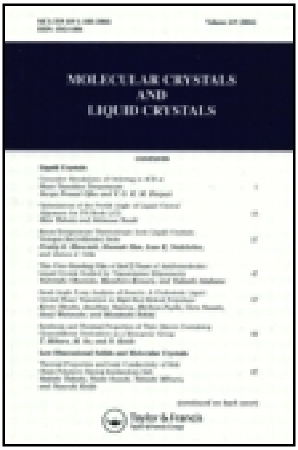

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Computer Simulation of Biphenyl-Phenyl Ester Liquid Crystals

Masafumi Yoshida [a] , Noriko Seo [b] , Kayako Hori [b] & Hirokazu Toriumi [c]

[a] Musashi Institute of Technology, Tamazutsumi 1-29-1, Setagaya-ku, Tokyo, 158-8557, Japan

[b] Graduate school of Humanities and Sciences, Ochanomizu University, Otsuka 2-1-1, Bunkyo-ku, Tokyo, 112-8610, Japan

[c] Graduate school of Arts and Sciences, The University of Tokyo, Komaba 3-8-1, Meguro-ku, Tokyo, 153-8902, Japan

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Computer Simulation of Biphenyl-Phenyl Ester Liquid Crystals

MASAFUMI YOSHIDA[a], NORIKO SEO[b], KAYAKO HORI[b] and HIROKAZU TORIUMI[c]

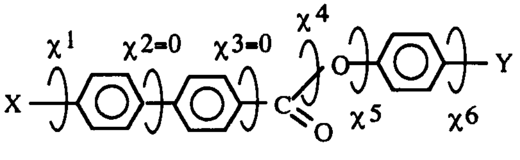
[a]*Musashi Institute of Technology, Tamazutsumi 1–29–1, Setagaya-ku, Tokyo 158–8557, Japan,* [b]*Graduate school of Humanities and Sciences, Ochanomizu University, Otsuka 2–1–1, Bunkyo-ku, Tokyo 112–8610, Japan and* [c]*Graduate school of Arts and Sciences, The University of Tokyo, Komaba 3–8–1, Meguro-ku, Tokyo 153–8902, Japan*

Molecular orbital (MO) calculation and molecular dynamics (MD) simulation were carried out for a set of smectic liquid crystalline molecules, 8O-O8 (4-octyloxyphenyl-4′-octyloxybiphenyl-4-carboxylate) and 8O-8 (4-octylphenyl-4′-octyloxybiphenyl-4-carboxylate), to understand the molecular origin of different crystalline structure formation and to predict their conformational property in liquid crystalline phases. The results of MO and MD analyses indicate that the structure of 8O-O8 and 8O-8 in crystalline phase is essentially determined by intramolecular interactions and the experimentally observed structure is chosen as a consequence of intermolecular packing constraints. This paper also reports the first application of two-molecular ab-initio calculation to liquid crystalline systems.

Keywords: molecular orbital calculation; molecular dynamics simulation; smectic liquid crystals; conformation; packing

INTRODUCTION

A biphenyl-phenyl ester group, -C_6H_4-C_6H_4-COO-C_6H_4-, is one of the most common structural constituents of smectic liquid crystalline molecules. A number of ferro- and antiferro-electric liquid crystalline molecules have been synthesized choosing this moiety as a mesogenic core group. For example, a well-known antiferroelectric compound MHPOBC, which has a chiral alkyl chain at one end of the core moiety, belongs to this series of compounds. The biphenyl-phenyl ester group can thus be regarded as an important structural prerequisite for the smectic phase formation, and therefore it is critically important to analyze its detailed conformational characteristics toward the full molecular understanding of the origin of smectic phase formation.



8O-O8	8O-8	MHPOBC
$X = OC_8H_{17}$	$X = OC_8H_{17}$	$X = OC_8H_{17}$
$Y = OC_8H_{17}$	$Y = C_8H_{17}$	$Y = COOC^*HCH_3C_6H_{13}$

FIGURE 1 Chemical structure of biphenyl-phenyl liquid crystals.

In recent studies, Seo and Hori [1] have carried out a single-crystal X-ray study of biphenyl-phenyl ester liquid crystals with normal alkyl (alkoxy) chains and found that they show various crystal modifications depending on the structure of terminal alkyl chains. Among them, the conformational and packing property observed for 8O-O8 (4-octyloxy-phenyl-4'-octyloxy-biphenyl-4-carboxylate) and 8O-8 (4-octylphenyl-4'-octyloxybiphenyl-4-carboxylate) is particularly interesting. Although these two compounds differ from each other only in the chemical structure of the substituting end chain Y (Figure 1), they exhibit distinctly different conformations in crystal structures. That is, in Figure 2, the octyloxy chain Y of 8O-O8 is oriented nearly parallel to the chain X and the molecule adopts an elongated shape, while the octyl chain of 8O-8 is oriented at an angle with respect to the phenyl-ring plane and thus the molecular conformation is distorted into a bent shape.

In our previous studies [2,3], we have developed a series of computational schemes for the conformational analysis of an antiferroelectric MHPOBC molecule in its smectic phases, including molecular orbital (MO) calculation and molecular dynamics (MD) simulation. These studies have shown (1) based on the MO calculations that the MHPOBC conformation observed in the crystalline phase [4] is one of the quasistable conformations and is stabilized by the packing effect and (2) based on the MD simulations that this quasistable conformation is maintained in crystalline and low-temperature smectic phases, but would transform into more stable elongated conformations in higher-temperature smectic phases [3].

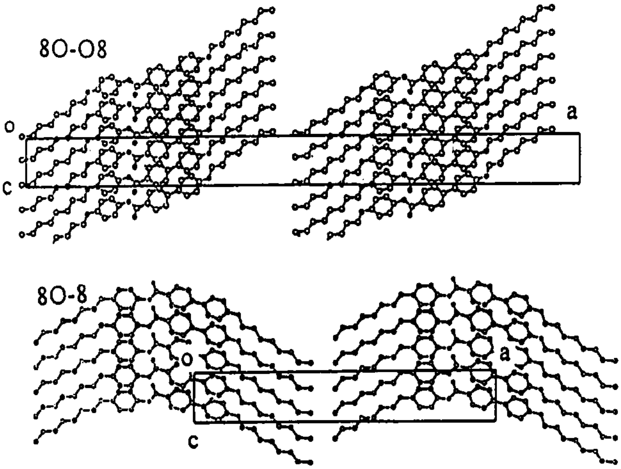


FIGURE 2 Crystal structure of 8O-O8 and 8O-8 observed by single crystal X-ray analysis.

In both crystalline and smectic liquid crystalline phases, intermolecular electrostatic and dispersion energy would be expected to compete with intramolecular conformational energy. That is, the molecular packing is determined by a quantitative balance between intramolecular and intermolecular interactions. Thus, in this study we expand our previous study and calculate the conformational and packing energies of 8O-O8 and 8O-8 to understand the microscopic origin of the formation of experimentally observed crystal packing structures. For this purpose, we first carry out single-molecule MO calculations for 8O-O8 and 8O-8 and then perform MD simulations to examine the effect of packing constraints on their conformational property. The results obtained in this study indicate that the molecular conformation of 8O-O8 and 8O-8 in crystalline phase is the one that is selected from several possible conformations with essentially the same energy (this energy is primary determined by intramolecular interactions, particularly those associated with the torsion potential about the core-alkyl linkage group) as a consequence of crystal packing effects. The coexistence of low energy conformations should then indicate that the 8O-O8 and 8O-8 molecules in high-temperature smectic phases would assume a number of possible conformations and therefore posses a considerable conformational flexibility.

CALCULATION

MO Calculation

The semiempirical molecular orbital calculation (MOPAC97, AM1, PM3) was carried out for 8O-O8 and 8O-8 on a SUN workstation. For simplicity, the bond lengths and the bond angles were fixed to the standard values. According to the X-ray analysis of a series of biphenyl-phenyl ester mesogens [11], the biphenyl ester core (C_6H_4-C_6H_4-COO) was assumed to be in a plane configuration and the octyl and octyloxy chains were fixed at the *trans* conformation. The intramolecular conformational energy, which corresponds to the heat of formation in MOPAC, was calculated for 1.8×10^5 conformers with varying the torsion angles $\chi 1$, $\chi 4$-$\chi 6$ (Figure 1) at every 15° intervals. The $\chi 1$, $\chi 4$-$\chi 6$ distribution curves were then calculated by assuming the Boltzmann distribution at 298K.

MD Simulation

The molecular dynamics (MD) simulation was carried out for a system of 1024 molecules on a HITACHI SR2201 parallel computer. The simulation cell was approximately 7 nm × 12 nm × 10 nm. The size effect was confirmed to be negligibly small though the periodic boundary condition was not imposed. The intermolecular energy U was defined as a sum of the pair-wise Coulombic and Lennard-Jones potentials between all united atoms,

$$U = \sum_{i>j} \sum_{i_m \in i,\, j_n \in j} \frac{q_{i_m} q_{j_n}}{4\pi\varepsilon_0 r_{i_m j_n}} + \left(\frac{A_{i_m j_n}}{r^{12}_{i_m j_n}} - \frac{B_{i_m j_n}}{r^{6}_{i_m j_n}} \right)$$

where i_m is m-th atom of i-th molecule, and q_{i_m} is its partial charge obtained from MO calculations (Gaussian94/RHF/6-31G(d,p)) for the corresponding conformation. The Lennard Jones parameters, A_{i_m, j_n} and B_{i_m, j_n}, were set to the OPLS values [5] which have been widely used in the MD simulation of organic compounds.

RESULTS AND DISCUSSION

MO Calculations

The rotamer distribution functions P(χi) (i = 1, 4-6) calculated for 1.8 × 10^5 conformers of 8O-O8 are shown in Figure 3-a together with the stable rotamer positions taken from the X-ray data. The $\chi 1$ rotamer distribution curve shows that the alkoxy chain X is in a plane position with respect to the biphenyl group and the $\chi 4$ and $\chi 5$ curves show that the phenyl group is twisted nearly perpendicular to the biphenyl ester plane. The $\chi 6$ rotamer distribution curve shows that the alkoxy chain Y is in plane of the adjacent phenyl group. In Figure 3-a, all the X-ray data coincide with the peaks of the distribution curves obtained by the MO calculation. This result should indicate that the molecular conformation in crystalline phase is not distorted from the stable conformation. In other words, the packing effect is not so large to change the molecular shape. The most stable conformation of 8O-O8 that corresponds to the X-ray data is illustrated in Figure 4.

The corresponding P(χi) curves calculated for 8O-8 are shown in Figure 3-b. The shape of the $\chi 1$, $\chi 4$, and $\chi 5$ distribution curves is essentially the same as that calculated for 8O-O8 in Figure 3-a. The only major difference is found in the $\chi 6$ distribution curve, where the peak located at $\chi 6 = 90^\circ$ indicates that the octyl chain Y is twisted nearly perpendicular to the adjacent phenyl group (see Figure 4). In both Figures 3-a and 3-b, calculations using the AM1 (○) and PM3 (●) parameters give slightly different $P(\chi i)$ distribution curves. This minor difference may arise from the fact that the PM3 parameters tend to overestimate the repulsive interactions between non-bonded hydrogen atoms, as is often reported. Generally, the results obtained using the AM1 parameters give a better agreement with experimental observations as seen in Figures 3-a and 3-b. The most stable structure of 8O-8 that corresponds to the X-ray data is illustrated in Figure 4 and compared with that of 8O-O8.

Here it should be noted that, because of the symmetry of the calculated $P(\chi i)$ distribution curves, both the 8O-O8 and 8O-8 molecules

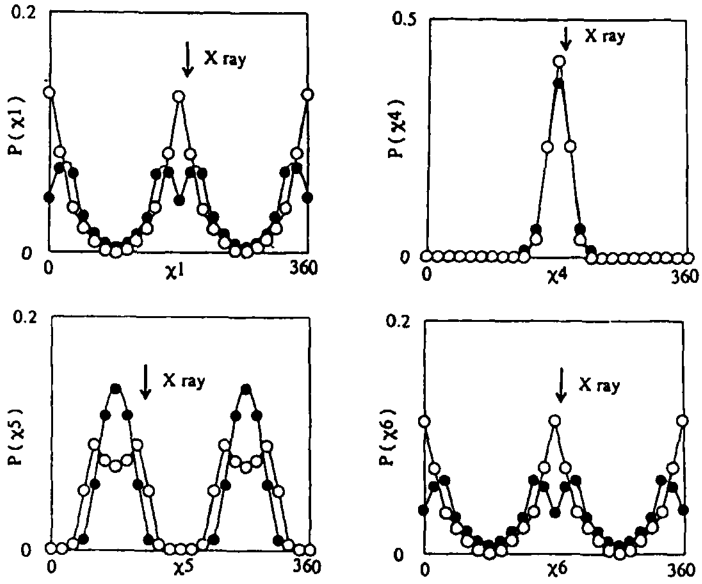


FIGURE 3-a Rotamer distribution curves $P(\chi i)$ for an isolated 8O-O8 molecule calculated by semiempirical MO, ○:AM1, ●: PM3.

can assume four different conformations with the same energy but with different shapes. Namely, for 8O-O8, the following four conformations are possible: A ($\chi1=0^\circ$, $\chi6=0^\circ$), B ($\chi1=0^\circ$, $\chi6=180^\circ$), C ($\chi1=180^\circ$, $\chi6=0^\circ$), D ($\chi1=180^\circ$, $\chi6=180^\circ$), with $\chi4=180^\circ$ and $\chi5=90^\circ$. Similarly, the 8O-8 molecule can assume the following four conformations: E ($\chi1=0^\circ$, $\chi6=90^\circ$), F ($\chi1=0^\circ$, $\chi6=270^\circ$), G ($\chi1=180^\circ$, $\chi6=90^\circ$), and H ($\chi1=180^\circ$, $\chi6=270^\circ$), with $\chi4=180^\circ$ and $\chi5=90^\circ$. The energy difference among these four conformers calculated for 8O-O8 and 8O-8 was found to be smaller than 0.1 kcal/mol.

Thus, it appears that the observed conformation shown in Figure 4 is not necessary the most stable conformation among the four possible candidates, but it is selected by the intermolecular packing effect. This point will be discussed in some more details in the next section. But, before closing this section, we would like to add some words about the

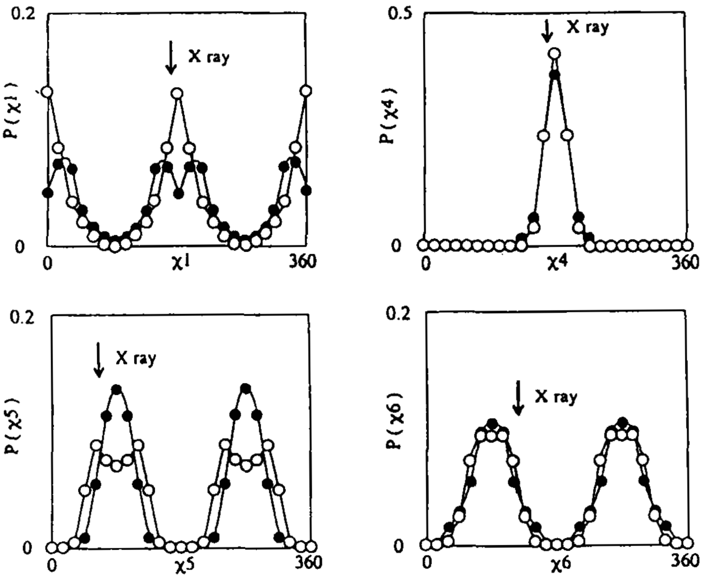


FIGURE 3-b Rotamer distribution curves P(χi) for an isolated 8O-8 molecule calculated by semiempirical MO, ○:AM1, ●: PM3.

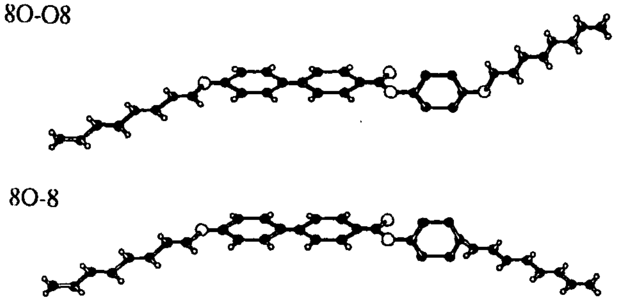


FIGURE 4 The most stable conformers of 8O-O8 and 8O-8 which correspond to the X-ray data.

nature of the two experimentally observed conformations in Figure 4. The most important point to note is that, among the four torsion angles χi discussed in Figure 3, only the $\chi 6$ value has practical importance in determining the overall molecular shape of 8O-O8 (elongated) and 8O-8 (bent) observed in crystalline phases. It should be evident that the ester C-O bond ($\chi 4$) has no conformational freedom and that the simultaneous $\chi 5$-$\chi 6$ rotation causes only the flip-flop rotation of the phenyl ring. Moreover, the P($\chi 1$) curve has the same angular distribution for 8O-O8 and 8O-8, both having the same octyloxy terminal chain. Thus, as seen in Figures 4, the chemical difference between 8O-O8 and 8O-8 is solely reflected into the $\chi 6$ torsion angle. The preferred $\chi 6 = 180^\circ$ (or 0°) angle results in the elongated molecular structure of 8O-O8 and the $\chi 6 = 90^\circ$ angle generates the bent structure of 8O-8. Nevertheless, as stated above, the energy difference between the experimentally observed conformation and other three possible conformations is smaller than 0.1 kcal/mol. This fact indicates that both 8O-O8 and 8O-8 in smectic phases should assume all these possible conformations, and thereby possessing a considerable conformational flexibility.

MD Simulation

The result of MO calculations given in Figure 3-a and 3-b has shown that the crystalline phase conformation of 8O-O8 and 8O-8 is chosen from four possible conformations by the intermolecular packing effect. The most honest tactics to discuss this selection mechanism is to perform the MD simulation for each of these four possible conformations or, alternatively, in the entire conformational space and calculate a contour map of intermolecular potential as a function of all the molecular configurations. Unfortunately, however, this calculation requires enormous computation time even if we use the most advanced supercomputer available today. Moreover, we have no information about the packing structure for the conformers other than that experimentally observed. Thus, the only possible approach that has certain physical meaning is to estimate the magnitudes of intra- and inter-molecular energies that would contribute to the stabilization of the observed crystalline structure by, for example, placing the 8O-O8 molecules in a hypothetical packing lattice that mimics the 8O-8 packing structure. MD simulation along this line was performed using the simulation cells shown in Figure 5. Here, the Cryst I and Cryst II correspond to the experimentally observed 8O-O8 and 8O-8 structures. The Cryst I' is an imaginary crystal of 8O-O8 where the conformation of the 8O-O8 molecule is distorted to the bent conformation that is observed for the

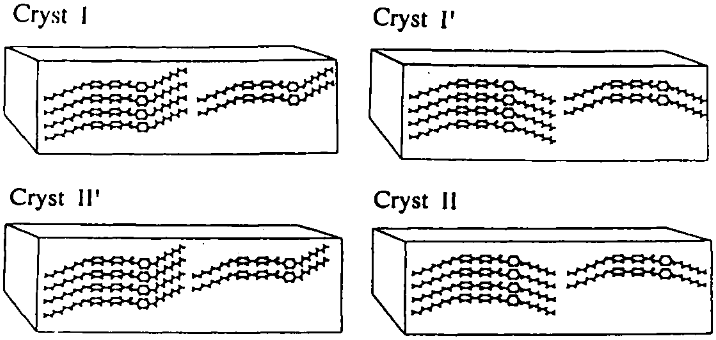


FIGURE 5 MD simulation systems. Cryst I and Cryst II represent the experimentally observed 8O-O8 and 8O-8 crystals. Cryst I' is an imaginary 8O-O8 crystal where the molecules are forced to the bent conformation; Cryst II' is an imaginary 8O-8 crystal where the molecules are forced to the elongated conformation.

8O-8 molecule. Similarly, the Cryst II' represents an imaginary 8O-8 crystal composed of the 8O-8 molecules forced to the elongated conformation that is observed for the 8O-O8 molecule. The intermolecular packing energies thus calculated for the two real (I and II) and the two imaginary (I' and II') crystals are summarized in Table I together with their intramolecular conformational energies (the values of partial charges were optimized by using an ab-initio program (Gaussian94/RHF/6-31G(d.p)) for the X-ray observed structures, i,e., Cryst I and II).

TABLE I Intermolecular and intramolecular energies of the four systems in Figure 5 obtained from MD and MO (Gaussian94/RHF/6-31G(d,p)) calculations.

(kcal/mol)	8O-O8 type packing	8O-8 type packing
8O-O8	Cryst I	Cryst I'
Intermolecular energy	- 59.12	- 59.41
Intramolecular energy	0.0	+ 0.46
Total	- 59.12	- 58.95
8O-8	Cryst II'	Cryst II
Intermolecular energy	- 56.84	- 58.38
Intramolecular energy	+ 5.04	0.0
Total	- 51.80	- 58.38

First, it should be noted, for 8O-8, that both intra- and and inter-molecular energies are lower in real structure (Cryst II) than in imaginary structure (Cryst II'). This result may indicate that, for molecules with bent structure, a chevron-type packing is more favored than a linear packing (to make more precise discussion we need to repeat similar MD simulations for bent molecules in a lattice with, for example, inverse chevron structure, chain intercalation, and so on). On the other hand, it is a little surprise to find that the packing energy of the 8O-O8 molecule is slightly higher in observed structure (Cryst I) than in imaginary structure (Cryst I'). Nevertheless, the total energy of Cryst I is lower than that of Cryst I' in agreement with experimental observations. This result implies that the excess of intermolecular packing energy can be compensated by intramolecular energy which is low for an elongated conformation. Again, we should note here that all these considerations, although they provide certain clue to understand the relative importance of intra- and inter-molecular interactions, are still suffering the effect of the artificialness of model simulation cell. Anticipating further development of MD engines, we may try a full optimization of the crystal packing structure of 8O-O8 and 8O-8.

Energy Partition in MO Calculations

We pointed out in a previous section that the primary difference in conformational property of 8O-O8 and 8O-8 is found in $\chi6$. That is, the octyloxy chain of 8O-O8 is in a plane of the adjacent phenyl group ($\chi6 = 0^\circ$), while the octyl chain of 8O-8 is oriented perpendicular to the adjacent phenyl group ($\chi6 = 90^\circ$). A quantum chemical origin of this difference may be discussed based on the results of MO calculations. In Figure 6 we plot the two energy components calculated by MO, i.e., the resonance energy and the steric hindrance (electrostatic) energy, as a function of the $\chi6$ torsion angle. It is clear that the resonance energy has a minimum value at $\chi6 = 0^\circ$ (in-plane conformation) for both 8O-O8 and 8O-8. The steric hindrance energy shows a similar angular dependence,

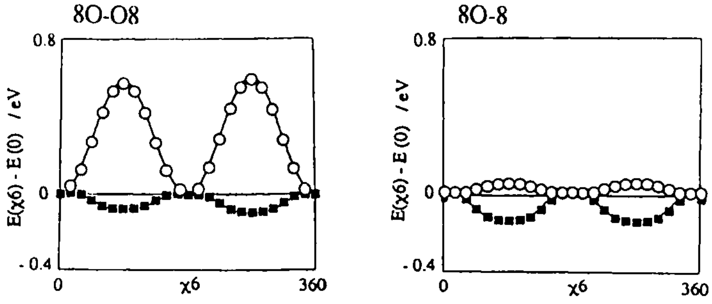


FIGURE 6 The $\chi6$ dependence of the resonance energy (○) and the electrostatic energy (■) calculated by semiempirical MO (AM1).

but its sign is negative in the entire $\chi 6$ region. Note here that the steric hindrance energy has essentially the same magnitude for both 8O-O8 and 8O-8, while the resonance energy of 8O-O8 shows a significantly large oscillation. Thus, the total energy (resonance energy + steric hindrance energy) has its minimum value at $\chi 6 = 0^\circ$ for 8O-O8 and at $\chi 6 = 90^\circ$ for 8O-8. This is the reason why the octyloxy chain of 8O-O8 is oriented to the in-plane direction relative to the phenyl plane, while the octyl chain of 8O-8 is oriented nearly perpendicular to the ring group. It should be noted that this discussion is not limited to 8O-O8 and 8O-8, but applies to all mesogenic molecules with normal alkyl and/or alkoxy chains attached to the phenyl ring groups.

Two Molecular ab-initio Calculations

The contribution of intramolecular interactions (such as non-bonded and electrostatic interactions) to the molecular conformational energy can be calculated by using the MO program. However, the contribution from the intermolecular electron-electron interactions is usually ignored. Although we naturally anticipate that this effect would be small in fluid-like liquid-crystalline phases, there are some possibilities that the molecular packing structure in crystalline phases is stabilized by this interaction. It may also be expected that higher order smectic phases including ferroelectric and antiferroelectric smectic phases can be stabilized in part by this type of intermolecular interactions. As a first step toward the full description of the intermolecular interactions, we carried out a two-molecular ab-initio calculation for a set of the nearest neighbor two molecules found in the 8O-O8 and 8O-8 crystals (Figure 2). The calculation was carried out by using the Q-Chem [6] and STO-3G basis set with the electron-electron correlations calculated by the MP2 method [7]. Some preliminary result of this ab-initio calculation is presented in Table II, where the values of the energy calculated for a single molecule (A) and for a pair of molecules (B) are listed. The difference between these two values (B-2A) should represent an excess stabilization energy arising from intermolecular interactions. The B-2A value is negative for both 8O-O8 and 8O-8 indicating that the two-molecular crystalline system is stabilized by intermolecular interactions. Moreover, the absolute magnitude of the B-2A value is found to be larger for 8O-O8 than 8O-8. This latter result agrees with the fact that 8O-O8 has a higher melting temperature. Although this two-molecular ab-initio calculation of liquid crystals is still preliminary, the aforementioned agreement with experimental observations indicates a potential applicability of this new technique to the prediction of the nature of intermolecular interactions between liquid crystalline molecules and of their macroscopic thermodynamic property.

TABLE II Intermolecular potential energy between the nearest pair of molecules in the observed 8O-O8 and 8O-8 crystals estimated by two molecular ab-initio MO calculations (Q-Chem/MP2/STO-3G).

		8O-O8	8O-8
Isolated molecule	A	-1632.5531 au	-1558.5115 au
Two molecule system	B	-3265.1110 au	-3117.0269 au
Intermolecular interaction	B-2A	-2.98 kcal/mol	-2.47 kcal/mol

CONCLUSION

In this study we carried out MO and MD analyses of smectic liquid crystalline molecules 8O-O8 and 8O-8 to understand the molecular origin of different crystalline structure formation in solid phases. The results of these analyses indicate that the biphenyl-phenyl ester mesogens with normal alkyl chains have several stable conformations with essentially the same energy and that the experimentally observed structure is chosen as a consequence of intermolecular packing constraints. It is also suggested that the 8O-O8 and 8O-8 molecules in liquid-like smectic phases should assume all these possible conformations and posses a considerable conformational flexibility

We have shown earlier [2,3] that the MHPOBC molecule, with the same biphenyl-phenyl ester core but a chiral alkyl chain, have several quasi-stable conformations that result from an asymmetric torsional potential about the C*-C (alkyl) bond. The conformation found in the crystalline phase corresponds to the second stable conformation calculated by MO and because of this reason MHPOBC exhibits a polymorphism in solid phases. In contrast to this, the 8O-O8 and 8O-8 molecules with normal alkyl chains have several stable conformations of similar energy rather than quasi-stable conformations with different energies. Comparison of these two observations may suggest that 8O-O8 and 8O-8 will not exhibit polymorphism and their phase transition involves conformational melting that liberates all possible conformations. The phase transition behavior of a series of biphenyl-phenyl ester smectic liquid crystals will be analyzed by MD simulation in future studies.

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