Computational Studies on CH/π Interactions

Tatsuya Takagi,* Akito Tanaka, Sanshiro Matsuo, Hironobu Maezaki, Mika Tani, Hideaki Fujiwara, and Yoshio Sasaki
Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamada-Oka, Suita, Osaka 565, Japan

Intermolecular interactions in CH/π systems have been studied by PCILO and *ab initio* MO methods to elucidate the origin of the attractive interactions. In the PCILO calculations, the van der Waals molecules of CH_4 + C_2H_n (n = 2 or 4) were more stable than that of CH_4 + C_2H_6, and the most stable arrangement was such that the carbon atom in methane is shifted from the C_2 axis perpendicular to the C–C–H plane of ethene. *Ab initio* MO results supported this conclusion and showed also that the main contributions to attractive CH/π interactions come from electrostatic and charge-transfer effects. These results were supported by electrostatic-potential maps of C_2H_4 and C_2H_6.

Saturated and unsaturated hydrocarbon systems are widely distributed in biological macromolecules, and inter- and intramolecular interactions involving these subsystems are expected to have direct effects upon higher order structures. In organic chemistry, the 'bulk repulsive concept'[1,2] is generally accepted as a basis for conformational analysis. However, attractive forces are sometimes calculated even for different alkyl/alkyl systems. For example, Kotos *et al.*[3] reported for methane dimer that the interaction energy and the most stable carbon–carbon distance are -1.256 kJ mol^{-1} and 0.428 nm, respectively, when dispersion energy obtained from empirical functions is added to an *ab initio* MO calculation. Lochmunn and Hobza[4] reported values of -0.5 kJ mol^{-1} and 0.35 nm obtained according to the PCILO method. In these studies, dispersion forces were reported to be a main contributor to the attractive forces.

Regarding alkyl/aryl systems, Nishio and co-workers[5] recently proposed the 'CH/π interaction hypothesis' in order to interpret the preference for the alkyl/aryl *gauche* conformer in different vicinal alkyl/aryl compounds. This hypothesis was supported by some molecular mechanical calculations[6] which also showed that dispersion forces are responsible for the greater part of the attractive interaction energies, whereas Nishio suggested that the attractive CH/π interaction resembles OH/π,[7] CH/*n*,[8] F/π,[9] and other weak hydrogen bonds such as are assumed for interactions between chloroform and aromatic hydrocarbons. Dispersion forces were also calculated to be responsible for the stacking of aromatic bases.[10] Kodama *et al.*[5f] calculated the interaction energies of the benzene plus methane system by the CNDO/2 method and obtained interaction energies of -4.8 kJ mol^{-1} for the most stable supermolecular structure.

We have examined the intermolecular interactions in the systems methane plus ethene, methane plus ethyne, and methane plus ethane, and have tested the CH/π interaction hypothesis by comparison of these systems. The *ab initio* MO and the PCILO methods were used; these methods are reported[11] to be successful when applied to true van der Waals molecules. Since the PCILO method requires a relatively short computing time, it was adopted for the various supermolecular structures, and the *ab initio* MO method was adopted for the limited supermolecular structures, for more detailed comparison between systems with and without π electrons.

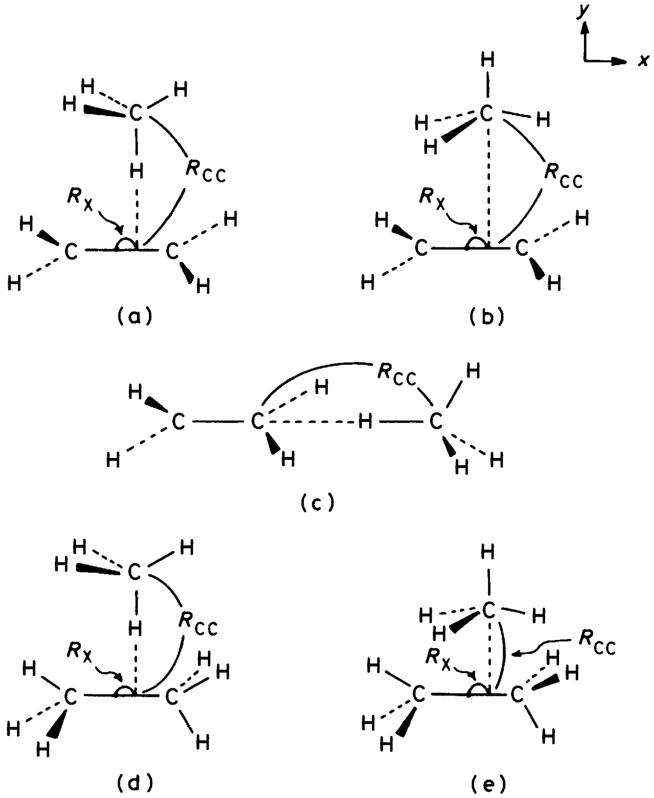

Figure 1. Mutual orientations of CH_4 and C_2H_n (n = 4 or 6) molecules considered in the present work

Calculation

PCILO calculations were carried out according to the QCPE program[12] after slight modifications. The IMSPAK program system[13] and its Osaka University version[14] (or our own version) were used for the *ab initio* MO calculations. Since dispersion energy is not included in the SCF calculation, it was evaluated by the second-order sum-of-state perturbation method,[15] employing equations (1) and (2), where A_0B_0 is the

$$\mathrm{DISP} = -\sum_{i}^{\mathrm{occ.}}\sum_{k}^{\mathrm{vac.}}\sum_{\mu}^{\mathrm{occ.}}\sum_{\nu}^{\mathrm{vac.}}\frac{|\langle A_0B_0|H'|A_{i\rightarrow k}B_{\mu\rightarrow\nu}\rangle|^2}{E_{i_A\rightarrow k_A,\,\mu_B\rightarrow\nu_B}-E_0} \quad (1)$$

$$= -4\sum_{i}^{\mathrm{occ.}}\sum_{k}^{\mathrm{vac.}}\sum_{\mu}^{\mathrm{occ.}}\sum_{\nu}^{\mathrm{vac.}}\frac{|\langle i_Ak_A|\mu_B\nu_B\rangle|^2}{E^{A}_{i\rightarrow k}+E^{B}_{\mu\rightarrow\nu}-E^{A}_{0}-E^{B}_{0}} \quad (2)$$

Hartree product of the Hartree–Fock wavefunctions for the ground states of molecules A and B, $A_{i\rightarrow k}B_{\mu\rightarrow\nu}$ is the Hartree product of the wavefunctions for the singly excited states of A

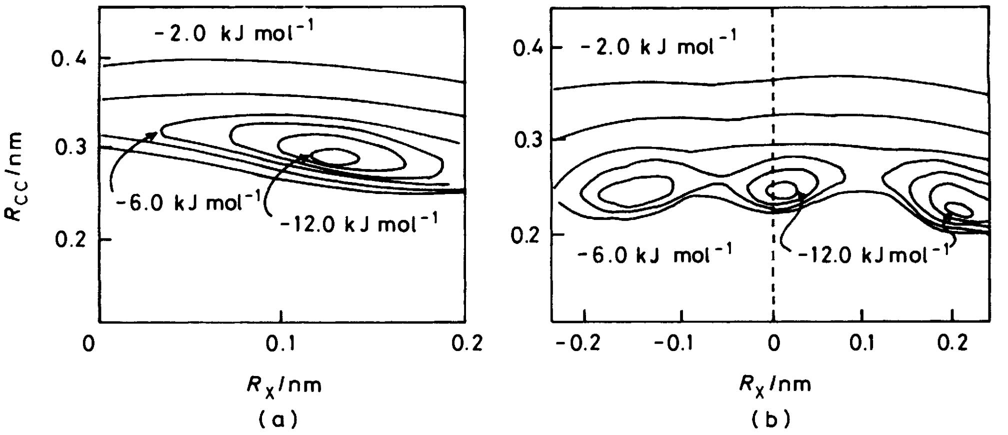

Figure 2. CH_4·C_2H_4 potential surfaces calculated by the semiempirical PCILO method. Supermolecular structures used are shown in Figure 1 (a) and (b)

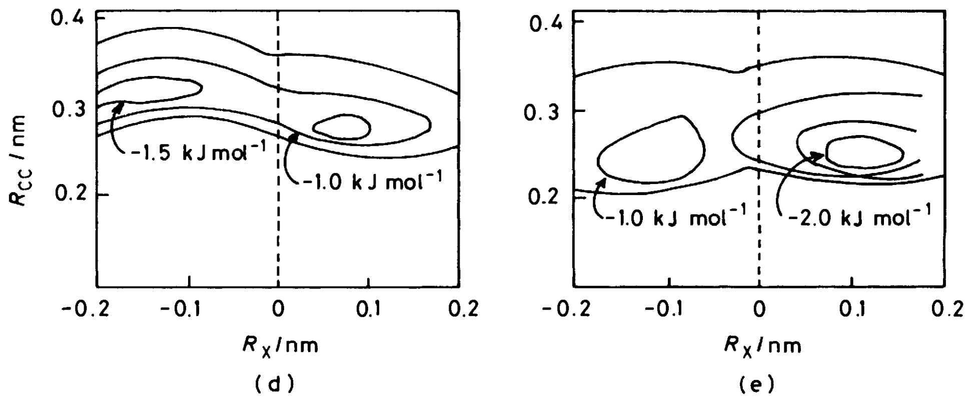

Figure 3. CH_4·C_2H_6 potential surfaces calculated by the semiempirical PCILO method. Supermolecular structures used are shown in Figure 1 (d) and (e)

and B, H′ is the molecular interaction part of the hamiltonian, and $\langle i_A k_A | \mu_B \nu_B \rangle$ is a two-electron integral over the Hartree–Fock MOs of isolated molecules. In a calculation of the hydrogen-bonding energy, this method has proved to be a fairly good approximation to an accurate calculation with a large basis set including electron correlations.[15,16] The program for this method was coded by the present authors, and was optimized for an integrated array processor. All monomer structures used for the MO calculations were taken from experimental data.[17] Some calculations of geometrical optimization for supermolecular structures showed that geometries of the monomer components did not change beyond the range of truncation error in the supermolecules, and so these geometries were not optimized. Numerical calculations were performed with a NEAC S1000 computer plus HFP (High-speed Fortran Processor) system at the Computation Center, Osaka University, and with a HITAC M-200H computer at the Computer Center for the Institute of Molecular Sciences.

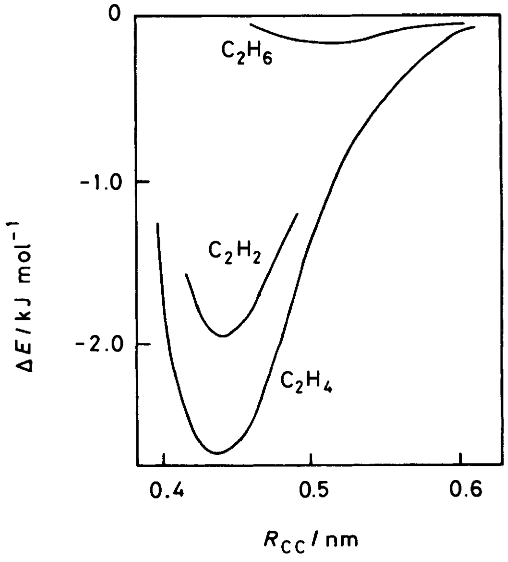

Figure 4. CH_4·C_2H_n (n = 2, 4, or 6) interaction energies, calculated by use of the 4-31G basis set

Results and Discussion

PCILO Calculations.—PCILO calculations for the C_2H_4 plus CH_4 system were carried out on the basis of supermolecular structures such as the one shown in Figure 1 (a) and (b). The resulting map of intermolecular potentials (Figure 2) showed that the carbon atom in methane is shifted from the C_2 axis perpendicular to the C–C–H plane of ethene in the most stable arrangement. This is consistent with a result reported by Kodama *et al.*[5f] for the benzene plus methane system. The calculations for the C_2H_2 plus CH_4 system showed the same feature. However, maximum interaction energies were very large in absolute value relative to the values from the literature,[5f] *viz.* −12.8 and −8.0 kJ mol^{-1} were calculated for the former and the latter, respectively. But on the basis of other supermolecular structures such as that shown in Figure 1 (c), the maximum interaction energy was only −1.5 kJ mol^{-1}. To investigate this problem further, the same calculation was applied to the C_2H_6 plus CH_4 system, which is devoid of π-electrons [Figure 1 (d) and (e)]. Although the most stable position of CH_4 was similar to that in the CH/π systems, the maximum interaction energy was calculated to be −2.3 kJ mol^{-1}, small in absolute value as compared with the other two systems (Figure 3). This fact supports the existence of 'CH/π interactions'.

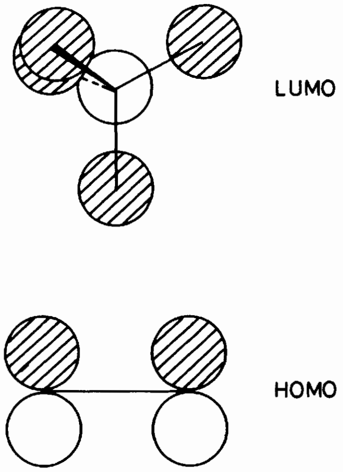

Figure 5. Shape of the HOMO of ethene and the LUMO of methane

Ab initio *Calculations.*—Although the PCILO method can be widely applied to the true van der Waals molecule, it is evident from papers hitherto published[11] that the method overestimates delocalization energies and underestimates interbond correlation energies. Therefore, an *ab initio* MO method with 4-31G basis set[18] was adopted here to calculate the energy components of CH/π interactions. The supermolecular structures used were similar to those in Figure 1 (a) and (d), but R_x was set to zero for the systematic comparison. The dependence of the total SCF interaction energies ΔE_{SCF} on the intermolecular distances R_{CC} is shown in Figure 4, which indicates that the CH/π systems are more stable than the CH_4 plus C_2H_6 system, in common with the results of the PCILO method. The potential minimum of the system containing ethene is deeper than that of the one containing ethyne. This order is the same as that calculated for the HF plus C_2H_n (n = 2 or 4) system.[19] Since ΔE_{SCF} does not contain the dispersion term, these results support the existence of specific CH/π interactions (similar to OH/π interactions).

Kitaura amd Morokuma[20] have provided a means for direct examination of the origin of molecular interactions. They have unambiguously defined components of the total interaction energy with the Hartree–Fock scheme, ΔE_{SCF}, as in equation (3),

$$\Delta E_{SCF} = \mathrm{ES} + \mathrm{PL} + \mathrm{EX} + \mathrm{CT} + \mathrm{MIX} \qquad (3)$$

where the individual components refer to electrostatic (ES), polarization (PL), exchange repulsion (EX), charge-transfer (CT), and higher order interaction (MIX) terms between various components. We have examined these analyses in terms of the characteristics of the CH/π interactions. The results of the energy-decomposition analyses (EDA) are shown in Table 1.

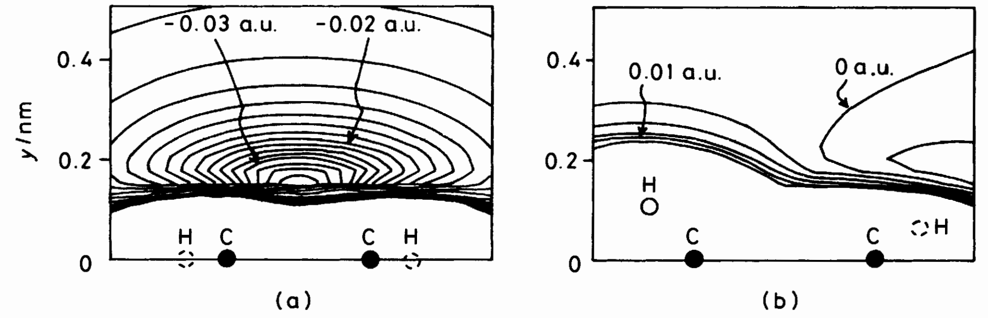

Figure 6. Molecular electrostatic potential maps in the *xy* planes: (a) C_2H_4, (b) C_2H_6

Table 1. Energy components and optimized intermolecular distances for the CH_4 (A) plus C_2H_n (B; n = 2, 4, or 6) systems calculated by use of the 4-31G basis set

		Interaction energy (kJ mol^{-1})								
n	R_{CC}/nm	ΔE	ΔE_{SCF}	ES	PL	EX	$CT_{A\rightarrow B}$	$CT_{B\rightarrow A}$	MIX	DISP
2	0.44	−2.75	−1.95	−0.56	−0.06	0.85	−0.07	−2.16	0.05	−0.80
4	0.44	−3.67	−2.68	−0.60	−0.07	0.99	−0.00	−3.00	0.00	−0.99
6	0.50	−1.01	−0.22	−0.33	−0.00	0.15	−0.34		−0.00	−0.79

Table 2. Energy components and optimized intermolecular distances for the CH_4 plus C_2H_4 system calculated by use of the MIDI $4^{*(*)}$ basis set

	Interaction energy (kJ mol^{-1})						
R_{CC}/nm	ΔE_{SCF}	ES	PL	EX	$CT_{A\rightarrow B}$	$CT_{B\rightarrow A}$	MIX
0.48	−1.21	−0.39	−0.04	0.36	−0.02	−1.14	−0.12

They indicate that the main contributions to the attractive CH/π interactions are the electrostatic term and the term for the charge transfer from the π-electron system to CH_4 ($CT_{B\rightarrow A}$).* Furthermore, population analyses showed weak charge transfer from the π-electron system to the methane molecule (0.0088 a.u. for the 4-31G basis set; no charge transfer was revealed for the CH_4 plus C_2H_6 system). This charge transfer may be caused by HOMO–LUMO interactions, as shown in Figure 5, which can explain the order of 'basicity' of the C_2H_4 and C_2H_2 molecules.† After all, these characteristics are similar to those found in CH/n[23] and in weak hydrogen-bonding systems.[24] The difference in the ES terms between the systems with and without π-electrons can be confirmed by molecular electrostatic potential (MEP) maps. The MEP maps for C_2H_6 and C_2H_4 are shown in Figure 6. Evidently, the MEP of C_2H_4 shows smaller negative values than that of C_2H_6 at the same positions; this indicates that the C_2H_4 molecule is more 'basic' than the C_2H_6 molecule. Dispersion energy (DISP) might be expected to be a main origin of attractive CH/π interactions, because π-electron systems possess larger polarizabilities than saturated systems. However, changes in this term are relatively small among the systems with and without π-electrons even if the proportions of the DISP term are large in the total attractive interaction energies. Therefore, it may be concluded safely that the DISP term is not a main cause of attractive CH/π interactions.

Acknowledgements

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* A basis set superposition error (BSSE)[21] could affect the values of the CT terms. However, energy differences between the CH/π and the CH/alkyl systems are important in the present discussion. For this purpose, the BSSEs in the two systems are expected largely to cancel out. The characteristics of the CH/π interactions as seen in Table 1 remain unchanged for the CH_4 plus C_2H_4 system after EDA using the $\mathrm{MIDI4}^{*(*)}$ basis set,[22] which can diminish the onset of BSSE (Table 2). Here, '*(*)' indicates that $\mathrm{MIDI4}^{**}$ is used for methane and $\mathrm{MIDI4}^{*}$ is used for ethene.

† E_{HOMO} is −0.369 98 a.u. for the ethene molecule and −0.402 80 a.u. for the ethyne molecule.