

Hydrogen-Bond-Like Nature of the CH/π Interaction as Evidenced by Crystallographic Database Analyses and Ab Initio Molecular Orbital Calculations

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Spatial distribution of CH hydrogen atoms with reference to a six-membered carbon aromatic ring was analyzed in the crystal structures deposited in the Cambridge Structural Database (CSD). The crystal data showed the propensity that the CH hydrogen atoms lie above the center of the aromatic ring to form interatomic CH/π contacts. Investigation of the effects of the CH proton acidity on the strength and the structure of the CH/π interaction has demonstrated that the distance between the hydrogen atom and the π plane (D_{pln}) decreases with increase of the CH proton acidity (D_{pln}: CCH_3 ≅ sp^2-CH > sp-CH ≅ Cl_2CH_2 > Cl_3CH), and that the C–H···π access angle (α) tends to approach 180° in the same order. Further, a negative correlation has been found between D_{pln} and α. The directional preferences are in accord with the property of conventional hydrogen bond, indicating a hydrogen-bond-like character of the CH/π interaction. In order to elucidate the intrinsic nature of the CH/π interaction, ab initio calculations [MP2/6-311++G(d,p)] were carried out for methane/benzene, ethylene/benzene, and acetylene/benzene complexes. Potential surfaces obtained for the three model supramolecules are consistent with the results from the CSD analyses.

Weak molecular interaction between a nonpolar (or weakly polar) CH bond and an electron-rich π-system has been recognized to be important in various fields of chemistry and biochemistry. This attractive force is termed the CH/π interaction.[1] Like the ordinary hydrogen bond, the concept of the CH/π interaction is useful for understanding the bases of chemical and biological phenomena such as chiral recognition,[2] self-assembly,[3] and the structure of proteins[4] and nucleic acids.[5] Despite its acceptance in various fields of chemistry, the nature of the CH/π interaction has remained controversial, because this interaction is very weak and difficult to distinguish from a trivial van der Waals attractive force.

The mechanism of CH/π interaction was studied from several different points of view. For instance, Suezawa et al. suggested that the CH/π interaction has a hydrogen-bond-like character, on the bases of electronic substituent effects on the conformational preference of a series of organic compounds.[6] Hunter et al.[7] and Saigo et al.[8] have shown that an electron-donating group on a phenyl ring caused strengthening of the aromatic CH/π interaction. Our previous statistical studies on crystal structures showed that the non-bonded CH/π distance tends to decrease with the increase of CH proton acidity.[9] On the ground of these facts, it now seems clear that the CH/π interaction does not simply originate from the dispersion force but involves interactions of an electronic nature.

Theoretically, Hirota et al. studied the issue by molecular mechanics calculations (MM2); they attributed the main origin of the CH/π interaction to the dispersion force.[10] Sakaki et al.[11] studied the nature of this interaction by ab initio calculations (MP2/MIDI4**) of methane/benzene and benzene/benzene complexes. They reported that the complexes preferred the T-shape geometry with a CH bond of the hydrocarbons pointing toward the center of the benzene ring. The CH/π interaction was ascribed primarily to the dispersion force with a minor contribution from the electrostatic interaction. Philp and Robinson[12] calculated (MP2/TZ2P) the potential surface of the CH/π(C≡C) interaction for an acetylene dimer, and found that the interaction energy is relatively insensitive to the position of the donating hydrogen atom along the bond vector of the accepting triple bond as well as to the C–H···π angle. Chakrabarti et al.[13] compared the stabilization energy of the CH/π interaction with those of other types of hydrogen bonds [MP2/6-31G(d,p)]. They reported that CH/π interaction and CH/N interaction become attractive only at the correlated level. More recently, Tsuzuki et al.[14] examined the stabilization energy of CH/π interactions, by high-level calculations (MP2/cc-pVQZ) of model hydrocarbon/benzene complexes in several geometries. They assigned the dispersion energy as the

most important contributor and suggested that the electrostatic force determines the directionality of the CH/π interaction. Contribution from the charge-transfer mechanism was also invoked to elucidate the nature of the CH/π interaction.[15,16] Oki et al.[16] reported that the global minimum configuration of an ethylene/benzene complex has a tilted C–H···π angle.

Despite these experimental and theoretical studies, unequivocal support for the inferred structural propensities has not been presented. Here we analyzed, systematically, the structural features of the CH/π interaction from both statistical and theoretical points of view. The observed directional preferences were compared with those of the conventional hydrogen bonds. We will show clear evidence for a hydrogen-bond-like character of the CH/π interaction.

Method

Database Analysis. The method of surveying CH/π contacts in the crystal structures deposited in the Cambridge Structural Database (CSD) was reported earlier.[9] A similar program was composed, by the use of a CSD software QUEST3D, to examine spatial relationship of CH groups with respect to a C_6 π system (Fig. 1). We chose the six-membered carbon aromatic ring since this is the system most extensively studied in view of its implications for chemistry and structural biology. Non-bonded short CH/π contacts were sought in compounds bearing at least one C_6 π system within the entire CSD (version 520: December 2000 release, 224 400 entries).[17] In order to collect as many data as possible, both organic and organometallic compounds were included in the search. Exclusion of organometallic compounds did not significantly affect the results.

Computational Method. The Gaussian 98 program[18] was used. The basis sets implemented in the program were employed without modification. Electron correlation energies were calculated by applying the second order Møller-Plesset perturbation theory (MP2).[19] The geometry, which was used for obtaining binding energies, was optimized for the isolated molecules (methane, ethylene, acetylene, and benzene) at the MP2/6-311++G(d,p) level of theory. High level approximations were necessary for estimating stabilization energies, since it was previously indicated that the use of small basis sets, such as cc-pVDZ or 6-311G(d,p), considerably underestimates binding energies.[20] The 6-311G++(d,p) basis sets were utilized in this study to determine the potential surfaces of the model complexes as precisely as possible; two diffuse functions were augmented for incorporating long-range interactions. Figure 2 shows the geometries of acetylene/benzene, ethylene/benzene, and methane/benzene complexes studied in the present work. In the case of the methane/benzene complex, two orientations were considered.

The basis set superposition error (BSSE) was corrected by the counterpoise method.[21] The process to assign the components of the intermolecular interactions (electrostatic, repulsion, and correlation energies) was the same as the method employed by Tsuzuki et al.[14] The distributed multipoles[22] were obtained from the MP2/6-311++G(d,p) densities, using GDMA coded by Stone.[23] The electrostatic interaction energies of the complexes were calculated as the interactions between the distributed multipoles by the use of ORIENT version 3.2.[24] It should be noted that the charge-transfer energies cannot be evaluated by this method. Therefore, the contribution from the charge-transfer energy to the CH/π interaction is

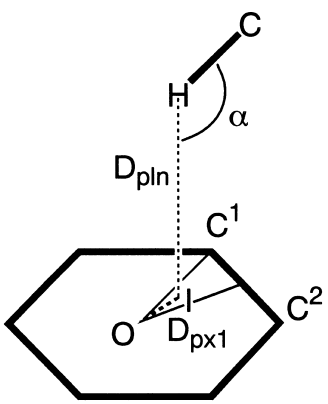

Fig. 1. Structural parameters used for surveying CH/π contacts in the CSD. O: Center of the ring. C^1: Carbon atom closest to H. C^2: Next closest carbon atom. D_{pln}: Distance from H to the aromatic π plane (line HI). D_{pxl}: Horizontal distance of H from the center of the aromatic ring (line IO). α: C–H···π access angle (∠ IHC).

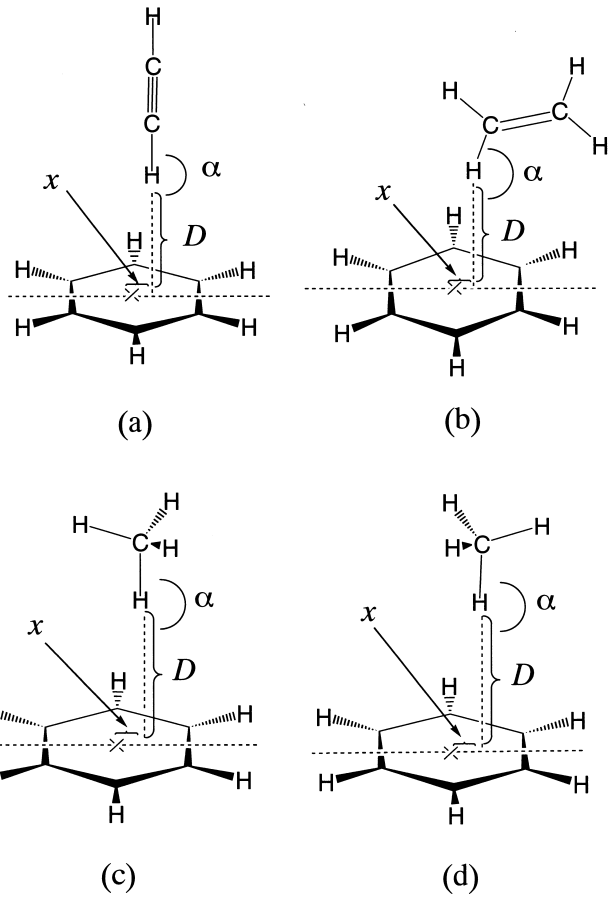

Fig. 2. Geometry of acetylene/benzene, ethylene/benzene, and methane/benzene complexes considered in this work. Definitions of the variables D and x are similar, but not the same, as those of D_{pln} and D_{pxl}, respectively, in Fig. 1.

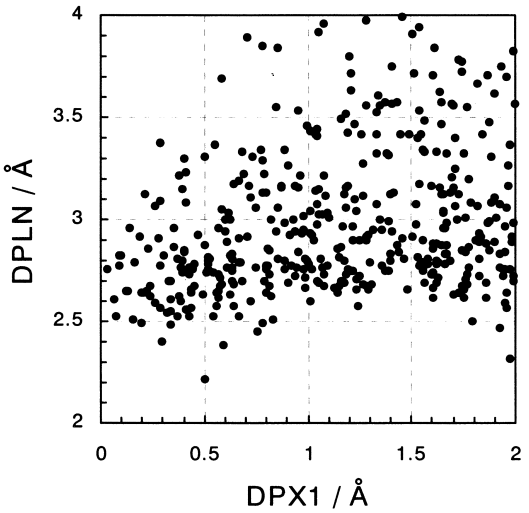

Fig. 3. Distribution of the sp^2-CH hydrogen atoms projected against a $D_{pxl} - D_{pln}$ plane (neutron data). D_{pxl}: Horizontal distance of H from the center of the aromatic ring. D_{pln}: Distance of H from the π plane.

not discussed in the present work.

Results and Discussion

Characterization of CH/π Interaction by Neutron Data. Evidence for the CH/π interaction would be obtained by measurement of the non-bonded distance between the CH hydrogen atom and the π ring. Therefore, spatial distribution of the CH hydrogen atoms with respect to the C_6 aromatic ring was examined. Figure 3 is a scattergram between D_{px1} (offset distance from the center of the ring) and D_{pln} (distance to the aromatic π plane) parameters obtained from neutron diffraction, which are more reliable than X-ray data for the positions of hydrogen atoms. Distribution of the CH hydrogen atoms is shown as a side-view to the aromatic ring. Here, the hydrogens are limited to aromatic CH (sp^2-CH) groups to minimize the chemical inhomogeneity. Note that a number of hydrogen atoms come over the π-plane (D_{px1} <1.4 Å). Figure 3 shows that sp^2-CH hydrogen atoms are more concentrated in the range of $D_{pln} < 2.9$ Å (van der Waals distance),[25] suggesting the existence of specific CH/π interactions between the two moieties.

Figure 4 shows histograms of the number of sp^2-CH's (neutron data) as a function of D_{px1} [(a): observed, (b): corrected by a factor of $1/D_{px1}$].[26] The number of the CH's increases slightly with D_{px1}, but the corrected data decreases and become almost constant outside the π ring ($D_{px1} > 1.4$ Å). It is clear that the CH hydrogen atom has a preference to place itself over the center of the aromatic ring.

Effects of the CH Proton Acidity. To investigate the effects of the CH proton acidity on the strength and the structure of the CH/π interaction, we categorized CH/π atomic contacts into six groups depending on the sort of CH's. Namely, (a) chloroform (Cl_3CH), (b) dichloromethane (Cl_2CH_2), (c) acetylenic CH (*sp*-CH), (d) aromatic CH (sp^2-CH), (e) aromatic CH (sp^2-CH) determined by neutron diffraction, and (f) methyl CH (CCH_3). Table 1 summarizes the mean values and the sample standard deviations of D_{pln} and α (uncorrected and corrected by a factor of $1/\sin\alpha$[27]).

Three features are apparent. First, the mean values of D_{pln}, α, and α(corrected) for (d) and (e) are almost the same to each other. This shows that the X-ray data can be used safely for investigating the CH/π interaction. Second, the mean value of D_{pln} decreases with increase of the CH proton acidity: $CCH_3 \cong sp^2$-CH > *sp*-CH $\cong Cl_2CH_2 > Cl_3CH$. This indicates that the strength of the CH/π interaction depends on the CH proton acidity. Third, the mean values of α and α(corrected) increase in the same order, i.e., $CCH_3 \cong sp^2$-CH < *sp*-CH $\cong Cl_2CH_2 < Cl_3CH$. Similar propensities have been reported for the ordinary hydrogen bonds[28] and the CH/O interaction.[29] It should be pointed out that the order has no relation with the steric hindrance around the interacting CH group; the stereochemical environments may be insignificant for the CH/π interaction.

Figure 5 shows the number of short CH/π contacts ($D_{pln} <$ 2.9 Å) as a function of D_{px1}. The CH hydrogen atoms have an obvious trend to position themselves just over the center of the aromatic ring ($D_{px1} \approx 0$ Å), except for *sp*-CH. The structural bias to bring the CH hydrogen atom toward the center of the ring gradually decreases from Cl_3CH to Cl_2CH_2, sp^2-CH, and

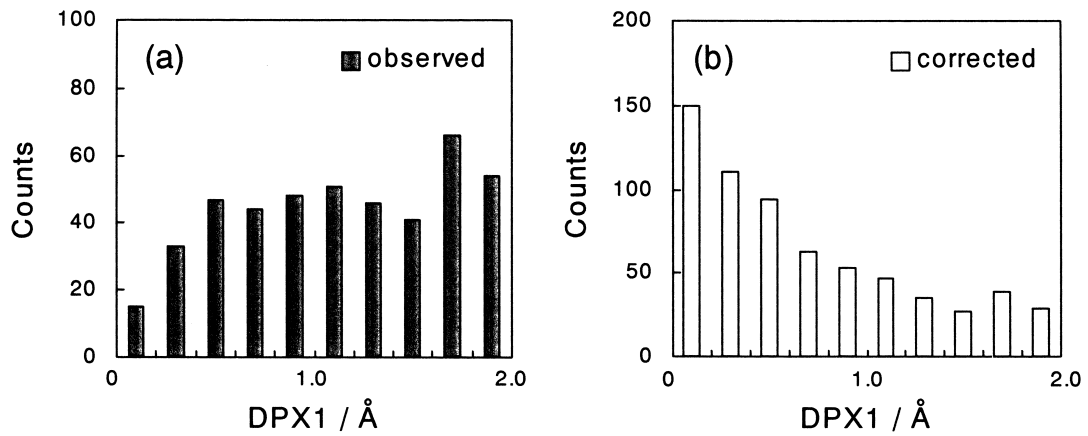

Fig. 4. Histograms showing the distribution of sp^2-CH hydrogen atoms (neutron data) against the distance from the center of the aromatic ring (D_{pxl}). (a) Observed. (b) Corrected by a factor of $1/D_{pxl}$.

Table 1. Summary of the CSD Analysis

Contact type	N[a)]	D_{pln} /Å[b)]	α / ° [c)]	α(corrected) / ° [d)]
(a) Cl_3CH/π	67	2.53±0.17	157±12	169±11
(b) Cl_2CH_2/π[e)]	648	2.62±0.15	151±13	159±14
(c) *sp*-CH/π	37	2.62±0.13	152±13	159±13
(d) sp^2-CH/π[f)]	11579	2.73±0.11	148±11	154±13
(e) sp^2-CH/π[g)]	161	2.70±0.11	146±9	149±11
(f) CCH_3/π[e)f)]	2391	2.75±0.10	148±13	157±15

a) The number of CH/π contacts observed in the ranges of $D_{px1} < 1.4$ Å and $D_{pln} < 2.9$ Å.
b) The mean values and the standard deviations of CH/π distance $D_{pln.}$
c) The mean values and the standard deviations of C–H···π access angle α.
d) The mean values and the standard deviations of C–H···π access angle α corrected by a factor of $1/\sin\alpha$.
e) Duplicate hits by two (Cl_2CH_2) or three (CCH_3) hydrogen atoms to a single aromatic ring were not counted.
f) Organic crystals with no disorder and $R \leq 5\%$.
g) Neutron data including organometallic compounds.

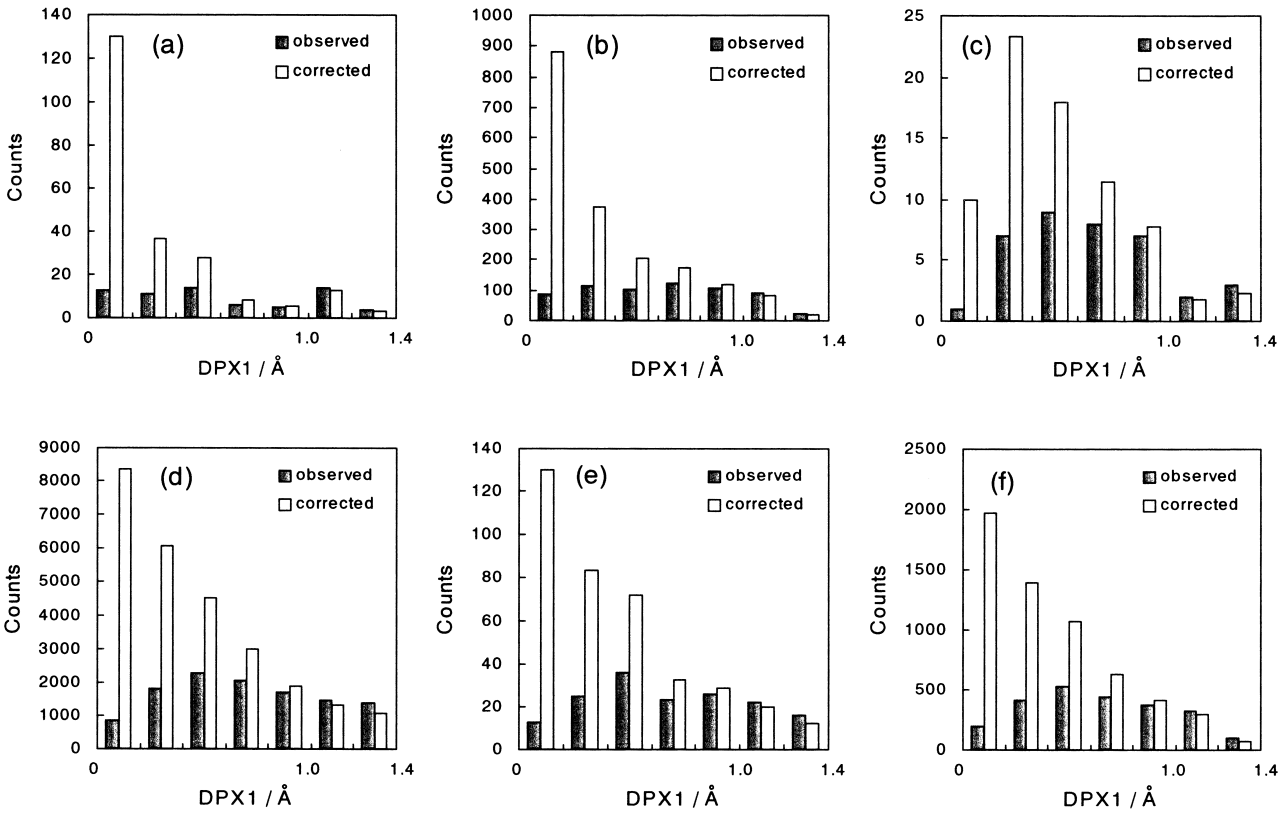

Fig. 5. Histograms showing the distribution of CH hydrogen atoms ($D_{pln} < 2.9$ Å) against the distance from the center of the ring (D_{pxl}). (a) Cl_3CH, (b) Cl_2CH_2, (c) *sp*-CH, (d) sp^2-CH (aromatic CH), (e) sp^2-CH (aromatic CH, neutron deta), (f) CCH_3. The data of only organic crystals with no disorder and $R \leq 5\%$ were used for (d) and (f). Open bars: observed. Shaded bars: corrected by a factor of $1/D_{pxl}$. D_{pxl}: Horizontal distance of H from the center of the ring.

then to CCH_3. For *sp*-CH [Fig. 5c], the peak seems to shift a bit from the center. This may be due to the small number of observations.

Figure 6 shows the number of short CH/π contacts ($D_{pln} <$ 2.9 Å, $D_{px1} < 1.4$ Å) as a function of α. The angle α is influenced by the nature of the CH group. For Cl_3CH and *sp*-CH, the CH bonds tend to access to the ring perpendicularly (peak at $\alpha \approx 180°$). For Cl_2CH_2 and sp^2-CH, the peak shifts to a smaller value, ca. 165° and 145°, respectively. The observed trends may reflect the stereochemical characteristics of the CH donor moieties. Chloroform and acetylenic CH bear only one hydrogen atom to interact, while Cl_2CH_2 and an aromatic group may form two non-bonded contacts with the π plane. In the case of CCH_3, the distribution seems to split into peaks at ca. 180° and 155°. This may be attributed to a variety of possible complex structures.

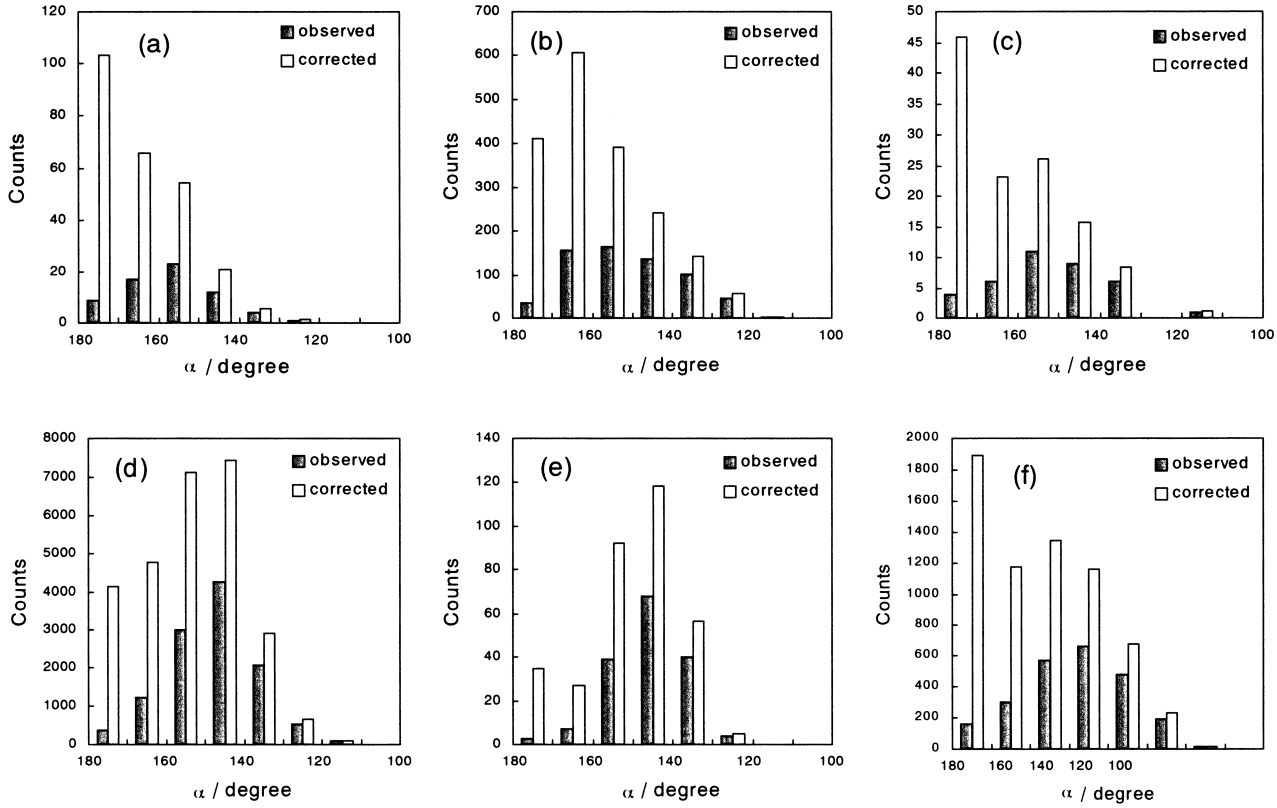

Fig. 6. Histograms showing the distribution of CH hydrogen atoms ($D_{\mathrm{pxl}} < 1.4$ Å, $D_{\mathrm{pln}} < 2.9$ Å) against the C–H···π access angle (α). (a) Cl_3CH, (b) Cl_2CH_2, (c) *sp*-CH, (d) sp^2-CH (aromatic CH), (e) sp^2-CH (aromatic CH, neutron data), (f) CCH_3. The data of only organic crystals with no disorder and $R \leq 5\%$ were used for (d) and (f). Open bars: observed. Shaded bars: corrected by a factor of 1/sin α.

To summarize, the mean non-bonded CH/π plane distance (D_{pln}) decreases with increasing CH acidity; the C–H···π access angle (α) tends to approach to 180° in the same order. The propensities are reasonable in view of a hydrogen-bond-like nature of the CH/π interaction, because similar propensities are unique for hydrogen bonds.[28]

Correlation between D_{pln} and α. Weak hydrogen bonds such as the CH/O[30] or CH/F[31] interactions exhibit a negative correlation between D_{pln} and α. To confirm the hydrogen-bond-like character of the CH/π interaction, correlation between D_{pln} and α was examined. In Fig. 7 are given scattergrams showing how the angle α is influenced by D_{pln} ($D_{\mathrm{px1}} <$ 1.4 Å). A remarkable propensity of the CH/π interaction is obtained: the shorter the non-bonded CH/π distance (D_{pln}), the more linear the C–H···X access angle (α). A similar negative correlation was reported for CH/π(Ph) interaction in cyclohexane derivatives,[32] CH/π(C≡C) interaction in acetylene compounds,[12] and XH/π(Ph) interaction (X = O, N) in organometallic crystals.[33] The plots of Fig. 7, however, show stronger correlation between D_{pln} and α. The discrepancy probably arose from the difference in the definition of the angle parameter; the previous works utilized the ring centroid···H–X or C···H–X angle, whereas we took the π plane···H–C angle as α. In any event, the distance versus angle plots examined so far show a similar overall trend. The hydrogen-bond-like character of CH/π interaction has been confirmed.

Figure 7 shows two additional interesting features. One is that the limit of D_{pln} values decreases with the CH acidity. The minimum D_{pln} is approximately 2.5 Å for CCH_3, 2.4 Å for sp^2-CH and *sp*-CH, and 2.3 Å for Cl_2CH_2 and Cl_3CH. This tendency agrees with the results presented in Table 1. The other point is that the slope (negative) seems to become slightly steeper as the CH acidity decreases. The features are in agreement with the previous suggestion that the CH/π interaction is not merely a dispersion force.[6–12]

Potential Surfaces of Model Complexes. Since the CH/π interaction is weak, orientation of the CH bond would readily be perturbed by the so-called packing force or stereochemical environments. The broadness of the data in Figs. 3–7 may reflect this. In order to investigate whether the structural preferences revealed by the CSD analyses are due to the intrinsic nature of the CH/π interaction or due to other reasons, we carried out high-level quantum chemical calculations on four structures of three isolated model complexes (Fig. 2).

Figure 8 shows the intermolecular interaction energies as a function of CH/π distance D. The position of the interacting hydrogen atom was fixed just above the center of the ring ($x =$ 0.0 Å). The access angle α was varied from 140° to 180°.

The potentials show minima at $D = 2.5$ Å for C_2H_2/C_6H_6 [geometry (a)], 2.65 Å for C_2H_4/C_6H_6 [geometry (b)], and 2.8 Å for CH_4/C_6H_6 [geometry (c) and (d)]. The results are consistent with those reported by Tsuzuki et al. for hydrocarbon/benzene complexes.[14] The binding energy increases as the CH proton acidity increases (-1.01, -1.74, and -2.37 kcal mol^{-1},

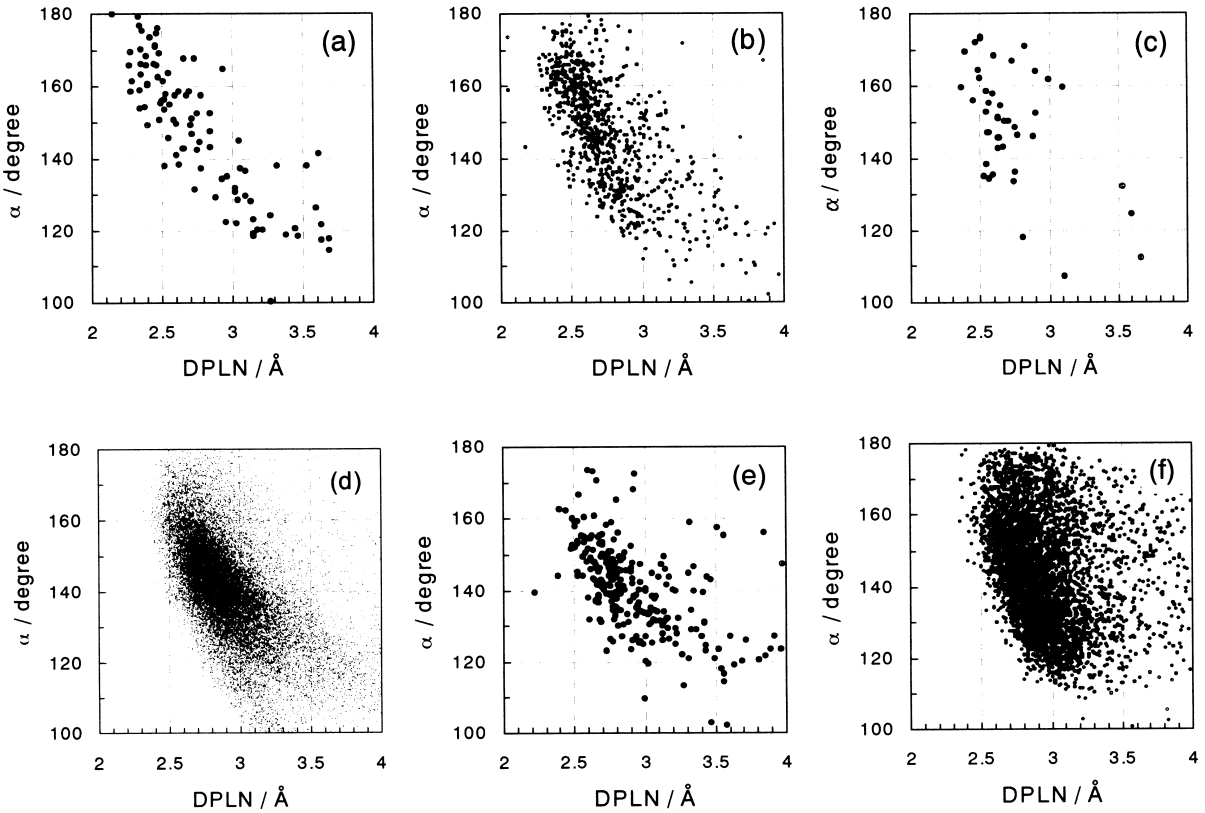

Fig. 7. Scatter plots showing dependence of the C–H···π access angle (α) on the CH/π plane distance (D_{pln}) in the range of $D_{\mathrm{pxl}} <$ 1.4 Å. (a) Cl_3CH, (b) Cl_2CH_2, (c) *sp*-CH, (d) sp^2-CH (aromatic CH), (e) sp^2-CH (aromatic CH, neutron data), (f) CCH_3. The data of only organic crystals with no disorder and $R \leq 5\%$ were used for (d) and (f).

respectively, for the methane, ethylene, and acetylene complexes), while the distance at the energy minimum decreases in this order. The observed tendency is in agreement with the results from the CSD analyses. Moreover, it is seen for all cases that the position of the energy minimum moves to a slightly larger value of D with the decrease of α. This is also consistent with the scatter plots shown in Fig. 7.

Figure 9 shows the potentials as a function of offset distance x with a fixed perpendicular distance: D = 2.5 Å for C_2H_2/C_6H_6, 2.65 Å for C_2H_4/C_6H_6, and 2.8 Å for CH_4/C_6H_6. The access angle α was varied from 140° to 180°.

For the acetylene [(a)] and methane [(c) and (d)] complexes, the potential curve (E_{total}) shows a global minimum at the center of the ring (x = 0.0 Å) when α = 180°. However, the potential well is offset by changing α to a smaller value. Thus, a shallow local minimum appeared at x = −0.2 Å when α = 160° for C_2H_2/C_6H_6 [geometry (a)] and at x = −0.1 Å when α = 160° for CH_4/C_6H_6 [geometry (c)]. For the ethylene complex [geometry (b)], on the other hand, the appearance of the potential curve is different from the other cases. Note that the global minimum appears when α = 160° and that the position of the minimum is offset from the center of the benzene ring (x = −0.1 Å). It is also notable that E_{total} becomes repulsive at α = 140°. This may be caused by the steric repulsion, which occurs between the other part of ethylene and the benzene ring. The result is consistent with the datum reported by Oki et al.[16] for the ethylene/benzene supramolecular system [MP2/6-31G(d,p)]: the energy minimum was obtained when the ethylene molecule was tilted 24° out of the normal vector of the π plane (corresponding to α 156°).

Figure 10 shows the angular dependence of the interaction energy as well as their components (electrostatic and correlation energies). The horizontal offset distance x was varied from −0.2 Å to +0.2 Å.

In the cases of acetylene/benzene [(a)] and methane/benzene [(c) and (d)] complexes, the energy minimum appears at α = 180° although the total interaction energy (E_{total}) does not vary appreciably between α = 180° and 140°. For the ethylene/benzene [(b)] complex, however, the situation is different: The global minimum shifts to α = 160°.

The structural preferences of the CH/π interaction obtained by ab initio calculations are in agreement with the results from the CSD analyses, though the potential surface is very flat with respect to x, α, and D. It therefore is obvious that the CH/π interaction is intrinsically orientation-dependent and hence has a hydrogen-bond-like character.

Stabilization Mechanism of the CH/π Interaction. The mechanism of the CH/π interaction was analyzed by estimation of the energetic components. The results are summarized in Table 2. It is seen that the major component of the CH/π interaction is the electron correlation energy (E_{corr}); this indicates that the CH/π interaction is primarily stabilized by a dispersion force. In addition, Table 2 shows that the change of the proton acidity significantly affects the interaction mechanism: the contribution from the electrostatic component E_{es} was calculated to be −1.83, −0.50, and −0.23 kcal mol^{-1}, respectively,

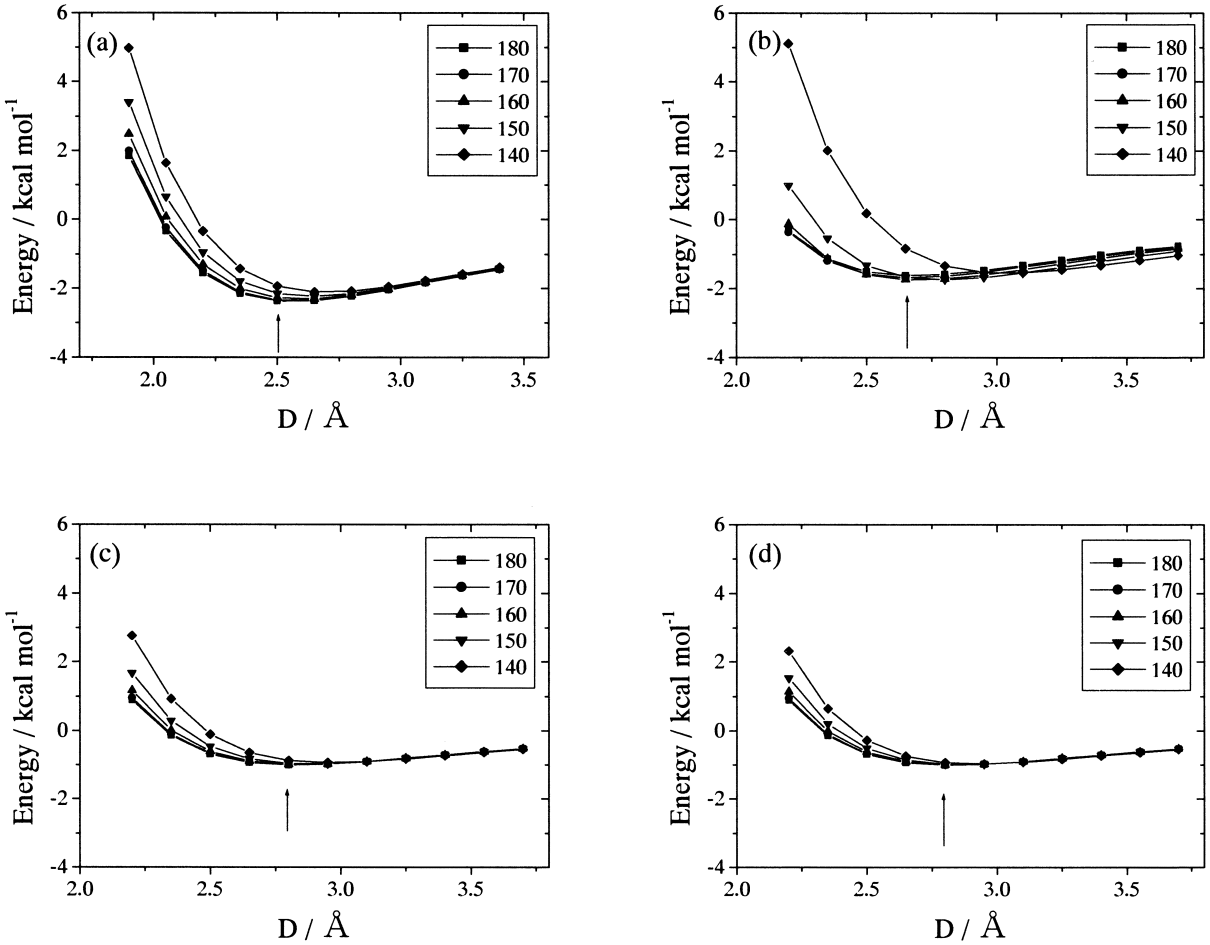

Fig. 8. Interaction potentials as a function of CH/π distance D (x = 0.0 Å) at various C–H···π access angle (α = 140°– 180°). Arrows indicate the potential minima. (a) C_2H_2/C_6H_6. (b) C_2H_4/C_6H_6. (c) CH_4/C_6H_6 in geometry (c). (d) CH_4/C_6H_6 in geometry (d).

Table 2. Total, Electrostatic, Exchange Repulsion, and Electron Correlation Energies of the CH/π Interaction for Acetylene/Benzene, Ethylene/Benzene, and Methane/Benzene Complexes[a)]

	C_2H_2/C_6H_6	C_2H_4/C_6H_6	CH_4/C_6H_6
E_{total} [b)]	−2.37	−1.74	−1.01
E_{es} [c)]	−1.83	−0.50	−0.23
E_{rep} [d)]	1.00	1.44	0.83
E_{corr} [e)]	−1.54	−2.69	−1.61
D [f)]	2.5	2.65	2.80
x [f)]	0.0	−0.1	0.0
α [f)]	180	160	180

a) Energies in kcal mol^{-1}.
b) Total MP2 interaction energies corrected for BSSE.
c) Electrostatic interaction energies.
d) Exchange repulsion energies.
e) Electron correlation (dispersion) energies.
f) See Fig. 2 for definitions of the structural parameters; D (Å), x (Å), and α(°).

for the acetylene, ethylene, and methane complexes. The results are consistent with those reported by Tsuzuki et al.[14]

Dependence of the total energy E_{total}, the correlation energy E_{corr}, and the electrostatic energy E_{es} on α is shown in Fig. 10. We see that the variance of E_{total} approximately parallels that of E_{es} for all the complexes and that the absolute value of E_{corr} increases with varying α to a smaller value. Also remarkable is the angular dependence of E_{es} for the acetylene complex [(a)], while in the other cases E_{es} does not show significant dependence on α. It was also found that the exchange repulsion energy (E_{rep}) greatly increases as the access angle (α) decreased (data not shown). The results indicate that the mechanism of the CH/π interaction is orientation-dependent, due probably to the contribution from the electrostatic energy.

Notwithstanding the common structural features discussed thus far, the CH/π interaction has a unique property different from the conventional hydrogen bond. Table 3 compares the contributions of E_{es}, E_{rep}, and E_{corr} in various hydrogen bonding interactions, collected from recent high level ab initio calculations. The electrostatic energy constitutes a major source of the OH/O hydrogen bond energy. Note that the electrostatic contribution decreases abruptly on going from OH/O[34] to OH/π and then to NH/π interaction,[35] while the electrostatic nature is only a minor factor for the CH/π interaction. On the contrary, the correlation energy remains practically constant. The CH/π interaction, consequently, is effective in polar media such as water[36] as well as in nonpolar organic solvents.

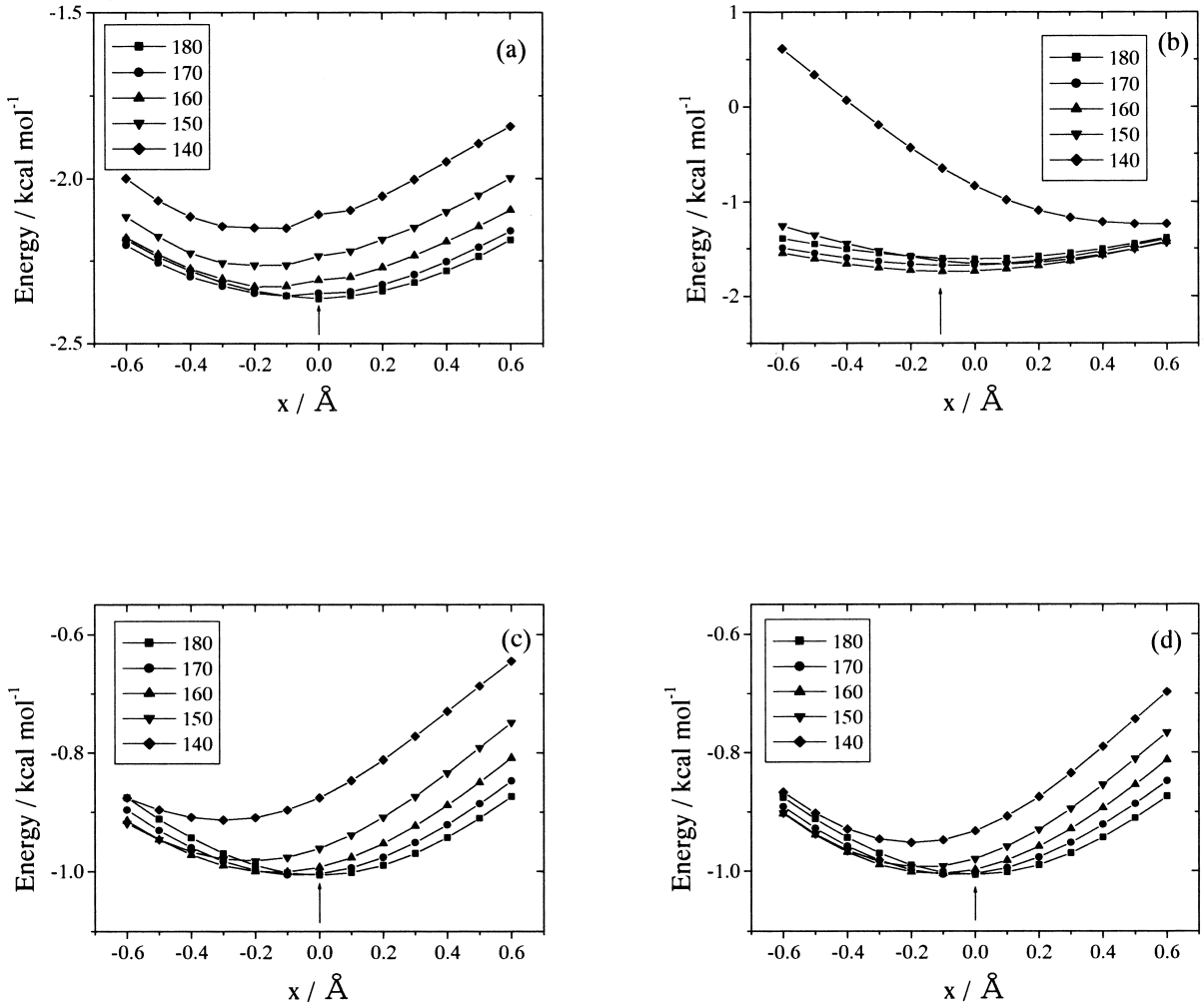

Fig. 9. Interaction potentials as a function of offset distance x from the center of the ring at various C–H···π access angles (α = 140°– 180°). Arrows indicate the potential minima. (a) C_2H_2/C_6H_6 (D = 2.5 Å). (b) C_2H_4/C_6H_6 (D = 2.65 Å). (c) CH_4/C_6H_6 in geometry (c) (D = 2.8 Å). (d) CH_4/C_6H_6 in geometry (d) (D = 2.8 Å).

Table 3. Energy Terms Contributing to Various Hydrogen Bonds

Type of H-bond	E_{total}[a)]	E_{es}[a)]	E_{rep}[a)]	E_{corr}[a)]	E_{es}/E_{total}
OH/O (H_2O/H_2O)[b)]	−5.23	−6.16	+5.09	−2.20	1.18
OH/π (H_2O/C_6H_6)[c)]	−3.02	−1.86	+1.07	−2.23	0.62
NH/π (NH_3/C_6H_6)[c)]	−2.22	−1.01	+1.14	−2.36	0.45
CH/π (CH_4/C_6H_6)[d)]	−1.45	−0.25	+1.10	−2.30	0.17
CH/π (CH_4/C_6H_6)[e)]	−1.01	−0.23	+0.83	−1.61	0.23

a) Energies in kcal mol^{-1}. E_{es}: electrostatic, E_{rep}: exchange repulsion, E_{corr}: correlation (dispersion) energy.
b) MP4/6-31+G(2d,2p) (Ref. 34).
c) MP2/cc-pVQZ (Ref. 35).
d) MP2/cc-pVQZ (Ref. 14).
e) MP2/6-311++G(d,p) (this work).

Conclusion

According to the crystallographic database analyses and ab initio calculations, the CH/π interaction has been shown to have a hydrogen-bond-like character. The following structural features of the CH/π interaction are common to well-established hydrogen bonds such as OH/O, OH/π, NH/π, and CH/O interactions.

1. The CH hydrogen atoms tend to lie above the center of the aromatic ring.

2. The mean non-bonded distance between the hydrogen atom and the π plane (D_{pln}) decreases with increase of the CH proton acidity (D_{pln}: sp^3-CH ≅ sp^2-CH > sp-CH ≅ Cl_2CH_2 > Cl_3CH).

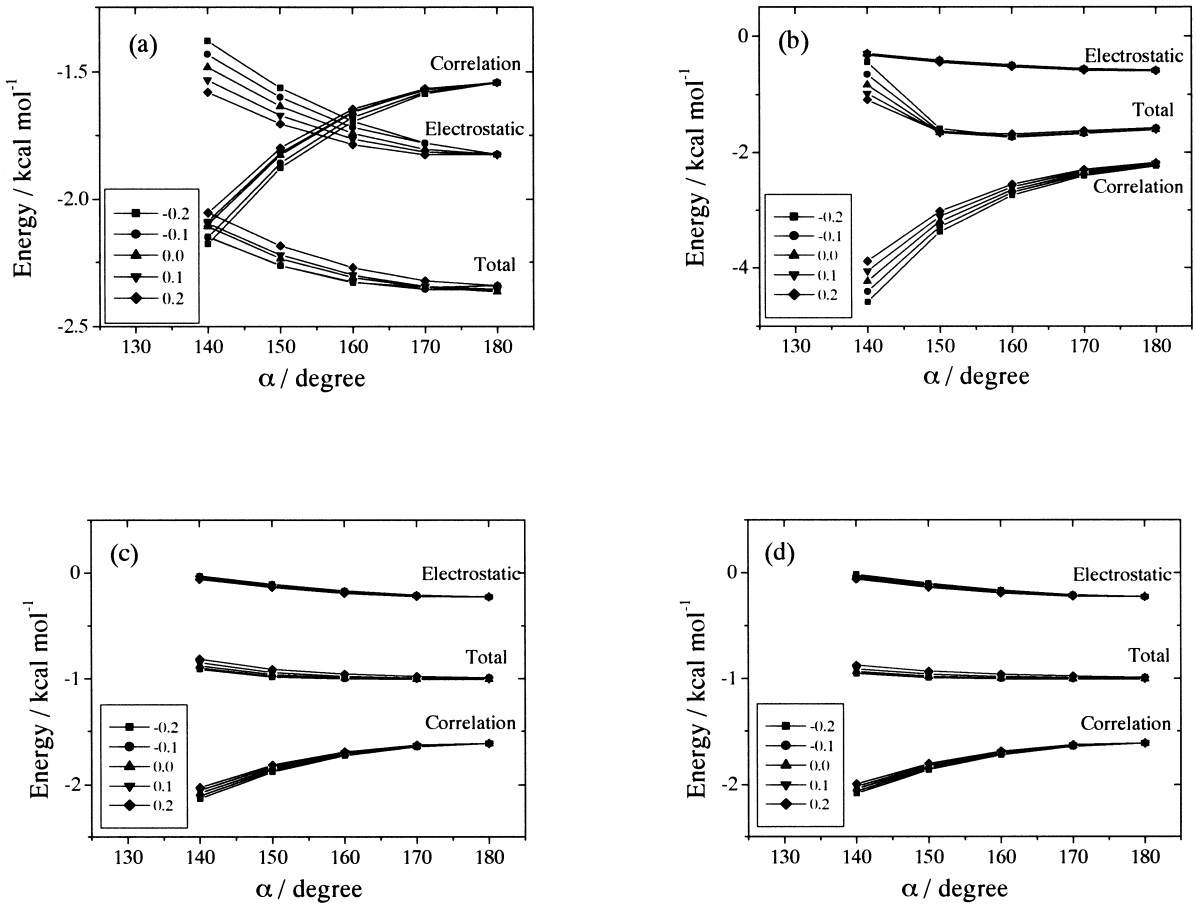

Fig. 10. Dependence of the interaction energies (E_{total}, total energy; E_{es}, electrostatic energy; E_{corr}, correlation energy) on the C–H···π access angle (α) at various offset distances ($x = -0.2$ Å – $+0.2$ Å). (a) C_2H_2/C_6H_6 ($D = 2.5$ Å). (b) C_2H_4/C_6H_6 ($D = 2.65$ Å). (c) CH_4/C_6H_6 in geometry (c) ($D = 2.8$ Å). (d) CH_4/C_6H_6 in geometry (d) ($D = 2.8$ Å).

3. The C–H···π access angles (α) tend to approach to 180° in the same order.

4. A distinct negative correlation exists between D_{pln} and α.

The structural propensities revealed by the CSD analyses are consistent with the results obtained by ab initio calculations. The angular dependence of CH is due neither to the so-called packing force nor to the stereochemical environments. The energetic components estimated for the intermolecular interactions suggest that the mechanism of the CH/π interaction is intrinsically orientation-dependent.

Interactions between hydrocarbon molecules and aromatic compounds were considered in the past as a mere van der Waals force or the "hydrophobic effect". This is inappropriate, in our view, because the interaction has intrinsic directional preferences similar to the hydrogen bond. The enthalpic contribution of a single CH/π interaction is very small, but these interactions usually occur simultaneously in multiple groups; the total energetic contribution may become considerable.

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