Theoretical Study on Mesogenic Core Structures of Nematic Liquid Crystalline Compounds

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The structures and intermolecular interaction energies of 10 dimers, included in the mesogenic core structures of typical liquid crystalline (LC) compounds, are obtained at the MP2/6-31G(d) level of theory. It is proved that the dispersion energy significantly contributes to the total interaction energy of these dimers. Even when bulky substituents are introduced into the core part, the interaction energy is still large. It is also revealed that when a long intermolecular distance is provided by a high steric repulsion originating from the linkage of two phenyl groups, the dispersion energy is significantly small. However, in this range of intermolecular distances, the electrostatic energy caused by a strong quadrupole—quadrupole attractive interaction plays a dominant role, and as a result, a rather stable dimer is formed. In all 10 dimers, the dispersion, electrostatic, and exchange—repulsion energies strongly depend on the geometrical orientation of the molecules. The calculated interaction energies of these dimers are also compared with the corresponding experimentally measured viscosities. The results suggest an explicit linear relationship between the interaction energies and viscosities.

1. Introduction

Much attention has been paid to the noncovalent interactions between molecules possessing aromatic groups in many fields of chemistry and biology, especially in material science.[1–6] Such investigations provide many suggestions not only for understanding the chemical and biochemical properties, but also for designing new materials which may be used for new electric devices.

Among other things, a remarkable development has been recently performed on liquid crystal (LC) displays and, as a result, a much higher precision and behavior are required from the LC compounds.[7–9] Many attempts have been made in order to propose new LC compounds possessing better optical and dielectric anisotropies.[8,10–14] In most of these studies, the physical properties of a single molecule in the LC compounds are estimated by using semiempirical molecular orbital (MO) theories. Some of them have reported that the AM1 method provides an extremely good prediction of the dielectric anisotropy ($\Delta\epsilon$) and optical birefringence (Δn) of nematic LC compounds on the basis of the well-known theories proposed by Vuks[12] and Maier and Meier,[13] when they are compared with dipole moments and polarizabilities.[14] On the other hand, it is more difficult to predict the bulk properties of LC molecules, such as rotational viscosities, clearing points, and elastic constants, because no macroscopic information could be obtained in these investigations. Instead, it might be worthwhile to study the bulk properties with molecular dynamics and Monte Carlo simulations, but many problems still remain to be solved.

Although less computational efforts are required when the semiempirical or nonempirical Hartree—Fock (HF) method is used, the dispersion energy is not taken into account in such

HF methods regarding the studies of intermolecular interactions. The dispersion energy should be most responsible in describing the aggregation behavior of aromatic molecules. For the appropriate estimation of the intermolecular interaction in such systems, more sophisticated MO methods need to be employed. So far, higher levels of theory have been used to obtain the intermolecular interaction energies or their two-body potentials only for relatively small molecules.[15–23] For instance, Hobza et al.[22] reported six minima for the benzene dimer and analyzed the intermolecular interaction energies using the second-order Møller—Plesset perturbation theory (MP2). Further investigation of the benzene dimer was performed by Tsuzuki et al.[23] using both the MP2 and coupled-cluster theory including single and double substitutions with noniterative triple excitations (CCSD(T)) near the basis-set limit. Both studies indicated that the dispersion and electrostatic quadrupole—quadrupole forces play significantly important roles as attractive terms in the interaction energies, and high levels of theory and large basis sets should be employed for reliable predictions.

The recent development of computers allows us to calculate large-size molecules at high levels of theory. Amovilli et al.[5] analyzed the intermolecular interaction between two 4-*n*-pentyl-4′-cyanobiphenyls (**5CB**, see Chart 1) using the fragmentation method developed with the MP2 method. In this investigation, they divided the molecule into *n*-pentane, benzene, and benzonitrile fragments, and estimated the interaction energies of each fragment pair.

The purpose of the present study is to understand the intermolecular interaction between the mesogenic core structures of nematic LC compounds. This paper reports the calculated results for the intermolecular interaction of the core structures in 10 dimers, and analyzes the interaction energy that is divided into several physical components. The rotational viscosities are also experimentally measured for these dimers, and are compared with the corresponding calculated results of the intermo-

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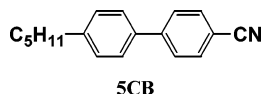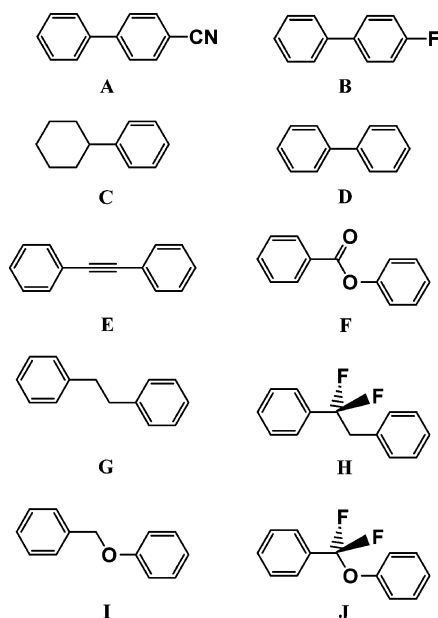   † Osaka Prefecture University.
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CHART 1

C$_5$H$_{11}$ ⬡—⬡—CN

5CB

CHART 2

⬡—⬡—CN

A

⬡—⬡—F

B

⬡—⬡

C

⬡—⬡

D

⬡—≡—⬡

E

⬡—C(=O)—O—⬡

F

⬡—⬡

G

⬡—CF₂—⬡

H

⬡—O—⬡

I

⬡—CF₂—O—⬡

J

Figure 1. Three optimized geometries for cyanobiphenyl dimer (**A**): **A-1**, antiparallel; **A-2**, parallel; and **A-3**, head-to-tail orientations.

TABLE 1: Intermolecular Interaction Energies [kcal/mol] for the Dimers of Cyanobiphenyl (A) and Fluorobiphenyl (B)[a]

	HF	MP2	ΔE[b]
A-1	6.22	−6.61	−12.83
A-2	8.03	−4.35	−12.38
A-3	−1.41	−1.94	−0.53
B-1	6.81	−4.69	−11.50
B-2	5.77	−4.08	−9.85
B-3	−0.35	−0.73	−0.38

[a] The 6-31G(d) basis set was used. [b] ΔE is the difference between the HF and MP2 interaction energies and is regarded as the dispersion energy.

Figure 2. Potential energy curves for cyanobiphenyl dimer (**A**) as a function of the distances between the center-of-masses of the monomers: HF, HF/6-31G(d) level of theory; and MP2, MP2/6-31G(d) level of theory.

lecular interaction energies. These analyses provide useful suggestions in order to understand the nature of the interaction in LC compounds and to design new core structures for better LC compounds.

2. Methods of Calculation and Experiment

The chemical structures of 10 dimers, illustrated in Chart 2, were fully optimized at the MP2/6-31G(d) level of theory.[24,25] The interaction energies were obtained by using a counterpoise method[26] in order to remove the basis-set superposition error (BSSE).[27] All calculations were performed with the GAMESS[28] and Gaussian 98[29] packages of program codes.

The rotational viscosities were measured in the temperature range of 20−95 °C, using the TVE-20L digital viscometer manufactured by TOKI SANGYO Co., Ltd. The standard liquids for calibrating viscometers were used to correct the absolute values of the viscosities.

3. Results and Discussion

3.1. Cyanobiphenyl Dimer (A). Since 4-*n*-pentyl-4-cyanobiphenyl (**5CB**) is one of the typical core parts of LC compounds exhibiting nematic phases,[30] the interaction between two cyanobiphenyl molecules (**A**) is analyzed at the MP2/6-31G(d) level of theory. Three energy minima are located for **A**, and their geometrical structures are illustrated in Figure 1. Although the dihedral angle of each intramolecular phenyl ring is about 40°, both phenyl rings are at the face-to-face position in **A-1** and **A-2**. Only the direction of the molecular rings is different in these structures. The reason **A-3** is an energy minimum is that it is stabilized by a hydrogen bond between the nitrogen atom of the cyano group and the hydrogen atom of the phenyl ring. Table 1 summarizes the interaction energies obtained by the HF and MP2 methods, and Figure 2 plots the potential energy curves as a function of the distance R between the center-of-masses of the single molecules. The most stable structure **A-1**
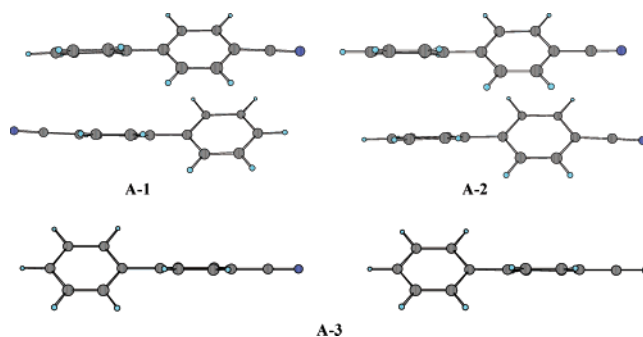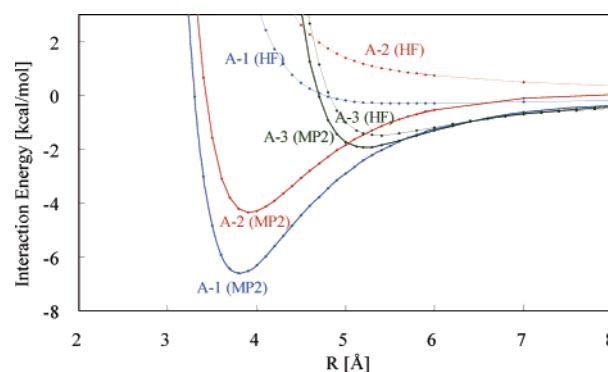
has a face-to-face antiparallel orientation. It is easy to understand the reason **A-1** and **A-2** are more stable than **A-3**; the face-to-face orientation of the phenyl rings produces a larger attractive dispersion energy (E_{disp}) in **A-1** and **A-2**, rather than that in **A-3**. The electrostatic attraction energy (E_{es}) in **A-1** is more effective than that in **A-2**, since the antiparallel orientation of the molecular rings provides a more effective dipole−dipole attraction. Additionally, the exchange−repulsion (E_{rep}) and repulsive quadrupole−quadrupole interactions become less effective because of its slipped-antiparallel phenyl orientation. This is supported by the fact that benzene dimer has a slipped-parallel structure possessing a small quadrupole−quadrupole repulsive E_{es} and large E_{disp}.[22,23]

It should be noted that the HF method significantly underestimates the interaction energies because the dispersion energy is not included within this approximation, and as a result, the energy minima of the dimers are estimated to be rather shallow. The dispersion energy (E_{disp}) in such dimers can be estimated by the counterpoise method[26] by using the HF and MP2

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energies for the monomers and dimers:

$$E_{disp} = E_{int(HF+MP2)} - E_{int(HF)}$$

(counterpoise corrected values)

where E_{int} is the total interaction energy obtained with the HF and HF+MP2 methods, respectively. This is usually called the "correlation term" in the expansion series of the intermolecular interaction energy, and is frequently employed in the analyses of intermolecular potential energy surfaces.[15,23,31,32] Therefore, we decided that the MP2 method should be employed in the present investigation.

The dispersion energy in **A-1** is estimated to be −12.8 kcal/mol at the MP2 level of theory. As a result, the depth of the energy minimum is −6.6 kcal/mol, while the HF method estimates only −0.3 kcal/mol at $R = 5.6$ Å. Thus, it is very important and necessary to include the correlation effects in order to consider the contribution of the dispersion energy in the discussion of intermolecular interactions.

The next stable **A-2** has a parallel orientation of the molecular rings (Figure 1). As shown in Figure 2, the HF energy curve for **A-2** does not have an energy minimum, while that for **A-1** has a shallow minimum (a depth of −0.3 kcal/mol). These results indicate that **A-2** has a larger repulsive E_{es} because of its geometrical orientation and, as a result, **A-2** is less stable than **A-1**. It is noted that the differences between the HF and MP2 curves are similar for both structures, which means that E_{disp} is compatible in these two structures (Table 1).

The head-to-tail structure of **A-3** is shown in Figure 1, and the interaction potential energy curves are plotted in Figure 2. The difference in the potential shapes between the HF and MP2 curves is rather small. In other words, the dispersion force is less effective (only −0.5 kcal/mol at most). Both the HF and the MP2 curves have a well-defined energy minimum (−1.5 (HF) and −1.9 (MP2) kcal/mol) caused by the strong dipole−dipole interaction (E_{es}). Since the dispersion energy rapidly disappears as R becomes long, the two energy curves are almost overlapped in the range of $R > 6.6$ Å. This is because the dispersion energy and dipole−dipole energy are proportional to R^{-6} and R^{-3}, respectively.[33]

On the basis of a multiple quantum NMR study, the dihedral angle of the biphenyl moiety of **5CB** in the nematic phase is estimated to be about 32°.[34] In the present study, the dihedral angle is calculated to be 41° for **A-1**, and is overestimated by 9°. Our result is very close to that observed in the gas phase.[35] In general, the potential energy curve along such an angle is very flat, since it is determined by the sensitive balance between the stabilization of the inter-ring π conjugation and the steric repulsion between the 2,2′- and 6,6′-hydrogen atoms.[36] Since it is also well-known that the aggregation induces a stronger conjugation between the phenyl rings,[37−39] it might be natural to obtain a larger angle in the present study in comparison with that observed in the nematic phase.

3.2. Structures and Interaction Energies of Fluorobiphenyl Dimer (B). The interaction energies were also calculated for the fluorobiphenyl dimer (**B**) in order to understand the substituent effects. Similar to the parent system **A**, three structures are located as energy minima, and the face-to-face structure (**B-1**) is the most stable. The interaction energy in **B-1** is estimated to be −4.7 kcal/mol, and is 1.9 kcal/mol smaller than that for **A-1** (Table 1). E_{disp} in **B-1** is smaller than that in **A-2** by 1.3 kcal/mol, because the number of π electrons in **B** is smaller than that in **A**. It should be noted that the single molecule in **B** has the dipole moment of 1.98 D at the MP2/6-31G(d)

TABLE 2: Intermolecular Interaction Energies [kcal/mol] for the Dimers of Phenylcyclohexane (C), Biphenyl (D), and Tolane (E)[a]

	HF	MP2	ΔE
C	3.86	−1.74	−5.60
D	6.66	−3.41	−10.08
E	6.89	−4.29	−11.18
F	3.35	−6.66	−10.00

[a] See Table 1.

level of theory, while a large dipole moment (5.68 D) is obtained for the single molecule in **A**. Therefore, it can be concluded that the interaction energy in **B-1** is smaller than that in **A-1** because of this large difference in the dipole moment as well as the difference in E_{disp} of the single molecules.

3.3. Intermolecular Interaction Energies of Mesogenic Core Structures. The intermolecular interaction energies are also analyzed in the dimers **C**, **D**, **E**, and **F** of phenylcyclohexane, biphenyl, tolane, and phenylbenzoate, where these are often employed as mesogenic core parts of the applicable LC compounds.[8,40,41] Even if several structures could be found as energy minima for these dimers, we decided that only an antiparallel structure similar to **A-1** and **B-1** is used for each dimer, since this structure is expected to be a global minimum.

Table 2 lists the MP2 interaction energies in **C**, **D**, **E**, and **F**. The reason **C** has the smallest interaction energy is caused by the small number of π electrons and by the steric repulsions between the bulky cyclohexyl rings. Because the single molecule in **F** has a large dipole moment (2.53 D), a large E_{es} is obtained for **F** when compared to the other dimers. This is the reason **F** has the largest interaction energy. It is noteworthy that E_{disp} plays a dominant role in determining the stability of the three hydrocarbon systems **C**, **D**, and **E**.

3.4. Relationship between Interaction Energies and Viscosities. The viscosity of the LC compounds is one of the key properties in determining the switching times as a display monitor.[42−44] However, it is still difficult to predict such macroscopic observables in the field of quantum chemistry. For several rodlike LC compounds, a linear relationship has been reported[45] between the viscosity and intermolecular interaction. In this section, we examine the relationship between the interaction energy in the present dimers and the viscosity of the corresponding LC compounds experimentally measured in our laboratory.

It is easy to guess that, if a dimer has weak intermolecular interaction, the corresponding LC compound has a low viscosity. In fact, our calculated results showing that **A-1** has a larger interaction energy than **B-1** are consistent with the fact that the LC compounds possessing fluoro substituents have a relatively low viscosity,[8,41,46] although the n-alkyl groups are replaced by a hydrogen atom in our computations. Since no useful experimental measurement of the viscosity was found for **C**, **D**, **E**, and **F** under the same conditions, we decided that the experimental measurements should be carried out on the viscosities of the corresponding compounds. According to our experimental measurements, **C**, **D**, **E**, and **F** have viscosities of 0.93, 1.25, 1.66, and 2.37 mPa·s at 75 °C, respectively. As **C**, **D**, **E**, and **F** have the interaction energies of −1.7, −3.4, −4.3, and −6.7 kcal/mol (see Table 2), respectively, some kind of relationship exists between the interaction energies in dimers and the viscosities in the liquids consisting of the corresponding LC compounds.

3.5. Effects of Flexible Linkages. In this section, we analyze the effects of the more flexible linkages, Ph−CX$_2$CH$_2$−Ph and Ph−CX$_2$O−Ph, in the mesogenic core part, where X was either
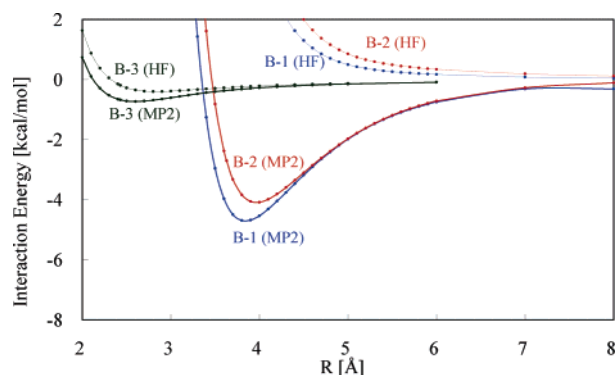
Figure 3. Potential energy curves for fluorobiphenyl dimer (**B**). See Figure 2.
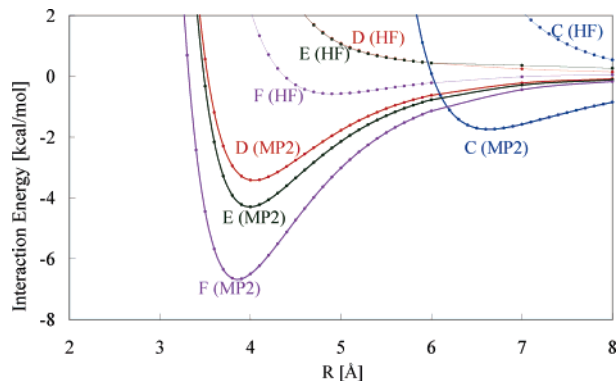

Figure 4. Potential energy curves for the dimers of phenylcyclohexane (**C**), biphenyl (**D**), tolane (**E**), and phenylbenzoate (**F**). See Figure 2.
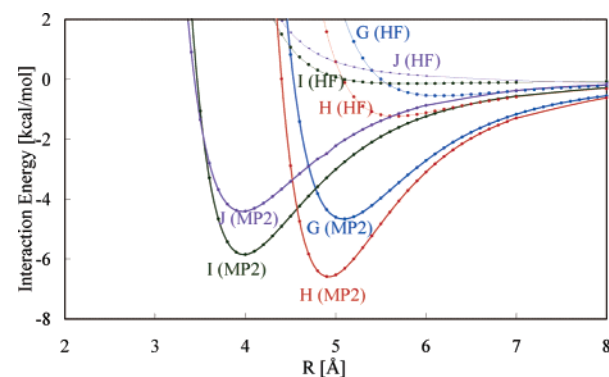

Figure 5. Potential energy curves for the dimers of bibenzyl (**G**), 1,1-difluoro-1,2-diphenylethane (**H**), benzyl phenyl ether (**I**), and difluorophenoxymethylbenzene (**J**). See Figure 2.

a fluorine or hydrogen atom,[8,9,46] instead of a direct linkage between the two phenyl rings. No intramolecular π conjugation would be observed between the phenyl rings connected by such linkages, therefore, we can discuss only the effects of geometrical orientation of the mesogenic core structures when the biphenyl dimer **D** is used as a reference system.

Figures 6−8 illustrate the optimized geometries of the dimers **G**, **H**, **I**, and **J**, in which the single molecules are bibenzyl, 1,1-difluoro-1,2-diphenylethane, benzyl phenyl ether, and difluorophenoxymethylbenzene, respectively. An energy minimum appears at $R = 5.1$ Å in **G**, while the biphenyl dimer (**D**) has an energy minimum at $R = 4.0$ Å. This is because the long and flexible linkage in **G** generates a steric repulsion between the monomers. Nevertheless, the interaction energy in **G** is 1.3 kcal/mol larger than that in **D**, and this is supported by the experimental measurement that the viscosity (1.41 mPa·s) of **G** is slightly higher than that of **D** (1.25 m·Pa·s) at 75 °C. The
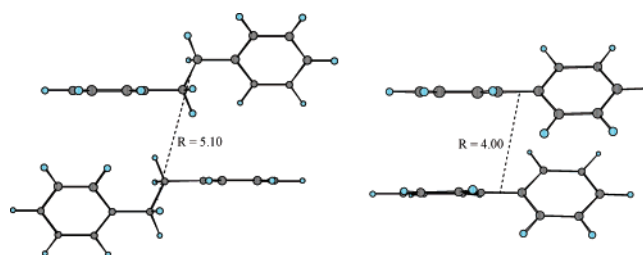

Figure 6. Bibenzyl dimer (**G**) (left) and biphenyl dimer (**D**) (right). R [Å] is the distance between the center-of-masses of the monomers.
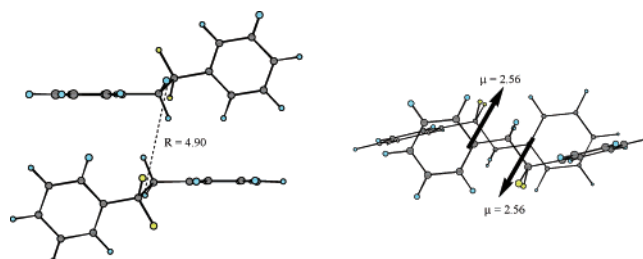

Figure 7. 1,1-Difluoro-1,2-diphenylethane dimer (**H**). See Figure 6. μ [Debye] is the dipole moment of the monomers.
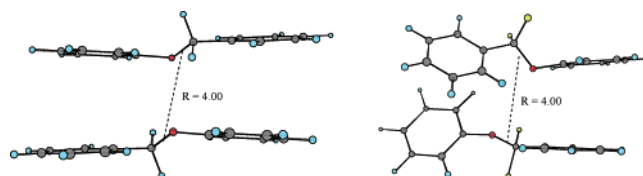

Figure 8. Benzylphenyl ether dimer (**I**) (left) and difluorophenoxymethylbenzene dimer (**J**) (right). See Figure 6.

TABLE 3: Intermolecular Interaction Energies [kcal/mol] for the Dimers of Bibenzyl (G), 1,1-Difluoro-1,2-diphenylethane (H), Benzyl Phenyl Ether (I), and Difluorophenoxymethylbenzene (J)[a]

	HF	MP2	ΔE
G	2.02	−4.66	−6.68
H	1.59	−6.59	−8.18
I	5.07	−5.85	−10.92
J	4.85	−4.40	−9.25

[a] See Table 1.

fact that **G** has an energy minimum at the longer R but a deeper energy minimum can be explained by the difference in their geometrical structures: **G** has a T-shaped orientation of phenyl rings on both sides because of its flexible linkage, while **D** has an antiparallel orientation. Therefore, **G** has a larger attractive E_{es} (quadrupole−quadrupole interaction), which produces a larger interaction energy in comparison with **D**. A lower viscosity and higher dielectric anisotropy ($\Delta\epsilon$) are generally required for better LC compounds.[8] It is already known that the introduction of fluoro substituents is the most effective method for this purpose. In fact, a lower viscosity (1.42 mPa·s) is observed for **J** rather than for **I** (1.59 mPa·s), and the interaction energy in the former was calculated to be 1.5 kcal/mol smaller than that in the latter.

On the contrary, even though fluorine atoms are present in **H**, it has a higher viscosity (2.25 at mPa·s), in comparison with **G** (1.41 mPa·s), and the interaction energy for **H** is larger than that for **G** by 1.9 kcal/mol. This reverse tendency can be explained by the difference in the geometrical structures: the steric hindrance of the ethylene linkage makes R much longer and leads to a T-shaped structures for both **G** and **H**. Addition-
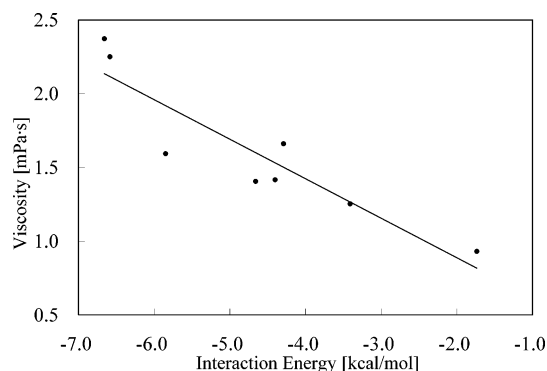
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Figure 9. Relationship between interaction energies and viscosities. The correlation coefficient is calculated to be 0.84.

ally, a larger E_{es} is obtained for the antiparallel structure of **H** (Figure 7), because the single molecule in **H** has a relatively large dipole moment (2.56 D) in contrast to the fact that an almost zero dipole moment is obtained for the single molecule in **G**.

Figure 9 plots the viscosities of compounds having mesogenic core structures of nematic LC versus the interaction energies in the corresponding dimers. The viscosities have been measured at 75 °C, where all of these compounds are in the liquid phase. The interaction energies are calculated for simple dimers corresponding to the LC compounds. As shown by the solid line in Figure 9, a linear relationship can be said to exist between the viscosities and interaction energies.

Since a stricter behavior has recently been requested for compounds in active matrix LC displays (AM-LCDs),[8,41,46] the mixtures of LC compounds are usually used in industrial processes in order to totally satisfy the various kinds of properties, such as viscosity, birefringence (Δn), and dielectric anisotropy ($\Delta \epsilon$), as LC compounds. For example, because phenylcyclohexane (**C**) has the lowest viscosity among the present compounds, this molecule is frequently mixed with other LC compounds in order to improve the response time of the LC displays. In addition, even though the compounds possessing difluoromethyleneoxy (**J**) as a core structure have the next lowest viscosity among the present compounds, **J** is considered to be one of the better core structures. This is because such compounds have a high dielectric anisotropy ($\Delta \epsilon$) and lower viscosity than **F**, **H**, and **I**, where $\Delta \epsilon$ is also high in **F**, **H**, and **I**. Note that the high $\Delta \epsilon$ means that the lower driving voltage and low viscosity produces shorter response times.[8,9,46] This fact suggests that it is very important for LC compounds to have well-balanced properties in AM-LCDs.

Vuks[12] and Maier and Meier[13] proposed theories in which $\Delta \epsilon$ and Δn can be calculated using molecular dipole moments and polarizabilities. It is rather easy to calculate such molecular dipole moments and polarizabilities with molecular orbital theories, so that their theories have been widely applied in the studies[8,14,16] for the design of new LC compounds. Therefore, based on the present results, we propose that when a new LC compound is designed, the interaction energy between the corresponding LC molecules should be estimated, in addition to the computation of the molecular dipole moments and polarizabilities. We can then analyze whether the LC compound has well-balanced properties of viscosity, as well as birefringence (Δn) and dielectric anisotropy ($\Delta \epsilon$).

4. Conclusion

The interaction energies are theoretically calculated for 10 dimers at the MP2/6-31G(d) level of theory. These dimers are

typical core parts of LC compounds. When an energy minimum has a parallel-displaced structure for phenyl rings, the dispersion energy plays a dominant role in the total interaction energy. On the other hand, when phenyl rings are oriented in a T-shaped structure, the dimer has a large electrostatic energy caused by a strong quadrupole−quadrupole attractive interaction, and as a result, its interaction energy is not very small as we have expected.

The viscosities of eight compounds possessing typical mesogenic core structures were also experimentally measured. The present study found an explicit linear relationship between the viscosities of the compounds and the interaction energies in the corresponding dimers. We believe that it is very useful to estimate the interaction energy in the newly designed dimers of LC compounds before their experimental synthesis.

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