J. Phys. Chem. A **2004,** *108,* 10311−10316

Magnitude of Interaction between *n*-Alkane Chains and Its Anisotropy: High-Level ab Initio Calculations of *n*-Butane, *n*-Petane, and *n*-Hexane Dimers

Seiji Tsuzuki,* Kazumasa Honda, Tadafumi Uchimaru, and Masuhiro Mikami

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

Received: April 12, 2004; In Final Form: August 27, 2004

Intermolecular interaction energies of *n*-butane, *n*-pentane, and *n*-hexane dimers were calculated at the MP2 level with a large basis set including multiple polarization functions. The comparison of the calculated interaction energies of five orientations of dimers for each *n*-alkane molecule, in which the main molecular axes of the two alkane chains are parallel, shows that the interaction between the two *n*-alkane chains has strong anisotropy. The antiparallel dimers (D_2 dimers of *n*-butane and *n*-hexane and C_{2h} dimer of *n*-pentane) have the largest interaction. The calculated interaction energies of the most stable *n*-butane, *n*-pentane, and *n*-hexane dimers are −2.80, −3.57, and −4.58 kcal/mol, respectively. The orientations of the most stable dimers are close to those of nearest neighboring *n*-alkane molecules (*n*-hexane to *n*-nonane) in the crystals. The calculated intermolecular interaction energies in the *n*-hexane crystal show that the intermolecular interaction (−4.23 kcal/mol) along the *a*-axis is substantially larger than those along the *b*- and *c*-axes.

Introduction

Nonbonding interactions of *n*-alkane chains are essential for the understanding of intermolecular interactions of organic molecules, which have alkyl chains such as alkanes, alcohols, thiols, esters, and carboxylic acids. Intermolecular 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 and Langmuir−Blodgett films.[4−11] The nonbonding interactions of *n*-alkane chains are also important for understanding structures and properties of polymers. An accurate interaction potential of *n*-alkane chains is essential for reliable force field simulations of these molecules. Detailed information on the nonbonding interactions of *n*-alkane chains is strongly needed.

Several experimental measurements have been reported on intermolecular interactions of small alkane molecules. Measurements of compressibility of a gas give the spherically averaged interaction potential of a molecule.[12] Heat of evaporation and heat of sublimation also provide averaged intermolecular interaction energy.[13,14] Crystal structures give detailed information on the shape of the potential at the van der Waals contact distance.[15] Measurements of the melting point alternation in *n*-alkanes show that the interactions between *n*-alkane chains have large anisotropy.[16]

Recently, ab initio molecular orbital calculation is becoming a powerful tool for studying intermolecular interactions.[17−19] 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.[19,20]

Many ab initio calculations of the methane dimer have been reported as the smallest model of the interaction between alkane molecules.[21−33] A few calculations of the ethane[28,33−35] and propane[33,36,37] dimers have also been reported. These calculations show that the calculated interaction energy has strong basis set dependence and HF calculations cannot evaluate the attraction. A very large basis set and an electron correlation correction are necessary to obtain accurate intermolecular interaction energy, as the major source of the attraction is dispersion force. The calculated interaction energies of methane dimers with a very large basis set near saturation were used for the fitting of force field parameters. Molecular dynamics simulations of liquid methane using the force field well reproduced the experimental liquid properties, which suggests the accuracy of the calculated interaction energies with the very large basis set.[27,32] Unfortunately, however, high-level ab initio calculations of the intermolecular interaction energies of longer *n*-alkanes have not yet been reported.

Although the experimental measurements and theoretical studies provide valuable pieces of information on the intermolecular interaction between *n*-alkane chains, there still remain several important and fundamental unsettled issues about the interaction between *n*-alkane chains. (1) Despite the broad interests in the interaction between *n*-alkane chains in many fields of chemistry, very little is known on the sizes of the intermolecular interaction energies between longer *n*-alkane molecules. (2) Another important issue is the anisotropy of the interaction between *n*-alkane chains. Experimental measurements such as melting point alternation of *n*-alkanes indicate that the interaction has anisotropy. However, the size of the anisotropy of the interaction has not yet been accurately evaluated.

In this paper, we have provided detailed evaluation of the intermolecular interaction energies of *n*-butane, *n*-pentane, and *n*-hexane dimers by high-level ab initio calculations. We have carefully evaluated the effects of basis set and electron correlation correction for the accurate calculation of the interaction energies. We have reported the size of the interaction energies of these *n*-alkane dimers and the magnitude of the anisotropy of the interactions. We have also calculated the intermolecular interaction energies between *n*-hexane molecules in the crystal

---

* Author to whom correspondence should be addressed. E-mail: s.tsuzuki@aist.go.jp. Member of Research Consortium for Synthetic Nano-Function Materials Project (SYNAF), National Institute of Advanced Industrial Science and Technology (AIST).

10.1021/jp048403z CCC: $27.50

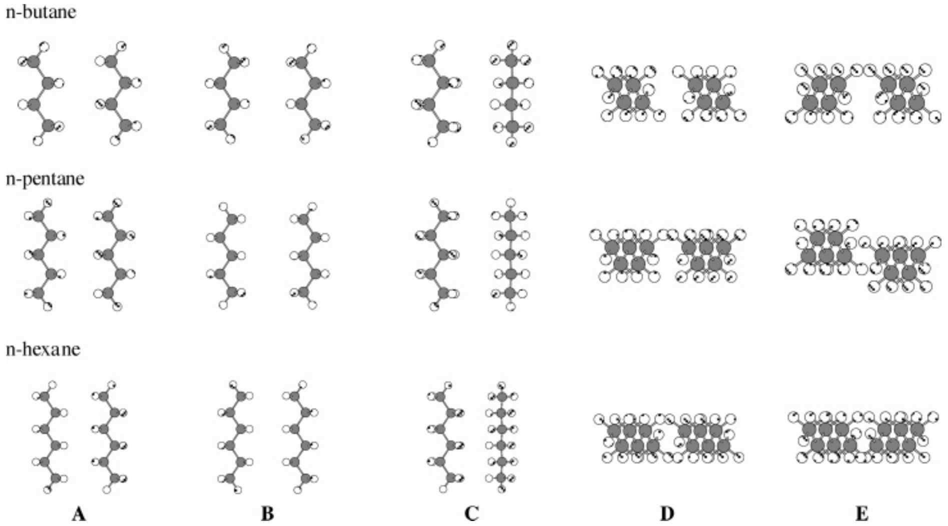

Figure 1. Geometries of *n*-alkane dimers. The details of the orientations of the dimers are shown in Figure 2.

and have discussed the anisotropy of the intermolecular interactions in the crystal.

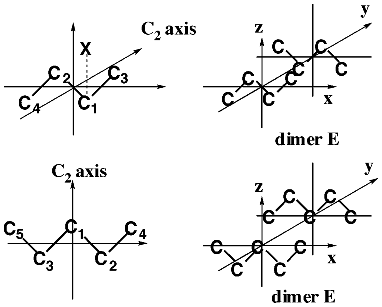

Figure 2. In all dimers of *n*-butane and *n*-hexane in Figure 1, the midpoints of C_1 and C_2 of the two molecules are on the *y*-axis and the C_2 axis of each molecule is parallel to *y*- or *z*-axis. In all dimers of *n*-pentane in Figure 1, the central methylene carbon atom (C_1) of the two molecules are put on the *y* axis and the C_2 axis of each molecule is parallel to *y*- or *z*-axis.

Computational Method

The Gaussian 98 program[38] was used for the ab initio molecular orbital calculations to evaluate total interaction energies. The basis sets implemented in the Gaussian program and a few modified basis sets were used. Electron correlation was accounted for at the MP2[39,40] and CCSD(T)[41] levels. The geometries of isolated *n*-alkane molecules were optimized at the MP2/6-31G* level. The optimized monomer geometries were used for the calculations of the dimers without further optimization. The intermolecular interaction energy potentials were calculated with changing the intermolecular separations. The use of the MP2/6-31G* level optimized geometries of monomers is adequate, as the MP2/6-31G* level optimized geometry of *n*-butane is close to that obtained using a large aug-cc-pVDZ level basis set. The largest difference between the bond distance in the two geometries is less than 0.01 Å and that of valence angle is less than 0.2°, respectively. The basis set superposition error (BSSE)[42] was corrected for all calculations using the counterpoise method.[43] The MP2 interaction energy at the basis set limit [$E_{\mathrm{MP2(limit)}}$] was estimated by the method proposed by Feller[44] from the calculated MP2 interaction energies using Dunning's correlation consistent basis sets (cc-pVXZ, X = D, T, and Q).[45,46] 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 $E_{\mathrm{MP2(limit)}}$ was then estimated by extrapolation. The aug(d,p)-6-311G** basis set is 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 [$\alpha_p(\mathrm{H}) = 0.1875$]. The aug(df,pd)-6-311G** basis set is the 6-311G** basis set augmented with the diffuse d functions and diffuse f functions on carbon atoms [$\alpha_f(\mathrm{C}) = 0.2$] and the diffuse p functions and diffuse d functions on hydrogen atoms [$\alpha_d(\mathrm{H}) = 0.25$].[33] Distributed multipoles[18,47] up to hexadecapole on all atoms were obtained from the MP2/6-311G** wave functions of isolated molecules using the CADPAC version 6.[48] The electrostatic energies of the dimers were calculated using the ORIENT version 3.2.[49] The electrostatic energies of the dimers were calculated as interactions between distributed multipoles of monomers. Distributed multipoles were used only to estimate the electrostatic energies. The geometries of *n*-hexane molecules observed in the crystal[16] were used for the calculations of interaction energies in the crystal. The positions of hydrogen atoms were optimized by the MP2/6-31G* level calculation of monomer before the calculations of the intermolecular interaction energies.

Results and Discussion

Geometries of *n*-Alkane Dimers. The intermolecular interaction energies of five orientation dimers (Figure 1) were calculated for each *n*-alkane to evaluate the anisotropy of the interaction. The details of the orientations of the dimers are shown in Figure 2. In all the *n*-butane and *n*-hexane dimers in Figure 1, the midpoints between the C_1 and C_2 atoms are put on the *y*-axis. The symmetry planes of the two molecules are coplanar in dimers A and B, perpendicular in dimer C, and parallel in dimers D and E. The bisector of the $C_2-C_1-C_3$ angle (C_1...X) is parallel to the *y*- or *z*-axis in the five dimers. In the five *n*-pentane dimers in Figure 1, the C_1 methylene carbon atoms are put on the *y*-axis and the C_2 axes of the two molecules are parallel to the *y*- or *z*-axis as shown in Figure 2. The C_2 axes are linear in dimers A and B, perpendicular in dimer C, parallel in dimer D, and antiparallel in dimer E.

Basis Set and Electron Correlation Effects. The intermolecular interaction energy of the *n*-butane dimers (Figure 1, dimer E) 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

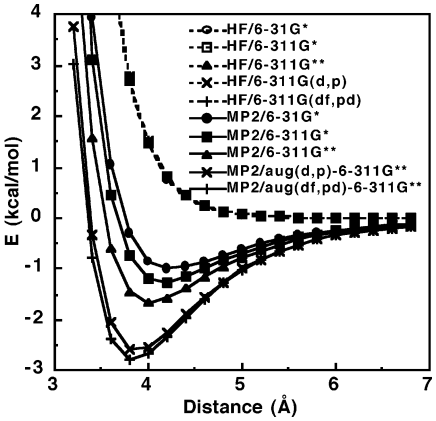

Figure 3. Calculated HF and MP2 interaction energies of the *n*-butane dimer E using several basis sets. The BSSE corrected interaction energies. See the text.

TABLE 1: Calculated HF and MP2 Interaction Energies of the *n*-Butane Dimer E Using Several Basis Sets[a]

basis set	bf[b]	E_{HF}[c]	E_{MP2}[c]
6-31G*	160	2.67	−0.30
6-311G*	204	2.75	−0.74
6-311G**	264	2.69	−1.45
aug(d,p)-6-311G**[d]	364	2.77	−2.59
aug(df,pd)-6-311G**[d]	520	2.78	−2.80
cc-pVDZ	212	2.75	−1.12
cc-pVTZ	520	2.78	−2.41
cc-pVQZ	1040	2.78	−2.78
aug-cc-pVDZ	364	2.78	−2.49
aug-cc-pVTZ	828	2.78	−2.86
basis set limit[e]			−2.93

[a] Energies in kcal/mol. The geometry of the dimer is shown in Figures 1 and 2. Intermolecular separation $R = 3.8$ Å. [b] Number of base functions used for the calculation of the *n*-butane dimer. [c] BSSE corrected interaction energies. [d] 6-311G** basis set augmented with diffuse polarization functions. See details in the text. [e] Estimated MP2 interaction energies at the basis set limit [$E_{\mathrm{MP2(limit)}}$] by the Feller's method from the calculated MP2 interaction energies using cc-pVXZ (X = D, T, and Q) basis sets. See the text.

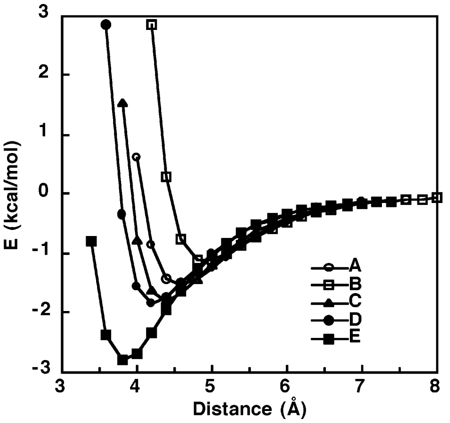

Figure 4. The calculated MP2 interaction energies of five orientation *n*-butane dimers.

as in the previously reported calculations of small alkane molecules.[33,35−37]

The inclusion of electron correlation considerably increases the attraction, which indicates that dispersion force is the major source of attraction. The significant basis set dependence shows that a large flexible basis set is necessary for the evaluation of the interactions of *n*-alkanes.

The MP2 level interaction energy at the basis set limit [$E_{\mathrm{MP2(limit)}}$] was estimated for the *n*-butane dimer E at the potential minimum (intermolecular separation $R = 3.8$ Å) by the method proposed by Feller.[44] The calculated MP2 interaction energies using the cc-pVXZ (X = D, T, and Q) basis sets were used for the estimation. The estimated $E_{\mathrm{MP2(limit)}}$ was −2.93 kcal/mol. Augmentation of diffuse functions to the small cc-pVDZ basis set considerably increases the calculated interaction energy. The calculated MP2 interaction energies with the cc-pVDZ and aug-cc-pVDZ basis sets are −1.12 and −2.49 kcal/mol, respectively. On the other hand, the augmentation to the large cc-pVTZ basis set does not largely change the calculated interaction energies. The calculated MP2 interaction energies with the cc-pVTZ and aug-cc-pVTZ basis sets are −2.41 and −2.86 kcal/mol, respectively. The small effect of the diffuse function shows that the cc-pVTZ basis set is close to saturation for the calculation of the dispersion energy. The effect of diffuse functions on the larger cc-pVQZ basis set will be smaller than that on the cc-pVTZ basis set. Therefore, we can obtain a sufficiently accurate $E_{\mathrm{MP2(limit)}}$ value by extrapolation from the calculated MP2 interaction energies using the cc-pVXZ (X = D, T, and Q) basis sets.

The calculated MP2 interaction energies using several basis sets are compared with the estimated $E_{\mathrm{MP2(limit)}}$ as summarized in Table 1. Although the aug(df,pd)-6-311G** basis set[33] employs small numbers of basis functions (520 basis functions for the *n*-butane dimer), the calculated interaction energy (−2.80 kcal/mol) is close to that calculated with the large cc-pVQZ basis sets[45,46] (−2.78 kcal/mol, 1040 basis functions) and the estimated $E_{\mathrm{MP2(limit)}}$. Because of the good performance of the aug(df,pd)-6-311G** basis set, we have carried out further calculations of the intermolecular interaction energies of *n*-alkane dimers with this basis set. The good performance of the aug(df,pd)-6-311G** basis set was also reported for the calculations of the interaction energies of small alkane molecules.[33]

The calculations of the propane dimer show that the effects of electron correlation beyond MP2 are not large. The calculated MP2/aug-cc-pVDZ interaction energy of the propane dimer (−1.72 kcal/mol) is very close to the CCSD(T)/aug-cc-pVDZ inteaction energy (−1.67 kcal/mol).[37] The good agreement of the MP2 level interaction energy with the corresponding CCSD(T) level one was also reported for methane dimer.[33] Therefore, we have used the MP2 method for calculations of the *n*-alkane dimers.

Intermolecular Interaction of *n*-Butane Dimer. The interaction energies of the five orientation dimers (Figure 1) were calculated at the MP2 level with changing the intermolecular separation (the distance between the midpoints of C_1 and C_2). The calculated interaction energies of the dimers are shown in Figure 4. The calculated interaction energies of the five dimers are not largely different when the intermolecular distances are larger than 5 Å.

On the other hand, the size of the interaction energy at the potential minimum depends strongly on the orientation of the dimer. The dimer E has the largest (most negative) interaction energy (−2.80 kcal/mol). The symmetrical planes of the two *n*-butane molecules are parallel and the two molecules have antiparallel orientation in the dimer E. The calculated interaction energy of the dimer E at the potential minimum is about 2.5 times as large as that of the dimer B (−1.13 kcal/mol).

Intermolecular Interaction of *n*-Pentane Dimer. The calculated MP2 level interaction energies of the five dimers are shown in Figure 5. The calculated interaction energies of the five dimers are not largely different when the intermolecular distances are larger than 5 Å and the depth of the potential

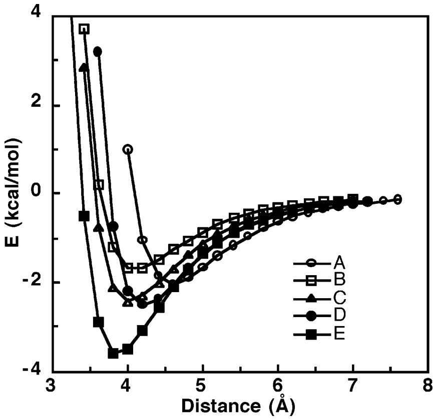

Figure 5. The calculated MP2 interaction energies of five orientation *n*-pentane dimers.

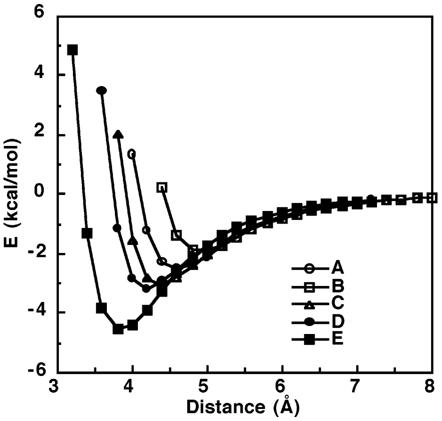

Figure 6. The calculated MP2 interaction energies of five orientation *n*-hexane dimers.

depends strongly on the orientation as in the *n*-butane dimer. The antiparallel dimer E has the largest interaction energy (−3.57 kcal/mol) at the potential minimum, which is 2.2 times as large as that of the dime B (−1.66 kcal/mol).

Intermolecular Interaction of *n*-Hexane Dimer. The calculated MP2 level interaction energies of the five dimers are shown in Figure 6. The orientation dependence of the calculated interaction energy is again small when the intermolecular distance is larger than 5 Å. The antiparallel dimer E has the largest interaction energy (−4.58 kcal/mol) at the potential minimum, which is 2.4 times as large as that of the dimer B (−1.90 kcal/mol).

The electrostatic (E_{es}), repulsion (E_{rep}), and correlation interaction (E_{corr}) energies of the five dimers at the potential minima are summarized in Table 2. 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 the interaction energy, which is the difference between the MP2/aug(df,pd)-6-311G** level interaction energy (E_{total}) and E_{HF}. The E_{corr} is mainly dispersion energy. In all the dimers, the E_{es} is negligible. The large E_{corr} indicates that the dispersion is the major source of the attraction.

TABLE 2: Calculated Interaction Energies of *n*-Hexane Dimers at the Potential Minima[a]

dimer	R(Å)[b]	E_{total}[c]	E_{es}[d]	E_{rep}[e]	E_{corr}[f]
A	4.6	−2.51	0.14	2.10	−4.75
B	5.0	−1.90	0.11	0.98	−2.99
C	4.4	−3.05	0.03	2.12	−5.20
D	4.2	−3.18	0.12	2.24	−5.53
E	3.8	−4.58	0.14	4.37	−9.09

[a] Energies in kcal/mol. [b] Intermolecular distance at the potential minimum. [c] MP2/aug(df,pd)-6-311G** level interaction energy. The BSSE corrected interaction energies. [d] Electrostatic energy calculated as the interaction between the distributed multipoles of monomers obtained from MP2/cc-pVTZ wave functions. See refs 18 and 47 for details. [e] Difference between the HF level interaction energy and E_{es}. E_{rep} is mainly exchange-repulsion energy. [f] Difference between the MP2 and HF level interaction energies. E_{corr} is mainly dispersion energy.

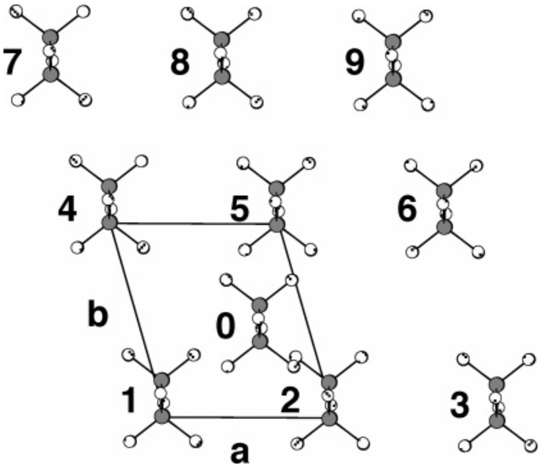

Figure 7. Schematic diagram of the crystal structure of *n*-hexane viewed from the parallel direction of the *n*-alkane chain. Nine molecules 1−9 at the same z position along with one molecule 0 at the z+1 position are depicted.

The E_{corr} value of the dimer E (−9.09 kcal/mol) is considerably larger (more negative) than those of other dimers, which shows that larger dispersion energy is the cause of the stability of the dimer E. The intermolecular distance of the dimer E at the potential minimum (3.8 Å) is substantially shorter than those of other dimers (4.2−5.0 Å). The antiparallel *n*-butane and *n*-pentane dimers E also have shorter intermolecular distances at the potential minima than the other dimers. This shows that the antiparallel orientation (dimer E) is the appropriate orientation for *n*-alkane dimers to have short intermolecular contact without serious steric repulsion and to increase the stabilization by dispersion force.

Although dispersion force is well known as the weak attractive force between rare gas atoms, our calculations show that the dispersion energy between *n*-alkane chains is substantially large. The calculated interaction energies (E_{total}) of the most stable *n*-butane, *n*-pentane, and *n*-hexane dimers are −2.80, −3.57, and −4.58 kcal/mol, respectively. The size of the intermolecular interaction energy of the *n*-hexane dimer is close to that of the water dimer (about −5 kcal/mol).[50] Our calculations suggest that the interaction energy between longer *n*-alkane chains is significantly large.

Intermolecular Interaction in *n*-Hexane Crystal. The intermolecular interaction energies of *n*-hexane molecules in the crystal (Figure 7) were calculated as summarized in Table 3. The calculated interaction energy between the nearest neighboring molecules (1−2 pair) in the crystal (−4.23 kca/mol) is close to the interaction energy of the most stable dimer E (−4.58 kcal/mol).

The interaction energy of the 1−2 pair is considerably larger than those of other pairs within the *ab*-plane (Figure 7). The interaction energies of 1−4 and 1−5 pairs (−2.51 and −1.49 kcal/mol) are only 59 and 35% of that of the 1−2 pair, respectively. The interaction energies with the molecules perpendicular to the plane (0−*n* pairs, n = 1−6) are not large

TABLE 3: Calculated Interaction Energies between *n*-Hexane Molecules in the Crystal[a]

pair	E_{total}	pair	E_{total}	pair	E_{total}
1−2	−4.23	1−7	−0.06	0−3	−0.03
1−3	−0.11	2−4	−0.32	0−4	−0.47
1−4	−2.51	0−1	−1.11	0−5	−0.63
1−5	−1.49	0−2	−0.53	0−6	−0.07

[a] Energies in kcal/mol. MP2/aug(df,pd)-6-311G** level interaction energy. The BSSE corrected interaction energies.

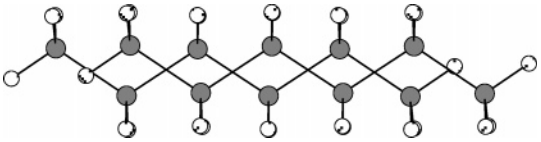

Figure 8. Orientation of the nearest neighboring *n*-hexane molecules (1 and 2 in Figure 7) in the crystal viewed from the perpendicular direction to the symmetry planes of the *n*-hexanes.

(−0.3 to −1.1 kcal/mol). The sizes of the calculated interaction energies indicate that the intermolecular interaction along the *a*-axis is substantially stronger than those along the *b*- and *c*-axes.

The orientation of the 1−2 pair is shown in Figure 8. Although *n*-hexane molecules slip as much as one methylene distance, the orientation of the 1−2 pair in the crystal is close to that of the dimer E.[16] The nearest neighboring *n*-alkane molecules (*n*-heptane to *n*-nonoane) in the crystal also have similar orientations.[16]

It is expected that molecules are packed so at to maximize the stability of the crystal. The similarity of the orientation of the most stable dimer and that of the nearest neighboring molecules in the crystal suggests that the interaction between the nearest neighboring molecules has the primary importance for the stabilization of these *n*-alkane crysatals.

However, the one methylene distance slipping suggests that the interactions with other molecules are also important for the crystal packing. The slipping decreases the interaction between the 1−2 pair, as this slipping increases the intermolecular distance. Therefore, the slipping must be important for enhancing the interaction with the other molecules along the *b*- and *c*-axes to maximize the stability of the crystal.

Conclusions

High-level ab initio calculations show that substantial attraction exists between *n*-alkane chains. The calculated intermolecular interaction energy of *n*-hexane (−4.58 kcal/mol) is close to that of the hydrogen-bonded water dimer (about −5 kcal/mol), which suggests that the interaction between longer *n*-alkane chains is significantly large. The interaction between *n*-alkane chains has strong anisotropy. The antiparallel dimers (D_2 dimers of *n*-butane and *n*-hexane and C_{2h} dimer of *n*-pentane) have the largest interaction energies because of short intermolecular separations. The orientations of the most stable *n*-alkane dimers are close to the orientations of the nearest neighboring *n*-alkane molecules in the crystals. The intermolecular interaction along the *a*-axis (the interaction between the nearest neighboring molecules) is substantially larger than those along the *b*- and *c*-axes.

Acknowledgment. This work was partly supported by NEDO under the Nanotechnology Materials Program, by NAREGI Nanoscience Project, Ministry of Education, Culture, Sports, Science, and Technology, Japan, and by KAKENHI 14209022. We thank Prof. K. Hiratani, Dr. Y. Nagawa, Dr. M. Kanesato, and Dr. H. Houjou for helpful discussion. We thank Tsukuba Advanced Computing Center for the provision of the computational facilities.

Supporting Information Available: Tables showing center number, atomic number, and coordinates of *n*-butane, *n*-penane, and *n*-hexane dimers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Jorgensen, W. *J. Am. Chem. Soc.* **1984**, *106*, 6638.

(2) Chen, B.; Siepmann, J. I. *J. Phys. Chem. B* **1999**, *103*, 5370.

(3) Wright, J. D. *Molecular Crystal*; Cambridge University Press: Cambridge, U.K., 1987.

(4) Meyer, E.; Howald, L.; Overney, R. M.; Heinzelmann, H.; Frommer, J.; Guntherodt, H. J.; Wagner, T.; Schier, H.; Roth, S. *Nature* **1991**, *349*, 398.

(5) Schwartz, D. K.; Garnaes, J.; Viswanathan, R. Zasadzinski, J. A. N. *Science* **1992**, *257*, 508.

(6) Camillone, N.; Chidsey, C. E. D.; Liu, G. Y.; Scoles, G. *J. Chem. Phys.* **1993**, *98*, 3503.

(7) Poirier, G. E.; Tarlov, M. J. *Langmuir* **1994**, *10*, 2853.

(8) Kricheldorf, H. R.; Schwarz, G.; Berghahn, M.; Deabajo. J.; Delacampa, J. *Macromolecules* **1994**, *27*, 2540.

(9) Rawicz, W.; Olbrich, K. C.; McIntosh, T.; Needham, D.; Evans, E. *Biophys. J.* **2000**, *79*, 328.

(10) Liu, G. Y.; Xu, S.; Qian, Y. L. *Acc. Chem. Res.* **2000**, *33*, 457.

(11) Malinsky, M. D.; Kelly, K. L.; Schatz, G. C.; Van Duyne, R. P. *J. Am. Chem. Soc.* **2001**, *123*, 1471.

(12) Dymond, J. H.; Rigby, M.; Smith, E. B. J. *J. Chem. Phys.* **1965**, *42*, 2801.

(13) Rossini, F. D.; Pitzer, K. S.; Arnett, R. L.; Braun, R. M.; Pimentel, G. C. *Selected Values of Physical and Thermodynamic Properited of Hydrocarbons and Related Compounds*; Carnegie Press: Pittsburgh, PA, 1953.

(14) Williams, D. E.; Starr, T. L. *Comput. Chem.* **1977**, *1*, 173.

(15) Allinger, N. L.; Miller, M. A.; VanCatledge, F. A. *J. Am. Chem. Soc.* **1967**, *89*, 4345.

(16) Boese, R.; Weiss, H.-C.; Blaeser, D. *Angew. Chem. Int. Ed.* **1999**, *38*, 988.

(17) Buckingham, A. D.; Fowler, P. W.; Hutson, J. M *Chem. Rev.* **1988**, *88*, 963.

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

(19) Chalasinski, G.; Szczesniak, M. M. *Chem. Rev.* **2000**, *100*, 4227.

(20) Tsuzuki, S.; Uchimaru, T.; Matsumura, K.; Mikami, M.; Tanabe, K. *J. Chem. Phys.* **1999**, *110*, 11906.

(21) Kolos, W.; Ranghino, G.; Clementi, E.; Novaro, O. *Int. J. Quantum Chem.* **1980**, *17*, 429.

(22) Williams, D. E.; Craycroft, D. J. *J. Phys. Chem.* **1987**, *91*, 6365.

(23) Szczesniak, M. M.; Chalasinski, G.; Cybulski, S. M.; Scheiner, S. *J. Chem. Phys.* **1990**, *93*, 4243.

(24) Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1991**, *95*, 2272.

(25) Novoa, J. J.; Whangbo, M.-H.; Williams, J. M. *J. Chem. Phys.* **1991**, *94*, 4835.

(26) Gay, D. H.; Dai, H.; Beck, D. R. *J. Chem. Phys.* **1991**, *95*, 9106.

(27) Tsuzuki, S.; Uchimaru, T.; Tanabe, K.; Kuwajima, S. *J. Phys. Chem.* **1994**, *98*, 1830.

(28) Tsuzuki, S.; Uchimaru, T.; Tanabe, K. *J. Mol. Struct. (THEOCHEM)* **1994**, *307*, 107.

(29) Nagy, J.; Weaver, D. F.; Smith, V. H. *Mol. Phys.* **1995**, *85*, 1179.

(30) Fraschini, E.; Stone, A. J. *J. Comput. Chem.* **1998**, *19*, 847.

(31) Tsuzuki, S.; Uchimaru, T.; Tanabe, K. *Chem. Phys. Lett.* **1998**, *287*, 202.

(32) Tsuzuki, S.; Uchimaru, T.; Tanabe, K. *Chem. Phys. Lett.* **1998**, *287*, 327.

(33) Tsuzuki, S.; Uchimaru, T.; Mikamki, M.; Tanabe, K. *J. Phys. Chem.* **1998**, *102*, 2091.

(34) Gupta, S.; Yang, J.; Kestner, N. R. *J. Chem. Phys.* **1988**, *89*, 3733.

(35) Rowley, R. L.; Yang, Y.; Pakkanen, T. A. *J. Chem. Phys.* **2001**, *114*, 6058.

(36) Jalkanen, J.-P.; Mahlanen, R.; Pakkanen, T. A.; Rowley, R. L. *J. Chem. Phys.* **2002**, *116*, 1303.

(37) Tsuzuki, S.; Uchimaru, T.; Mikamki, M.; Tanabe, K. *J. Phys. Chem. A* **2002**, *106*, 3687.

(38) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; 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;* Gaussian, Inc.: Pittsburgh, PA, 1998.

(39) M*ϕ*ller, 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) Feller, D. *J. Chem. Phys.* **1992**, *96*, 6104.

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

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

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

(48) Amos, R. D.*CADPAC: The Cambridge Analytical Derivatives Package, Issue 6*, Tech. rep., University of Cambridge, 1995, A suite of quantum chemistry programs developed by Amos, R. D. with contributions from Alberts, I. L.; Andrews, J. S.; Colwell, S. M.; Handy, N. C.; Jayatilaka, D.; Knowles, P. J.; Kobayashi, R.; Laidig, K. E.; Laming, G.; Lee, A. M.; Maslen, P. E.; Murray, C. W.; Rice, J. E.; Simandiras, E. D.; Stone, A. J.; Su, M. D.; Tozer, D. J.

(49) 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, U.K., 1995.

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