller than that of a carbon atom, which suggests that the dispersion interaction between carbon atoms of benzene ring and the carbon atom of the C−H bond is mainly responsible for the attraction in the CH/π complexes.

The rotation of methane and chloromethane does not largely change the calculated interaction energies of the CH/π complexes, if the distance between benzene and the carbon atom of the C−H bond was fixed. The very small change of the interaction energy associated with the rotation of the C−H bond also suggests that the hydrogen atom is not important for the attraction.

Origin of Strong Attraction between Benzene and Chlorinated Methanes. The strong attraction between benzene and chloroform was reported. The aromatic-solvent induced shift of ^{1}HNMR spectra shows that the C−H bond of chloroform positions above the benzene ring.[64−67] The strong attraction in the benzene-chloroform complex was called CH/π hydrogen bonding. High-level ab initio calculations also show the existence of strong attraction between the benzene and chloroform ($E_{total} = -5.64$ kcal/mol).[7] The strong attraction was explained by the strong acidity of the hydrogen atom of chloroform, which increases the attractive electrostatic interaction. It was also claimed that the strong acidity increases the charge-transfer interaction between benzene and chloroform.

However, ab initio calculations show that the dispersion interaction is mainly responsible for the strong attraction in the benzene−chloroform complex. The electrostatic interaction is not the primary source of the strong attraction in the complex. The E_{corr} of the chloroform complex (−7.85 kcal/mol) is 5.55 kcal/mol greater than that of the methane complex (−2.30 kcal/mol), whereas the E_{es} of the chloroform complex (−2.42 kcal/mol) is only 2.18 kcal/mol greater than that of the methane complex (−0.25 kcal/mol).[68] The distance dependence of the calculated interaction energy (Figure 2c) suggests that charge-transfer (short-range interaction) is not the major source of the attraction.

The large E_{corr} values of the chlorinated methane complexes suggest that dispersion interaction between chlorine atoms and benzene is the cause of large E_{corr} values, as chlorine atoms have a large polarizability. The E_{corr} values of the chlorinated methane complexes are considerably larger than those of the corresponding fluorinated methane complexes, which clearly indicates that the dispersion interaction with chlorine atoms contributes largely to the E_{corr}, as polarizability of a fluorine atom is considerably smaller than that of a chlorine atom.

The calculations suggest that dispersion interaction between benzene and chlorine atoms, which is not the CH/π interaction (interaction between C−H bond and π system), largely contributes to the attraction between the benzene and chloroform. The strong attraction in the benzene-chloroform complex is not the evidence of strong CH/π interaction in the complex.

Comparison with the Hydrogen Bond. The comparison of the typical (nonactivated) CH/π interaction with the hydrogen bond (Table 1) show that the nature of the typical CH/π interaction is completely different from that of the hydrogen bond: (1) The typical CH/π interaction is very weak compared with the hydrogen bond.[62,69] (2) The dispersion interaction is the major source of attraction in the typical CH/π interaction and electrostatic contribution is very small, whereas the electrostatic interaction contributes largely to the attraction in the hydrogen bond. (3) The directionality of the interaction energy of the typical CH/π interaction is very weak. On the other hand the interaction energy of the π−hydrogen bond has a strong orientation dependence. The conventional hydrogen bond has larger directionality than the π-hydrogen bond.

The calculated electrostatic and dispersion contributions to the attraction in the benzene−acetylene complex suggest that the nature of the activated CH/π interaction in this complex has a little similarity with the π−hydrogen bond. The sizes of electrostatic and dispersion contributions in the acetylene complex (−2.01 and −2.26 kcal/mol) are close to those in the benzene−water complex (−1.86 and −2.23 kcal/mol). Apparently, the electrostatic contribution is the cause of the weak directionality of the interaction energy of the benzene−acetylene complex.[12−14] On the other hand, more isotropic dispersion interaction is the major source of attraction in the benzene−chloroform complex. Although the size of the electrostatic interaction in the chloroform complex (−2.42 kcal/mol) is close to that in the acetylene complex, the electrostatic interaction in the chloroform complex is much weaker than the dispersion interaction (−7.85 kcal/mol).

Roles of CH/π Interaction in Controlling Structures of Molecular Assemblies. The typical CH/π interaction (methane, ethylene and monosubstituted methane complexes) will not play crucial roles in controlling molecular orientation in molecular assemblies. The typical CH/π interaction is very weak. The contribution of electrostatic interaction to the attraction is very small. Therefore, the orientation dependence of the typical CH/π interaction energy is very small (nearly negligible), as we have discussed before.

The activated CH/π interaction (acetylene and substituted methanes with two or three electron withdrawing groups) may possibly play a little role in controlling molecular orientation in molecular assemblies. The activated CH/π interaction is not very weak. The interaction energy has weak orientation dependence.

The above discussion clearly shows that the type of C−H bond is critical for understanding the roles of the CH/π interaction in molecular assemblies. Although large numbers of CH/π contacts were found in crystals, most of the C−H bonds in the nature are typical C−H bonds, which suggests that large parts of the observed CH/π interaction are not crucial in controlling the molecular orientation in the crystal. Recently Dunitz and Gavezzotti have pointed out that molecules may be in van der Waals contact in crystals without having a particularly attractive interaction, but just enabling the close packing of the crystal.[70]

Conclusions

Dispersion interaction is the major source of attraction even if substituents are attached to the interacting C−H bond. Electrostatic interaction also contributes to the attraction in the activated CH/π interaction (acetylene and di- or trisubstituted methanes). The substituted methane complexes have larger (more negative) interaction energies than the methane complex, as the substituents increase the dispersion interaction. The dispersion interaction between the benzene and chlorine atoms, which is not the CH/π interaction, contributes largely to the very large attraction in the chlorinated methane complexes.

The nature of the typical (nonactivated) CH/π interaction is completely different from the hydrogen bond. The typical CH/π interaction is substantially weaker than the hydrogen bond. The major source of attraction in the typical CH/π interaction is the dispersion interaction, whereas the highly orientation dependent electrostatic interaction is mainly responsible for the attraction in the hydrogen bond. The orientation dependence of the interaction energy of the typical CH/π interaction is very weak compared with the hydrogen bond due to the small contribution of the electrostatic interaction. The large dispersion contribution in the typical CH/π interaction suggests that the hydrogen atom of the C−H bond is not essential for the attraction, as the atomic polarizability of hydrogen is small.

Although it was sometimes claimed that the CH/π interaction is important in determining the structures of molecular assemblies without considering the type of the interacting C−H bond, the very weak directionality of the interaction energy of the typical CH/π interaction suggests that the typical CH/π interaction does not play crucial roles in controlling the molecular orientation in molecular assemblies. Our calculations show that the typical CH/π interaction should be distinguished from the hydrogen bond. It may be appealing to call the CH/π interaction as a weak hydrogen bond, but it will mislead the nature of the typical CH/π interaction and its roles in molecular assemblies.

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Supporting Information Available: Detailed discussion on the effects of basis set and electron correlation. Estimation procedure of the CCSD(T) level interaction energy at the basis set limit. Calculated HF, MP2, and CCSD(T) level interaction energies of CH/π complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond*; Oxford University Press: New York, 1999.

(2) Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π interaction*; Wiley-VCH: New York, 1998.

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

(4) Shibasaki, K.; Fujii, A.; Mikami, N.; Tsuzuki, S. *J. Phys. Chem. A* **2006**, *110*, 4397.

(5) Umezawa, Y.; Tsuboyama, S.; Honda, K.; Uzawa, J.; Nishio, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1207.

(6) Stone, A. J. *Chem. Phys. Lett.* **1993**, *211*, 101.

(7) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Phys. Chem. A* **2002**, *106*, 4423.

(8) Buckingham, A. D.; Fowler, P. W. *J. Chem. Phys.* **1983**, *79*, 6426.

(9) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 2018.

(10) *The theory of intermolecular forces*; Stone, A. J., Ed.; Clarendon Press: Oxford, U.K., 1996.

(11) Jones, M., Jr. *Organic chemistry*, 2nd ed.; W. W. Norton & Company, Inc.: New York, 2000.

(12) Philip, D.; Robinson, M. A. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1643.

(13) Takahashi, O.; Kohno, Y.; Iwasaki, S.; Saito, K.; Iwaoka, M.; Tomoda, S.; Umezawa, Y.; Tsuboyama, S.; Nishio, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 2421.

(14) Takahashi, O.; Kohno, Y.; Saito K. *Chem. Phys. Lett*. **2003**, *378*, 509.

(15) Fujii, A.; Morita, S.; Miyazaki, M.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2004**, *108*, 2652.

(16) Kodama, Y.; Nishihata, K.; Nishio, M.; Nakagawa, N. *Tetrahedron Lett.* **1977**, 2105.

(17) Takagi, T.; Tanaka, A.; Matsuo, S.; Maezaki, H.; Tani, M.; Fujiwara, H.; Sasaki, Y. *J. Chem. Soc., Perkin 2* **1987**, 1015.

(18) Sakaki, S.; Kato, K.; Miyazaki, T.; Musashi, Y.; Ohkubo, K.; Ihara, H.; Hirayama, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 659.

(19) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Phys. Chem. A* **1999**, *103*, 8265.

(20) Oki, M.; Takano, S.; Toyota, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2221.

(21) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.

(22) Novoa, J. J.; Mota, F. *Chem. Phys. Lett.* **2000**, *318*, 345.

(23) Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323.

(24) Tsuzuki, S.; Houjou, H.; Nagawa, Y.; Hiratani, K. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1951.

(25) Takahashi, O.; Kohno, Y.; Iwasaki, S.; Saito, K.; Iwaoka, M.; Tomoda, S.; Umezawa, Y.; Tsuboyama, S.; Nishio, M. *Bull. Chem. Soc. Jpn*. **2001**, *74*, 2421.

(26) Ribas, J.; Cubero, E.; Luque, F. J.; Orozco, M. J. *J. Org. Chem.* **2002**, *67*, 7057.

(27) Ugozzoli, F.; Arduini, A.; Massera, C.; Pochini, A.; Secchi, A. *New J. Chem.* **2002**, *26*, 1718.

(28) Sundararajan, K.; Sankaran, K.; Viswanathan, K. S.; Kulkarni, A. D.; Gadre, S. R. *J. Phys. Chem. A* **2002**, *106*, 1504.

(29) Sundararajan, K.; Viswanathan, K. S.; Kulkarni, A. D.; Gadre, S. R. *J. Mol. Struct.* **2002**, *613*, 209.

(30) Medakovic, V. B.; Milcic, M. K.; Bogdanovic, G. A.; Zaric, S. D. *J. Inorg. Biochem.* **2004**, *98*, 1867.

(31) Linares, M.; Pellegatti, A.; Roussel, C. *J. Mol. Struct. Theochem* **2004**, *680*, 169.

(32) Kobayashi, Y.; Saigo, K. *J. Am. Chem. Soc.* **2005**, *127*, 15054.

(33) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem*. **1996**, *100*, 18790.

(34) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104.

(35) Tsuzuki, S.; Honda, K.; Azumi, R. *J. Am. Chem. Soc.* **2002**, *124*, 12200.

(36) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M. *J. Chem. Phys.* **2004**, *120*, 647.

(37) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(39) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

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

(41) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys*. **1987**, *87*, 5968.

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

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

(44) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(45) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (Ehama, 1993).

(46) Feller, D. J. *Chem. Phys*. **1992**, *96*, 6104.

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

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

(49) CADPAC: The Cambridge Analytical Derivatives Package, Issue 6, Technol. rep., University of Cambridge, 1995, A suite of quantum chemistry programs developed by Amos, R. D. et al.

(50) 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.

(51) Curtiess, L. A.; Frurip, D. J.; Blander, M. *J. Chem. Phys.* **1979**, *71*, 2703.

(52) Feyereisen, M. W.; Feller, D.; Dixon, D. A. *J. Phys. Chem.* **1996**, *100*, 2993.

(53) Leutwyler, S. *Chem. Phys. Lett.* **1984**, *107*, 284.

(54) Gonohe, N.; Suzuki, N.; Abe, H.; Mikami, N.; Ito, M. *Chem. Phys. Lett.* **1983**, *94*, 549.

(55) Gotch, A.; Zwier, T. S. *J. Chem. Phys.* **1992**, *96*, 3388.

(56) Schauer, M.; Bernstein, E. R. *J. Chem. Phys.* **1985**, *82*, 726.

(57) Carrasquillo, E.; Zwier, T. S.; Levy, D. H. *J. Chem. Phys.* **1985**, *83*, 4990.

(58) Shelley, M. Y.; Dai, H.-L.; Troxler, T. *J. Chem. Phys.* **1999**, *110*, 9081.

(59) Ramos, C.; Winter, P. R.; Stearns, J. A.; Zwier, T. S. *J. Phys. Chem. A* **2003**, *107*, 10280.

(60) Gotch, A. J.; Pribble, R. N.; Ensminger, A.; Zwier, T. S. *Laser Chem.* **1994**, *13*, 187.

(61) The repulsion between benzene and chlorine atom is the cause of the positive interaction energy of the benzene-chloromethane complex when $\theta = 180°$.

(62) Tsuzuki, S.; Honda, K.; Uchimaru, T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2000**, *122*, 11450.

(63) The interaction energy of the activated CH/π interaction (benzene−acetylene complex) has weak orientation dependence (refs 12−14).

(64) Reeves, L. W.; Schneider, W. G. *Can. J. Chem.* **1957**, *35*, 5, 251.

(65) Johnson Jr., C. E.; Bovey, F. A. *J. Chem. Phys.* **1958**, *29*, 1012.

(66) Zurcher, R. F. *Helv. Chim. Acta* **1961**, *44*, 1380.

(67) Ehama, R.; Tsushima, M.; Yuzuri, T.; Suezawa, H.; Sakakibara, K.; M. Hirota.*Bull. Chem. Soc. Jpn.* **1993**, *66*, 814.

(68) Although electrostatic interaction in the benzene-chloroform complex is substantially weaker than dispersion interaction, electrostatic interaction plays a crucial role in stabilizing the orientation in which the C−H bond points toward the benzene ring. The total interaction [$E_{\mathrm{CCSD(T)(limit)}}$] of this orientation benzene-chloroform complex (Figure 1) is −5.64 kcal/mol, whereas that of the reverse orientation complex is −2.42 kcal/mol, which shows that the former complex is 3.22 kcal/mol more stable than the later one. The E_{es} of the former orientation is attractive (−2.42 kcal/mol), whereas that of the later one is repulsive (0.45 kcal/mol). The difference of E_{es} (2.87 kcal/mol) is close to the difference of the total interaction energy, which shows that highly orientation dependent electrostatic interaction mainly determines the stable orientation of the benzene-chloroform complex.

(69) Tsuzuki, S.; Luthi, H. P. *J. Chem. Phys.* **2001**, *114*, 3949.

(70) Dunitz, J. D.; Gavezzotti, A. *Cryst. Growth Des.* **2005**, *5*, 2180.