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High Level ab Initio Calculations of Intermolecular Interaction of Propane Dimer: Orientation Dependence of Interaction Energy

Seiji Tsuzuki,* Tadafumi Uchimaru, Masuhiro Mikami, and Kazutoshi Tanabe

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan

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Intermolecular interaction of the propane dimer was calculated with the MP2 level electron correlation correction using several basis sets up to the cc-pVQZ. The calculated interaction energy greatly depends on the basis set. Small basis sets underestimate the attraction considerably. The effects of electron correlation beyond MP2 are not large. Intermolecular interaction energies of 23 orientations of propane dimers were calculated at the MP2 level with a large basis set including multiple polarization functions. In all dimers, the inclusion of electron correlation considerably increases the attraction. The dispersion interaction is found to be the major source of attraction, whereas the electrostatic interaction is very small. The C_{2h} dimer in which the two C_2 axes of propane monomers have antiparallel orientation has the largest binding energy. The separation between the two methylene carbon atoms at the potential minimum in this dimer is the shortest among the 23 dimers. The short separation, which increases the dispersion energy, is the cause of the large binding energy of the C_{2h} dimer. The estimated MP2 and CCSD(T) interaction energies of the propane dimer at the basis set limit are −1.99 and −1.94 kcal/mol, respectively.

Introduction

Nonbonding interactions of hydrocarbon molecules are essential for the understanding of intermolecular interactions of organic molecules which have alkyl chains such as alkanes, alcohols, thiols, esters, and carboxylic acids. Nonbonding interactions of these molecules control their liquid-phase properties,[1,2] crystal packing,[3] and three-dimensional structures of their assemblies such as self-organized monolayers on metal surfaces[4,5] and Langmuir−Blodgett films.[6,7] Accurate intermolecular interaction potentials of these molecules are necessary for the understanding of structures and properties of their assemblies and are also strongly needed by those who carry out molecular dynamics simulations of these molecules.

Several experimental data such as the compressibility of a gas, the heat of evaporation of a liquid, the heat of sublimation of a crystal, and the crystal structure provide useful information on intermolecular interaction. However, it is still difficult to accurately determine potential energy surfaces of interacting molecules only from these experimental data. Experimental measurements can cover only a limited region of the potential energy surface. Whereas measurements of the compressibility of gas give the spherically averaged interaction potential of a molecule, the anisotropy of interaction cannot be evaluated from this measurement. Neither heat of evaporation nor sublimation energy give any information about the anisotropy of potential. From measurements of crystal structures, the shape of the potential at the van der Waals contact distance can be revealed. However, the shape of the potential in the other region is not covered by the measurements of crystal.

Recently, ab initio molecular orbital calculations are becoming a powerful tool to study intermolecular interactions.[8−10] Ab initio calculations of small molecules show that sufficiently accurate interaction energy can be obtained, if a reasonably large basis set is used and electron correlation is properly corrected.[10,11] Intermolecular interaction energy of the methane dimer has been calculated repeatedly as the smallest model to study the interaction between hydrocarbon molecules.[12−24] A few calculations of the intermolecular interaction energy of the ethane dimer have been reported.[19,24−26]

Propane is the smallest hydrocarbon molecule which has a methylene (CH_2) unit. Methylene is an important unit for organic molecules which have an alkyl chain. Therefore, the propane dimer interaction is essential for the understanding of intermolecular interactions of these molecules. Unfortunately, however, very little has been reported on the intermolecular interaction of the propane dimer.[24,25,27] Gupta et al. reported the MP2 level calculations of four orientations of propane dimers using small 6-31G and 6-31G* basis sets.[25] Recently, our group reported MP2 level calculations of a single orientation propane dimer using several basis sets.[24] Although the calculations reported by Gupta et al. were impressive when they were reported, the basis sets used are too small to evaluate the interaction energy accurately. Recent ab initio calculations of small hydrocarbon molecules show that a large flexible basis set including multiple polarization functions is necessary for the evaluation of weak intermolecular interactions and that small basis sets underestimate the attractive interaction considerably.[15,19,22,24,28,29] Very recently, Jalkane et al. reported MP2/6-311+G(2df,2pd) level calculations of propane dimers.[30]

Detailed information on the orientation dependence of the interaction energy is important for the understanding of the propane dimer interaction. Ab initio calculations of several orientation propane dimers using a reasonably large basis set are necessary for this purpose. In addition, the effect of electron correlation beyond MP2 has not yet been confirmed. Sometimes an MP2 level calculation is not a suitable approximation to evalutate intermolecular interaction between hydrocarbon molecules. Recently reported ab initio calculations of the benzene dimer show that the MP2 level calculations overestimate the attraction considerably compared to the more reliable CCSD(T) level calculations.[28,31]

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

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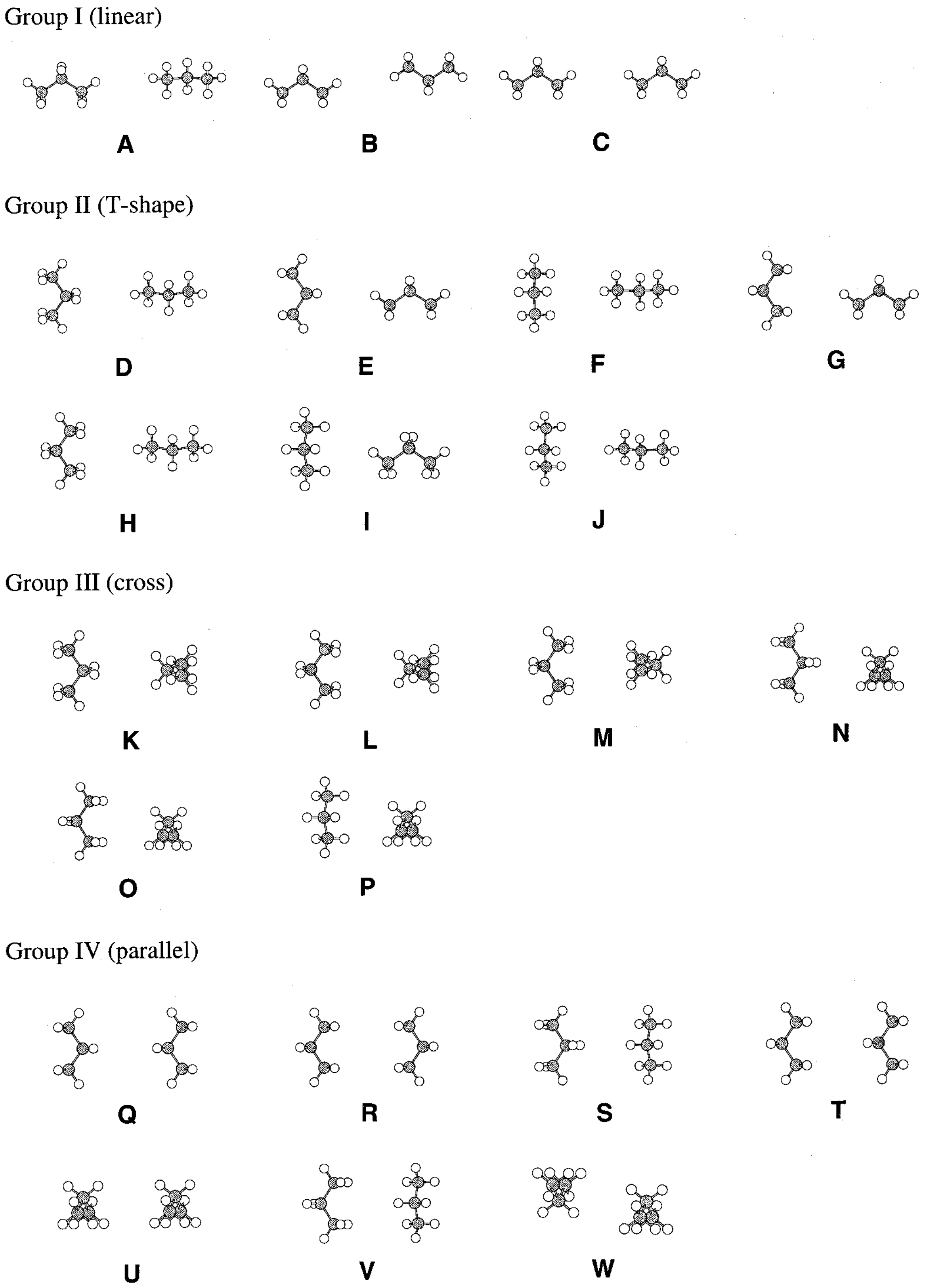

Figure 1. Geometries of 23 orientation propane dimers. The two methylene carbon atoms are on the *x* axis. The C_2 axis and the chain axis of each propane monomer are parallel to *x*, *y*, or *z* axis as shown Figure 2. The dimers are classified according to the orientation of chain axes of two propane molecules. See text.

In this paper, we have carried out the MP2 level calculations of 23 orientations of propane dimers using a large basis set including multiple polarization functions to study the orientation dependence of the interaction energy. We have also discussed the cause of the orientation dependence of the interaction energy. In addition, we have evaluated the effects of the basis set and electron correlation beyond MP2 and estimated the MP2 and CCSD(T) interaction energies of the propane dimer at the basis set limit.

Computational Method

The Gaussian 94 and 98 programs[32,33] were used for the ab initio molecular orbital calculations. The geometry of the isolated propane molecule was optimized at the MP2/6-31G* level[34] and was used for the calculations of dimers. The Dunning's correlation consistent basis sets (cc-pVXZ and aug-cc-pVXZ, X = D, T, and Q)[35−37] and modified 6-311G* basis sets [the aug(d,p)-6-311G** and aug(df,pd)-6-311G**] were used.[24] The aug(d,p)-6-311G** basis set is the 6-311G** basis set[38] augmented with diffuse d functions on carbon atoms ($\alpha_d(C) = 0.1565$) and diffuse p functions on hydrogen atoms ($\alpha_p(H) = 0.1875$). The aug(df,pd)-6-311G** basis set is the 6-311G** basis set augmented with diffuse d and f functions on carbon atoms ($\alpha_d(C) = 0.1565$ and $\alpha_f(C) = 0.2$) and diffuse p and d functions on hydrogen atoms ($\alpha_p(H) = 0.1875$ and $\alpha_d(H) = 0.25$). Electron correlation was accounted for at the

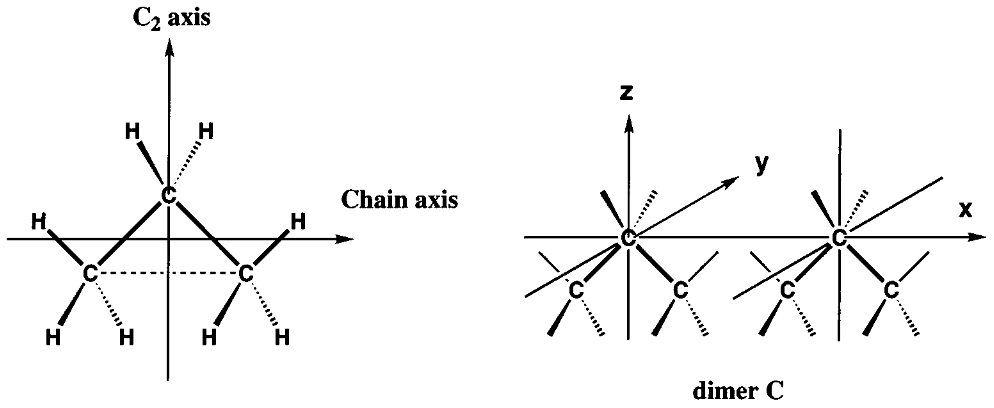

Figure 2. In all dimers in Figure 1, the methylene carbon atoms are on the *x* axis and the C_2 axis and the chain axis of each propane monomer are parallel to *x*, *y*, or *z* axis. The chain axis is parallel to the broken line which connects the two methyl carbon atoms. The orientation of the dimer C is shown for an example.

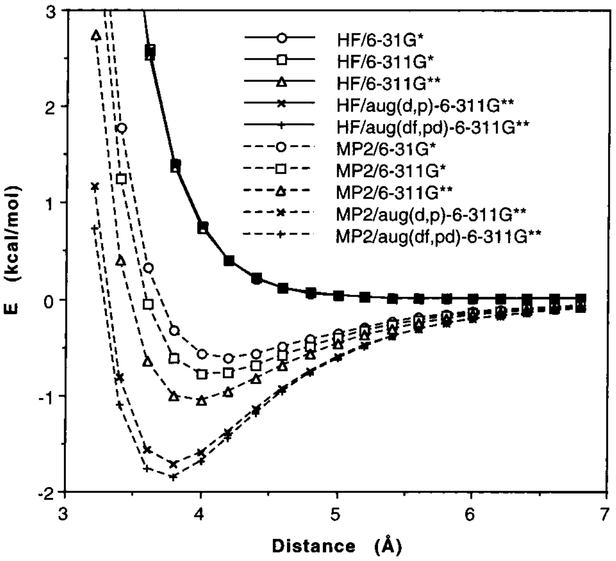

Figure 3. Calculated HF and MP2 interaction energies of the propane dimer W using several basis sets. The BSSE corrected interaction energies. See text.

MP2[39,40] and CCSD(T) levels.[41] The basis set superposition error (BSSE)[42] was corrected for all calculations by using the counterpoise method.[43] The MP2 interaction energy at the basis set limit was estimated with the method proposed by Feller.[44] Distributed multipoles[9,45] up to hexadecapole on all atoms were obtained from the MP2/cc-pVTZ wave functions of an isolated molecule using CADPAC version 6.[46] The electrostatic energies of the dimers were calculated using ORIENT version 3.2.[47] The electrostatic energies of the dimers were calculated as the interactions between distributed multipoles of monomers. The geometries of propane dimers considered in this work (23 orientations) are shown in Figure 1. In all dimers, the two methylene carbons are put on *x* axis. The C_2 axis and the chain axis (See Figure 2) of each propane monomer are parallel to the *x*, *y*, or *z* axis.

Results and Discussion

Effects of Basis Set and Electron Correlation. The interaction energy of the propane dimer (Figure 1, dimer W) was calculated at the HF and MP2 levels using several basis sets as shown in Figure 3. The basis set dependence of the HF interaction energy is not large, whereas the MP2 interaction energy strongly depends on the basis set. Small basis sets (6-31G* and 6-311G*) greatly underestimate the attraction as previously reported in the calculations of other small hydrocarbon molecules. The inclusion of electron correlation considerably increases the attraction. This indicates that the dispersion interaction is the major source of the attraction. The significant basis set dependence shows that a large flexible basis set is necessary for the evaluation of the propane dimer interaction. We have used the aug(df,pd)-6-311G** basis set for the calculations of the 23 orientation dimers. Although this basis set is a medium size basis set, the calculated intermolecular interaction energies of small hydrocarbon molecules using this basis set are close to those using the large cc-pVQZ and cc-pV5Z basis sets.[24]

Interaction Energies of 23 Orientation Dimers. The MP2 intermolecular interaction energies of the 23 orientation dimers (Figure 1) were calculated with changing the intermolecular separation (*R*, the distance between the two methylene carbons). The interaction energies (E_{total}) of the dimers at the potential minima are summarized in Table 1. The 23 orientation dimers can be classified into four groups (linear, T-shape, cross, and parallel) according to the orientation of the chain axes of two propane monomers as shown in Figure 1. The chain axis is parallel to the line connecting the two methyl carbon atoms of a propane molecule as shown in Figure 2.

The group I (linear) includes the three dimers A−C. In these dimers, the chain axes are nearly linear. The calculated interaction energy potentials of the dimers are shown in Figure 4. The potentials have their minima at $R = 6.8-7.0$ Å. The calculated interaction energies at the potential minima ($-0.29 \sim -0.30$ kcal/mol) are very small because of the large intermolecular separations.

The potentials of the group II (T-shape) dimers D−J have their minima at $R = 5.2-6.0$ Å as shown in Figure 5. These separations are shorter than those of the group I dimers. The calculated interaction energies at the potential minima ($-0.50 \sim -0.95$ kcal/mol) are larger (more negative) than those of the group I dimers. The potentials of the dimers G and H have their minima at $R = 6.0$ Å. The separations of these dimers are larger than those of the other group II dimers ($R = 5.0-5.2$ Å). In the dimers G and H, the two methyl groups of the left side propane molecule have the close contact with a methyl group of the right side propane. The steric repulsion because of the close contact would be the cause of the larger separations.

The potentials of the group III (cross) dimers K−P have their minima at $R = 3.8-5.6$ Å as shown in Figure 6. The dimer M has the exceptionally large separation ($R = 5.6$ Å) because of the repulsion of methyl groups. The separations of the other group III dimers (3.8−4.8 Å) are shorter than those of the group

TABLE 1: Intermolecular Separations and Calculated Interaction Energies of the 23 Propane Dimers at the Potential Minima[a]

dimer	R^b	$E_{total}{}^c$	$E_{es}{}^d$	$E_{rep}{}^e$	$E_{corr}{}^f$
Linear					
A	7.0	−0.29	0.02	0.15	−0.46
B	6.8	−0.30	0.01	0.25	−0.56
C	7.0	−0.29	0.01	0.20	−0.51
T-Shape					
D	5.4	−0.50	−0.02	0.34	−0.82
E	5.4	−0.51	−0.04	0.34	−0.82
F	5.4	−0.67	−0.00	0.48	−1.14
G	6.0	−0.73	−0.03	0.70	−1.40
H	6.0	−0.76	−0.01	0.60	−1.35
I	5.2	−0.79	−0.04	0.91	−1.65
J	5.2	−0.95	0.00	0.83	−1.79
Cross					
K	3.8	−0.73	0.08	0.66	−1.47
L	4.8	−0.92	−0.00	0.58	−1.50
M	5.6	−1.14	0.03	0.88	−2.05
N	3.8	−1.25	−0.00	1.03	−2.27
O	4.8	−1.29	0.00	1.18	−2.47
P	4.0	−1.46	0.01	1.35	−2.82
Parallel					
Q	4.0	−0.62	0.05	0.48	−1.14
R	5.8	−0.92	0.09	0.71	−1.72
S	4.0	−1.08	−0.01	0.66	−1.73
T	4.6	−1.09	0.05	0.79	−1.93
U	4.2	−1.20	0.08	1.12	−2.40
V	4.8	−1.31	0.07	1.09	−2.47
W	3.8	−1.85	0.06	1.34	−3.26

[a] Energies in kcal/mol. Distance in Å. The BSSE corrected interaction energies. The geometries of dimers are shown in Figure 1. [b] The separations of methylene carbon atoms of two propanes at the potential minima. See Figures 1 and 2. [c] Calculated MP2 interaction energies using the aug(df,pd)-6-311G** basis set. [d] Electrostatic energies. See text. [e] Repulsion energies. E_{rep} is the difference between the HF/aug(df,pd)-6-311G** interaction energy (E_{HF}) and the E_{es}. [f] Correlation interaction energies. E_{corr} is the contribution of electron correlation on interaction energy, which is the difference between the MP2 interaction energy (E_{total}) and the E_{HF}. E_{corr} is mainly dispersion energy.

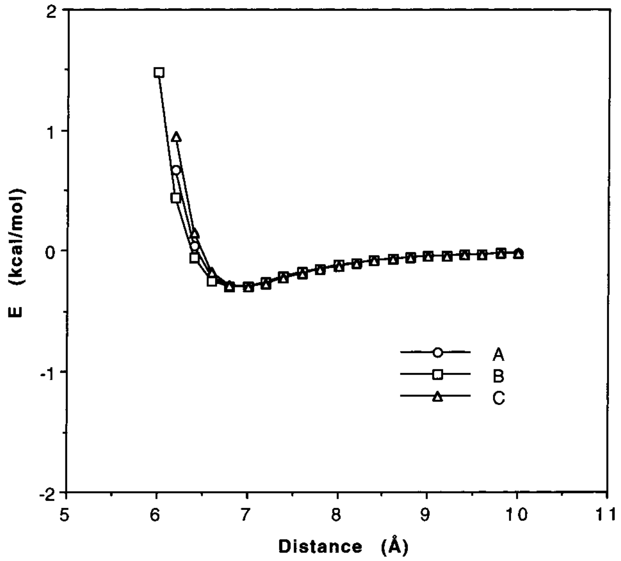

Figure 4. Calculated MP2/aug(df,pd)-6-311G** interaction energies of group I (linear) dimers A−C. BSSE corrected interaction energies.

II dimers. The calculated interaction energies of the four dimers M−P at the potential minima (−1.14 ∼ −1.46 kcal/mol) are larger than those of the group II dimers. The interaction energies of the dimers K and L (−0.73 and −0.92 kcal/mol, respectively) are close to those of the group II dimers.

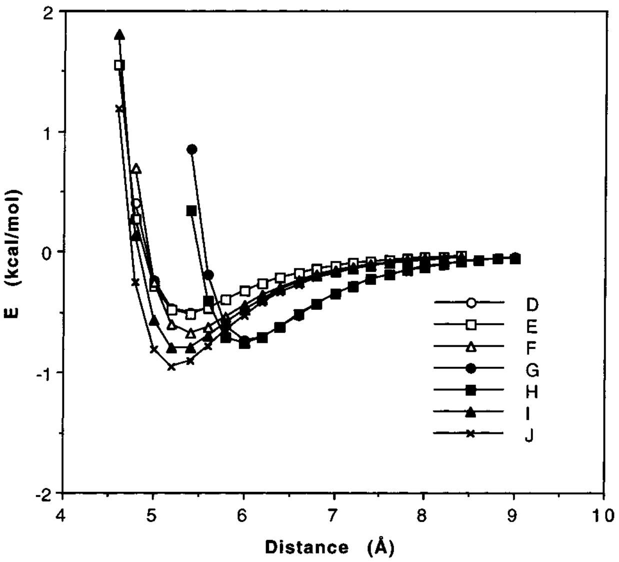

Figure 5. Calculated MP2/aug(df,pd)-6-311G** interaction energies of group II (T-shape) dimers D−J. BSSE corrected interaction energies.

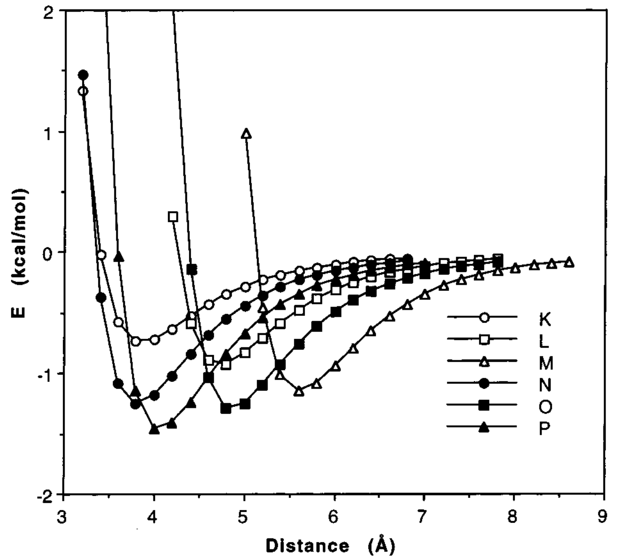

Figure 6. Calculated MP2/aug(df,pd)-6-311G** interaction energies of group III (cross) dimers K−P. BSSE corrected interaction energies.

The potentials of the group IV (parallel) dimers Q−W have their minima at R = 3.8−5.8 Å as shown in Figure 7. These separations are close to those of the group III dimers. The dimer R has the large separation (R = 5.8 Å). The separations of the other group IV dimers are R = 3.8−4.8 Å. The calculated interaction energy considerably depends on the orientation of the dimers. The calculated interaction energies of the dimers Q−V at the potential minima (−0.62 ∼ −1.31 kcal/mol) are close to those of the group III dimers. The dimer W, in which the two C_2 axes have antiparallel orientation, has the largest (most negative) interaction energy (−1.85 kcal/mol) at the potential minimum (R = 3.8 Å).

Origin of the Orientation Dependence of Dimer Interaction Energy. The electrostatic (E_{es}), repulsive (E_{rep}), and correlation interaction (E_{corr}) energies of the dimers at their potential minima are summarized in Table 1. The E_{rep} is the difference between the HF/aug(df,pd)-6-311G** level interaction energy (E_{HF}) and the E_{es}. The E_{rep} is mainly exchange-repulsion energy, but it also contains other terms. The E_{corr} is the contribution of electron correlation on interaction energy, which is the difference between the MP2/aug(df,pd)-6-311G** level interaction energy

TABLE 2: Interaction Energies of the Propane Dimer Calculated with Electron Correlation Correction by Several Methods[a]

basis set	HF	MP2	MP3	MP4(SDTQ)	CCSD	CCSD(T)	ΔCCSD(T)[b]
6-31G*	1.35	−0.37	−0.27	−0.34	−0.11	−0.30	0.06
6-311G**	1.36	−1.05	−0.80	−0.97	−0.62	−0.91	0.14
cc-pVDZ	1.39	−0.86	−0.62	−0.77	−0.45	−0.71	0.15
aug-cc-pVDZ	1.41	−1.72	−1.42	−1.75	−1.25	−1.67	0.05

[a] Energies in kcal/mol. The BSSE corrected interaction energies. The optimized geometry at the MP2/6-311G** level was used. See Figure 8. [b] The CCSD(T) correction term. The difference between the CCSD(T) and MP2 interaction energies.

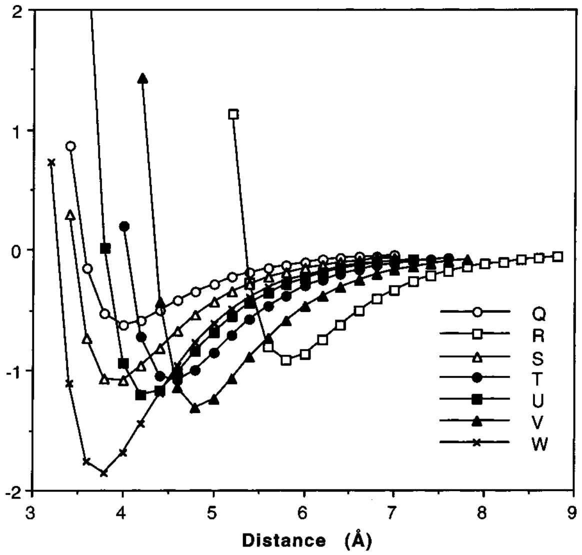

Figure 7. Calculated MP2/aug(df,pd)-6-311G** interaction energies of group IV (parallel) dimers Q−W. BSSE corrected interaction energies.

(E_{total}) and the E_{HF}. The E_{corr} is mainly dispersion energy. In all dimers, the E_{es} is negligible. The large E_{corr} indicates that the dispersion interaction is the major source of attraction.

The dimer W has the largest (most negative) E_{corr} (−3.26 kcal/mol), which indicates that the large dispersion interaction is the cause of the largest binding energy of this dimer. The smallest intermolecular separation (R = 3.8 Å) is a cause of the largest E_{corr} of this dimer. The potentials of the dimers K and N also have their minima at R = 3.8 Å. However, the E_{corr} of these dimers (−1.47 and −2.27 kcal/mol, respectively) are substantially smaller than that of the dimer W. The other dimers have larger separations at their potential minima (R = 4.0−7.0 Å). The dispersion interaction has its origin in the polarization of the propane molecules. The polarization of carbon atoms is mainly responsible for the dispersion energy in the propane dimer, because the atomic polarizability of hydrogen is considerably smaller than that of carbon. Therefore, short C···C contact increases the dispersion interaction. The dimer W has larger number of short C···C contact than the other dimers. This would be the cause of the large attraction in the dimer W.

Optimized Geometry of the Dimer. The geometry of the propane dimer was optimized at the MP2/6-311G** level. The geometry of the dimer W (R = 3.8 Å) was used for the initial geometry. The geometries of monomers were frozen during the optimization. The optimized geometry is shown in Figure 8. The optimized geometry has C_{2h} symmetry. The distance between the two methylene carbons (R) is 3.855 Å. The angle θ is 94.7°.

Electron Correlation beyond MP2. The interaction energy of the dimer (Figure 8, MP2/6-311G** level optimized geometry) was calculated with electron correlation correction by using the MP3, MP4(SDTQ), CCSD, and CCSD(T) methods as summarized in Table 2. The CCSD interaction energy is smaller (less negative) than the CCSD(T) one. The MP2, MP3, and MP4(SDTQ) interaction energies are not largely different from the CCSD(T) ones.

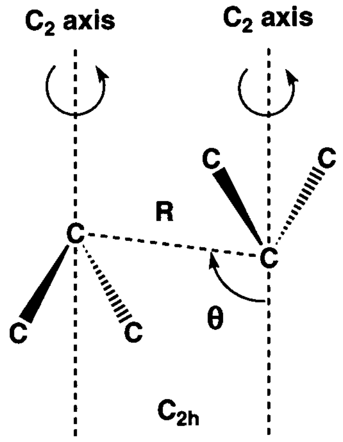

Figure 8. MP2/6-311G** level optimized geometry of the propane dimer. R = 3.855 Å and θ = 94.7°.

TABLE 3: Calculated HF and MP2 Interaction Energies of the Propane Dimer Using Several Basis Sets[a]

basis set	bf[b]	E_{HF}	E_{MP2}
6-31G*	122	1.35	−0.37
6-311G**	204	1.36	−1.05
cc-pVDZ	164	1.39	−0.86
cc-pVTZ	404	1.40	−1.64
cc-pVQZ	810	1.40	−1.88
aug-cc-pVDZ	282	1.41	−1.72
aug(d,p)−6-311G**[c]	282	1.40	−1.78
aug(df,pd)−6-311G**[d]	404	1.40	−1.91
$E_{\mathrm{MP2(limit)}}$[e]			−1.99
ΔCCSD(T)[f]			0.05
$E_{\mathrm{CCSD(T)(limit)}}$[g]			−1.94

[a] Energies in kcal/mol. The BSSE corrected interaction energies. The optimized geometry at the MP2/6-311G** level was used. See Figure 8. [b] Number of basis functions employed for the calculation of the propane dimer. [c] The 6-311G** basis set augmented with diffuse d functions on carbon atoms ($\alpha_d(\mathrm{C}) = 0.1565$) and diffuse p functions on hydrogen atoms ($\alpha_p(\mathrm{H}) = 0.1875$). [d] The 6-311G** basis set augmented with diffuse d and f functions on carbon atoms ($\alpha_d(\mathrm{C}) = 0.1565$ and $\alpha_f(\mathrm{C}) = 0.2$) and diffuse p and d functions on hydrogen atoms ($\alpha_p(\mathrm{H}) = 0.1875$ and $\alpha_d(\mathrm{H}) = 0.25$). [e] The estimated MP2 interaction energies at the basis set limit. See text. [f] The CCSD(T) correction term. The difference between the calculated CCSD(T) and MP2 interaction energies using the aug-cc-pVDZ basis set. [g] The estimated CCSD(T) interaction energies at the basis set limit. The sum of the $E_{\mathrm{MP2(limit)}}$ and the ΔCCSD(T). See text.

Interaction Energy at the Basis Set Limit. The MP2 interaction energy of the dimer (Figure 8, MP2/6-311G** level optimized geometry) was calculated using the cc-pVXZ (X = D, T, and Q) basis sets as summarized in Table 3. The MP2 interaction energy of the dimer at the basis set limit [$E_{\mathrm{MP2(limit)}}$] was estimated from the calculated MP2 interaction energies with the method proposed by Feller.[44] In Feller's method, the calculated interaction energies were fitted to the form $a + b\exp(-cX)$ (where X is 2 for cc-pVDZ, 3 for cc-pVTZ, etc). The MP2 energy at the basis limit ($E_{\mathrm{MP2(limit)}}$) was then estimated by extrapolation. The estimated $E_{\mathrm{MP2(limit)}}$ is -1.99 kcal/mol. The $E_{\mathrm{MP2(limit)}}$ was also estimated using the form $a + bX^{-3}$ (ref 48). The estimated $E_{\mathrm{MP2(limit)}}$ using this form (-2.01 kcal/mol) is very close to that obtained using the form proposed by Feller. The calculated MP2 interaction energy with the aug(df,pd)-6-311G** basis set (-1.91 kcal/mol, respectively) is close to the estimated $E_{\mathrm{MP2(limit)}}$. The MP2/6-311+G(2df,2pd) interaction energy of the propane dimer reported by Jalkanen et al. (-1.6125 kcal/mol) is slightly (about 15%) smaller than this value.[30] The good agreement indicates that sufficiently accurate interaction energies are calculated with the aug(df,pd)-6-311G** basis set. The MP2 interaction energy was also calculated using the aug(df,pd)-6-311G** basis set with {3s3p2d} bond functions proposed by Tao and Pan ($\alpha_s = 0.9$, 0.3, and 0.1; $\alpha_p = 0.9$, 0.3, and 0.1; $\alpha_d = 0.6$ and 0.2).[49] The bond functions were centered at the midpoint of the two methylene carbons. The calculated MP2 interaction energy was -1.93 kcal/mol. The effect of the bond functions is very small (-0.02 kcal/mol), which indicates that the aug(df,pd)-6-311G** basis set is very close to saturation. The CCSD(T) interaction energy of the dimer at the basis set limit [$E_{\mathrm{CCSD(T)(limit)}}$] was estimated from the $E_{\mathrm{MP2(limit)}}$ and a CCSD(T) correction term [ΔCCSD(T)]. The ΔCCSD(T) [the difference between the CCSD(T) and MP2 interaction energies] obtained using the aug-cc-pVDZ basis set (0.05 kcal/mol) was used for the estimation. The estimated $E_{\mathrm{CCSD(T)(limit)}}$ [sum of $E_{\mathrm{MP2(limit)}}$ and ΔCCSD(T)] was -1.94 kcal/mol.

Conclusion

The calculations of the 23 orientations of propane dimers show that the interaction energy strongly depends on dimer orientation. The C_{2h} dimer in which two C_2 axes of propane monomers have antiparallel orientation has the largest binding energy. The electrostatic energy is negligible in all dimers. The C_{2h} dimer has large number of close C⋯C contact and therefore has the large dispersion energy. This would be the cause of the large binding energy of this dimer.

The calculated MP2 interaction energy strongly depends on the basis set. The effects of electron correlation beyond MP2 are not large. The calculated MP2 interaction energy is not largely different from the CCSD(T) one. The estimated MP2 and CCSD(T) interaction energies of the propane dimer at the basis set limit are -1.99 and -1.94 kcal/mol, respectively.

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