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Spontaneous Chirality Induction and Enantiomer Separation in Liquid Crystals Composed of Achiral Rod-Shaped 4-Arylbenzoate Esters

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Abstract: The discovery of spontaneously induced chirality and enantiomeric separation in liquid crystal and soft crystal systems composed of achiral rod-shaped 4-arylbenzoate esters is described. Negligibly small circular dichroism (CD) signals are produced in the smectic A (SmA) phases of these substances, and the signals were found to increase with increasing smectic order. Since the advent of chirality occurs in freely suspended films, it is not a consequence of surface effects. Both positive and negative CD signals are observed with equal probability at different positions in these films. Vibrational CD spectroscopy and theoretical calculations are used to analyze the conformational changes that are associated with the induced chirality of the rod-shaped molecules. The results show that the phenomenon is caused by the twisting of biphenyl bond associated with the ester moiety in 4-arylbenzoate esters.

1. Introduction

Spontaneous separations of enantiomers (deracemization) have been observed in many racemic molecular systems.[1,2] The earliest and most famous example is found in studies by Pasteur, which showed that a solution of racemic tartaric acid salts forms physically separable crystals containing the individual enantiomers.[3] Since that time, numerous observation of deracemization of racemic mixtures by way of formation of homogeneous two-dimensional or three-dimensional crystals have been made.[4]

Liquid crystals that are derived from racemic materials, even when they are in fluid smectic phases, rarely form local conglomerates in which one of the two enantiomers predominates.[5] This situation changed with the discovery that liquid crystals generated from bent-core type banana-shaped achiral molecules undergo spontaneous formation of chiral, enantiomerically enriched conglomerates.[6] The discovery of the spontaneous deracemization in bent-core mesogens stimulated a large number of studies focusing on the chirality of mesogenic systems.[7] The ensuing efforts uncovered two types of chirality induction. One is layer chirality, which originates from the tilt of bent molecules from the normal of the smectic layer.[8] In addition, spontaneous chiral segregation was observed to take place in the B_4 and dark conglomerate phases,[9,10] and was attributed to twisted molecular conformations by polarized Fourier-transformed infrared (FT-IR) spectroscopy,[11] nuclear magnetic resonance (NMR).[12−14] The observation of large degrees of optical activity, i.e., rotatory power or circular dichroism (CD), from each of the chiral domains was interpreted in terms of the molecular superstructures that are produced.[15] Recently, helical superstructures of both phases were clarified mainly by freeze-fractured electron microscopy and X-ray analysis.[16,17]

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Bent-core mesogens are highly unusual examples of induced chirality since they are associated with achiral (not racemic) molecules that spontaneously segregate into two enantiomerically related domains in liquid crystalline phases (not crystal phases). Recently, it was suggested that spontaneous chiral segregation might take place with achiral rod-shaped compounds.[18] However, this proposal has been the subject of wide debate owing to the possible intervention of surface effects and the absence of strong supporting evidence.[19] Although unusual features exhibited by rodlike ester molecules have been demonstrated[20,21] and interpreted later,[22] symmetry breaking with rod-shaped molecular systems has not been demonstrated yet.

In this article, we describe observations made in CD studies of rodlike achiral molecules in sandwich cells and in freely suspended films. This effort has led to the significant discovery that even simple rodlike molecules, if they contain phenylene ester moieties, could exhibit spontaneous chirality induction and enantiomer separation in which two optically active forms are spatially separated. Vibrational CD (VCD) spectroscopy was employed to show that a molecular twist occurring at the ester linkages in these substances is the cause of the axial chirality that develops in these molecules. Unlike those previously reported to display chirality induction, the achiral 4,4′-biphenylcarboxylate esters used in this investigation are not banana-shaped, nor are any chiral dopants or environments employed. Instead, the esters displaying induced chirality are members of a common class of low-molecular weight LC materials[23] that form smectic (Sm) liquid crystals (LCs).

2. Results

2.1. Texture Observation. Two types of simple rod-shaped molecules, possessing alkyl **1** and semifluoroalkyl **2** terminated phenylene ester structures, were used in this investigation (Figure 1). The detailed synthesis and basic characterization is described in the Supporting Information (1−3). Note that all the molecules show only conventional smectic phases but not phases characteristic to bent-core molecules. This means that the molecules are categorized into rod-shapes, although a slight bent structure has resulted from the ester linkage.

Upon cooling from the isotropic to SmA, a fan texture is displayed. The molecules were homeotropically aligned by shearing in the SmA phase and a dark texture was produced owing to the lack of birefringence. This observation confirmed the presence of homeotropically well aligned LC molecules. When the temperature is lowered to room temperature (RT), the SmA phase is converted into a material with an ansiotropic texture, in spite of the fact that a negligible change of layer spacing is expected during the cooling process. This finding suggests that a slight layer deformation might be taking place. POM images showing these characteristics in **1−6**, **1−7**, **1−8**, and **2** are shown in Figure S4 (Supporting Information).

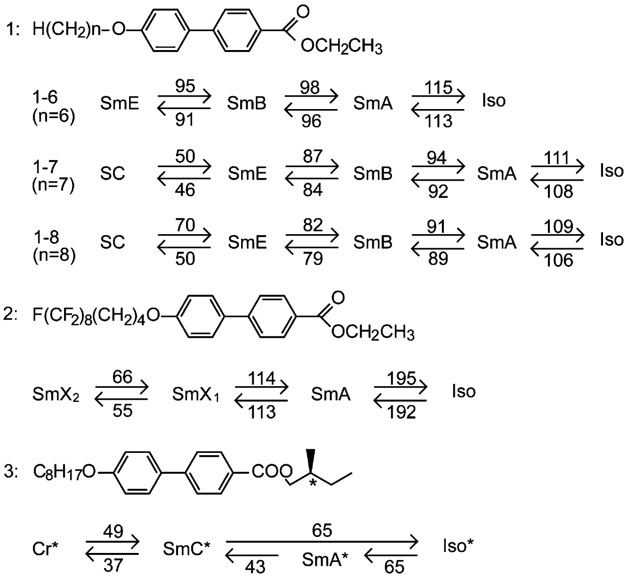

Figure 1. Chemical structures and phase behaviors of LC molecules. Chemical structures and phase sequences of **1−6**, **1−7**, **1−8**, and **2**. The structure of the chiral dopant **3** is also shown. All transition temperatures are in degrees Celsius.

2.2. CD Measurements. CD measurements were conducted as described in the Supporting Information (11). In Figure 2a−d are shown typical CD spectra at RT of samples comprised of compounds **1−6**, **1−7**, **1−8**, and **2**, respectively. The spectra contain position-dependent positive and negative signals with maxima and minima at 270 nm. This result indicates that spontaneous induction of chirality and enantiomeric separation have taken place. Positive and negative CD signals for compounds **1** also develop around 310 nm in a manner that correlates with the terminal chain length.

In order to rule out the influence of birefringence on the CD signals, two experiments were conducted. The first involved making CD spectral measurements at each point in rotating the sample about the optical beam (Figure 2e−h). Also, the CD experiments were carried out multiple times (10 for **1** and 20 for **2**) at different positions of the samples in the homeotropic cells. Measurements at each sample position were also performed at different sample rotations. The mean values of the measurement made are given in Figure 2i−l. The results of the first experiments show that the CD spectra are largely unchanged when the rotation angle is altered, confirming that the contribution of birefringence to the CD signals is negligible (see Supporting Information, Figure S5). The observations made in the second experiment are also consistent with this conclusion. After 10 or 20 runs, the peak intensities and signs seen in the CD spectra are randomly distributed and the signal intensities are relatively large. Thus, it is possible to conclude that chirality induction and enantiomer separation in these systems is a consequence of the random generation of axial conformational asymmetry in the manner that has been reported for LCs produced from achiral banana-shaped molecules.[9]

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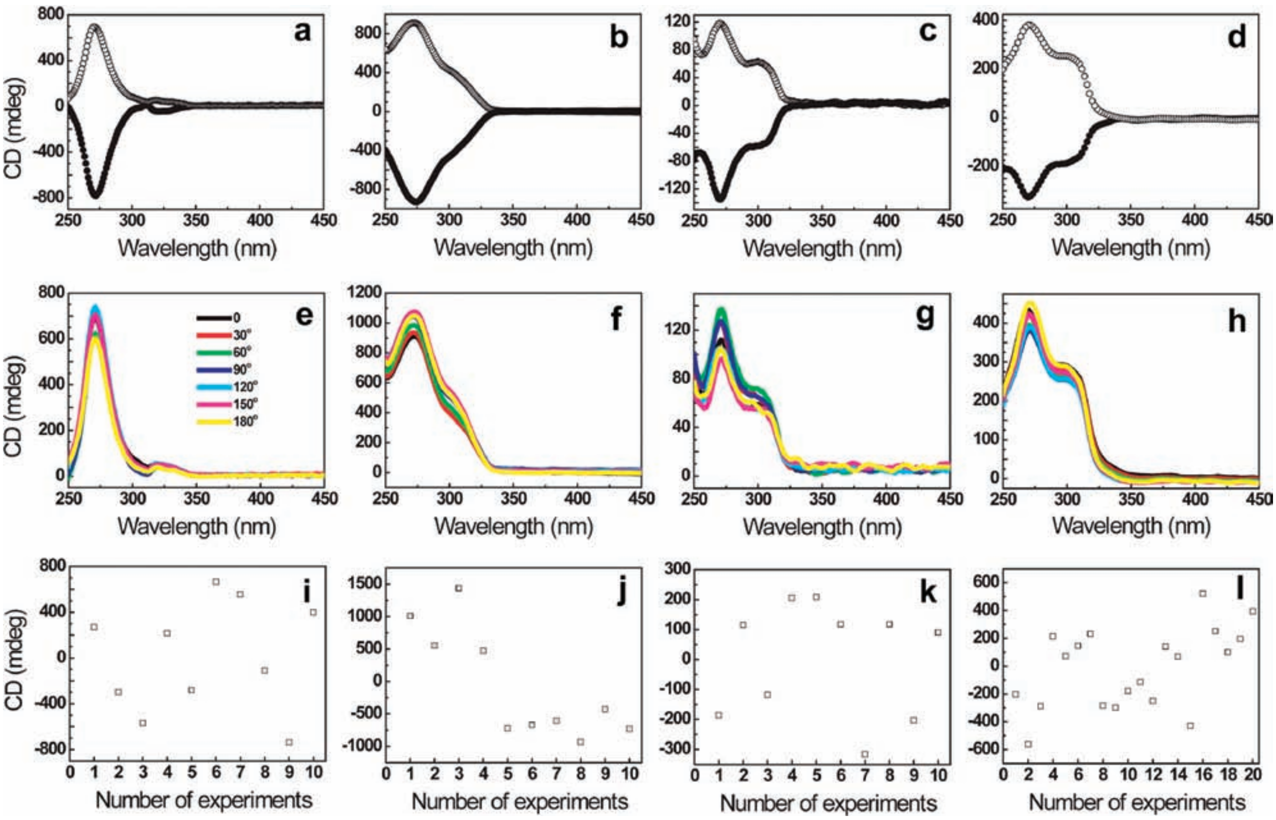

Figure 2. CD spectra of homeotropically aligned cells. (a−d) CD spectra from different enantiomeric domains, (e−h) CD spectra taken by rotating cells about the cell surface normal, and (**i**−**l**) maximum CD signal intensities for 10 or 20 experiments. The first, second, third, and fourth rows are for compounds **1**−**6**, **1**−**7**, **1**−**8**, and **2**. The experiments e−h certify negligible contribution of birefringence to the CD signals. The repeated experiments i−l suggest the formation of segregated right- and left-handed chiral domains with equal probability.

2.3. Phase-Dependent CD Spectroscopy. To determine in which phase chirality and enantiomer separation occurs, CD measurements were carried out as a function of temperature. Although typically it is difficult for LC molecules to retain homeotropic alignment during heating and cooling cycles, compounds **1**−**8** and **2** have the advantageous property that homeotropic alignment in the cells is retained even after heating to obtain isotropic phases. For the phase dependent CD measurements, the homeotropically aligned sample was prepared in the same manner above, and then mounted on stage, equipped with temperature control capabilities at RT. The sample (**1**−**8**) was heated to its isotropic temperature and subsequently cooled to RT at a rate of 2 °C/min. In-situ CD measurements were made in each phase. As shown by comparing Figure 4a and Figure S4 (third row, Supporting Information), the texture seen at RT becomes nearly homeotropic after heating and cooling cycles. The samples generated in this way were used for recording temperature dependent CD spectra.

CD spectra of compounds **1**−**8** recorded during the cooling process are given in Figure 3b. As can be ascertained by inspecting the spectra, CD signals were not predominant in the isotropic (120 °C) and SmA phases (100 and 90 °C) of **1**−**8**. Notably, CD signals start to appear from the SmB phase (84 °C, 80 °C), and these signals remain at the same intensity in the SmE phase (70 °C, 60 °C). The observations indicate that chirality induction and enantiomer separation take place in the SmB phase, which is definitely different from the crystalline phase.

In Figure 3c are displayed the original CD signal (red circles) recorded at the same sample position after a heating and cooling cycle (blue circles). The sign of CD signals change from position to position as well. It is obvious that the helicity of the sample undergoes a change during the cycle, indicating that the enantiomeric integrity of the molecular system is generated in a random manner that is consistently followed in repeated cycles (Figure 2i−l). In Figure 3d are shown CD spectra of compound **2** recorded at various temperatures during the heating process. A remarkably large CD signal is observed in the SmX_2 phase (50 °C), which abruptly decreases in conversion to the SmX_1 phase (70 °C) and remains nearly unchanged in this phase (90 °C, 110 °C). Finally, the CD signal is negligible in both SmA (130 °C) and isotropic (210 °C).

2.4. The Effect of a Chiral Dopant. The results presented above demonstrate that the two enantiomeric domains, generated by the spontaneous chirality induction taking place in the SmB phase of phenylene esters, are formed with equal probabilities. Additional studies demonstrate that a chiral dopant has a pronounced effect on the ratio of the enantiomeric forms produced in the chirality induction process. For this purpose, we chose compound **3** as a chiral dopant (see Figure 1) and compound **1**−**8** as a parent material. The temperature dependence of CD spectra of **3** was recorded in each phase generated by the cooling process. Negligible CD signals were observed in the SmA phase of the pure compound **3**, indicating that no chiral structure is formed by the LC molecules (Supporting Information, Figure S6A). Noticeable CD signals at 290 and 265 nm appear and a striped fan-shaped texture pattern develops upon cooling from SmC*. The CD spectral pattern observed in this phase is similar to that of **1**−**8** with the only difference being a CD sign reversal that abruptly takes place upon crystallization at 37 °C.

A mixture of **1**−**8** and **3** (5 wt %) was obtained by adding 9.5 mg of **1**−**8** and 0.5 mg of **2** to 5 mL of chloroform,

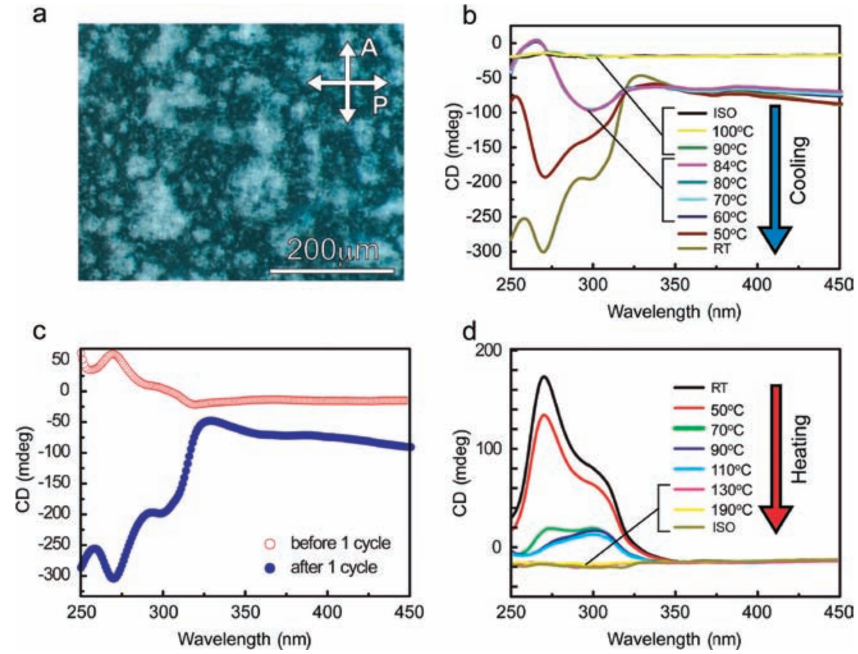

Figure 3. Temperature dependence of CD spectra. (a) Photomicrograph of compounds **1**−**8** observed at RT after heating to the isotropic phase. (b) CD spectra of **1**−**8** measured on cooling. Chiral induction and enantiomer separation starts to occur in the lowest-temperature region of SmB. (c) CD signals for compounds **1**−**8** observed at RT before and after one heating and cooling cycle. Different enantiomeric domains emerge in a random manner at the same sample position. (d) CD spectra of **2** measured on heating. The signal gradually decreases with increasing temperature and disappears in the SmA phase.

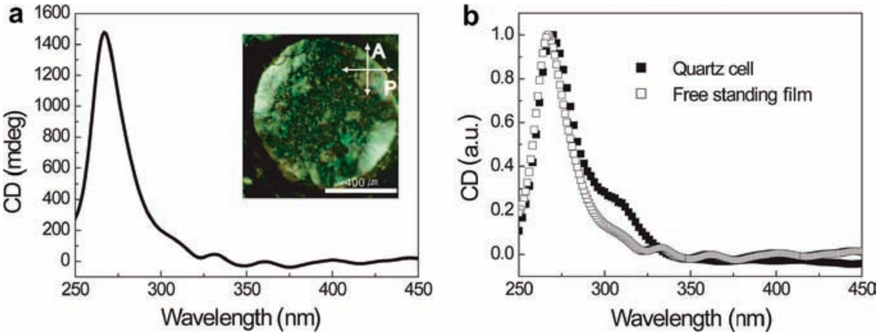

Figure 4. CD spectra of freely suspended film. (a) CD spectrum observed in a freely suspended film of the compound **2**. A photomicrograph of the film sample is also shown in the inset. (b) Comparison of CD spectra in a sandwich cell and a freely suspended film.

sonicating for 60 min, and evaporating the solvent in a drying oven at 60 °C. Other mixtures of **1**−**8** and **3** (10 wt % and 20 wt %) were obtained in a similar manner. Next, mixtures of **1**−**8** and **3** were subjected to POM and CD analysis. It is known that chiral dopants induce an imbalance in the size of the chiral domain but that they do not affect the twisting power in each chiral domain.[24] In order to probe this behavior, CD measurements at different positions and at a fixed position with decreasing temperatures were conducted. CD spectra (Supporting Information, Figure S6B) recorded on a 20 wt % mixture of **3** and **1**−**8** show clearly observed negative CD signals of about equal intensities, independent of the position probed. Importantly, amplification of the intensity of the CD signal by **3** is not observed, and the wavelength of the CD peak is not changed. Thus, the results demonstrate that the chiral dopant does not affect the twisting power of the chiral superstructure. In other words, the twisting power or chiral superstructure is a consequence of the inherent nature of the LC rod-shaped molecules containing ester moieties, and the only role played by the chiral dopant is to govern the sense of chiral superstructure.

2.5. Measurements on a Freely Suspended Film. To remove the possibility that surface effects are causing the chiral induction, POM observations and CD measurements were made using freely suspended films. These films were created by drawing **2** in its isotropic phase over a hole of 800 μm diameter followed by cooling to RT at a rate of 5 °C/min. Inspection of the inset image in Figure 4a shows that a grayish textured, free-standing film exists in the $\mathrm{SmX_2}$ phase (40 °C), indicating that LC molecules are homeotropically aligned between the air boundaries. The CD spectrum recorded on this film (Figure 4a) contains a high-intensity signal with a maximum at 270 nm. The POM images of SmA, $\mathrm{SmX_1}$, and $\mathrm{SmX_2}$ are shown in Figure S7A−C (Supporting Information). The birefringence effect on the CD signal is negligible as confirmed by rotating the film about its surface normal (the light propagation direction) (Supporting Information, Figure S7D). A comparison of normalized CD spectra of the freely suspended LC film of **2** and the LC system in a sandwich cell is displayed in Figure 4b. Both samples give rise to almost the same CD spectra, differing only by a slight shift of the main peak. These findings make it perfectly clear that spontaneous chirality induction and enantiomer spatial separation discovered in these LC systems composed of rod-structured achiral substances is not caused by surface phenomena.

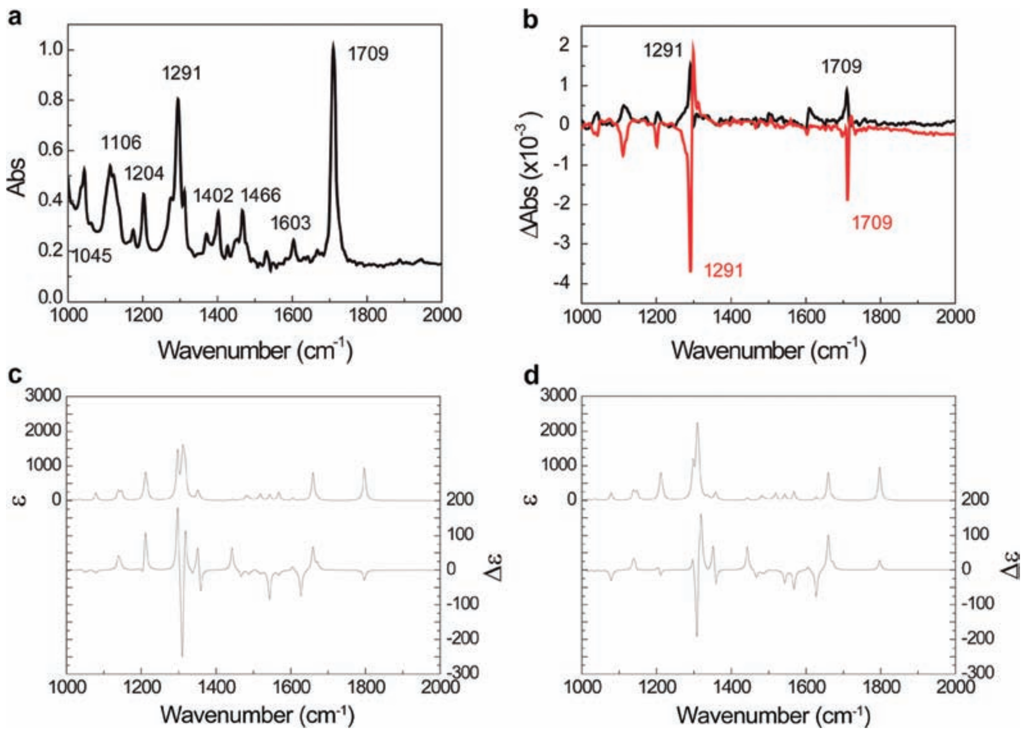

Figure 5. FT-IR and VCD spectrum. (a) Experimental FT-IR and (b) VCD spectrum of compounds **1**−**8**. (c) Calculated FT-IR and VCD spectra of conformer 1, and (d) those of conformer 2 of methyl 4-(*p*-methoxyphenyl)benzoate.

2.6. Vibrational CD Measurements. Vibrational circular dichroism (VCD) spectroscopy, a CD measurement in infrared (IR) region, serves as a powerful methodology to elucidate conformational changes associated with the advent of chirality. We measured VCD spectra at RT, as described in the Supporting Information (11). Inspection of the IR spectrum of the sample (Figure 5a) shows that most of the absorption bands, except for those at 1204, 1402, 1466, and 1603 cm^{-1}, are attributable to ester related vibrations (Supporting Information, (S8) Table 1). Particularly indicative are the two major peaks at 1291 cm^{-1} and 1709 cm^{-1} which correspond to ester C−O and C═O stretching, respectively. In Figure 5b are displayed VCD spectra at two different positions in the cell. The VCD spectra clearly contain two strong signals of opposite sign at 1291 cm^{-1} and 1709 cm^{-1}. Three other peaks are also observed in the ester-related, low wavenumber, vibrational region. Importantly, all of the signals seen in the VCD spectra originate from vibrations related to the ester linkage having opposite twist conformations. Thus, it is possible to conclude that conformational twisting at the ester linkage is the origin of axial chirality induced in this LC system comprised of rod-shaped molecules containing appended ester moieties. Later we will show that in reality the twisting occurs at the biphenyl bond which is associated with the ester moiety.

In order to gain additional information, optical and CD measurements were made on two pyrimidine derivatives that form LC phases but do not contain ester groups (Supporting Information, Figure S9). These compounds have phase sequences of Iso (78 °C), SmA (74 °C), SmC (42 °C), Cryst and Iso (66 °C), N (58 °C), SmA (47 °C), SmC (27.5 °C) Cryst, respectively. CD spectral analysis of these substances did not reveal the presence of any meaningful signals at RT (Supporting Information, Figure S9). Although not a completely unambiguous test because the compounds possess different phase sequences from those of the ester-containing compounds, the findings suggest that ester moieties in the rodlike liquid crystals play significant roles in the spontaneous chiral induction process.

3. Discussion

The results presented above clearly show that the achiral rod-shaped, ester-containing molecules investigated in this effort undergo spontaneous formation of axially chiral molecules that separate into two enantiomeric domains. To more clearly understand the occurrence of this spontaneous enantiomeric resolution process, density functional theory calculations (B3LYP/6-31(d,p))[25] were performed to determine the stable conformations of a simple model ester, methyl 4-(*p*-methoxyphenyl)benzoate. In Figure 6 is shown a plot of potential energy as a function of dihedral angle at the biphenyl linkage between the two aromatic rings. The results show that the C−O and C═O bonds in the ester group are coplanar with the adjacent aromatic ring, irrespective of the dihedral angle between the two aromatic rings. In addition, two equal energy conformers are found to have energy minima, and both have their enantiomeric forms. As a result, four energy minima exist (Figure 6) that correspond to conformations in which the dihedral angle between the two aromatic rings is ∼35°. The potential barriers for interconversion of the enantiomers is found to be ∼1.76 kcal/mol in both of these conformers, being higher than the thermal energy (∼0.6 kcal/mol) at RT. Based on the results of the calculations, it seems reasonable that both conformers represent chiral forms that are responsible for the enantiomeric separation process in the present LC systems consisting of rod-shaped molecules.

IR and VCD spectra were calculated for the two energy minimum conformations 1 and 2 (Figure 5c and d). Two key

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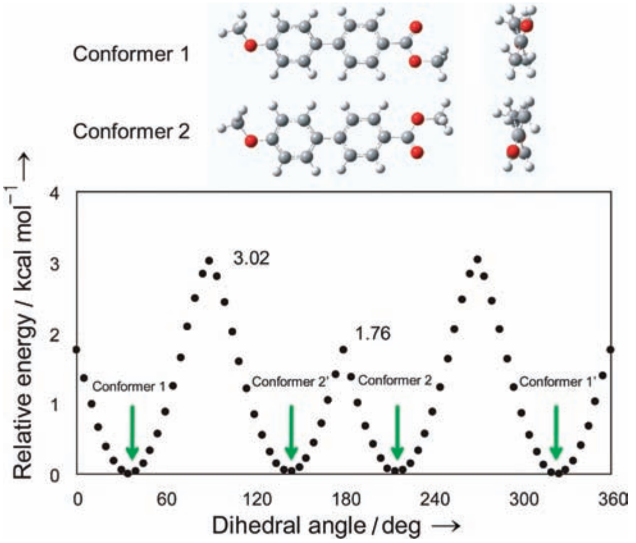

Figure 6. Calculated potential energies of the model compound, methyl 4-(*p*-methoxyphenyl)benzoate, as a function of dihedral angle between two aromatic rings. Two stable conformations (shown at the top) with equal energies exist.

observations are made in inspecting the calculated spectra. First, both spectra, and in particular the VCD spectra, show a marked intensity dependence on molecular conformation. Second, the C═O stretching band at ~1800 cm^{-1} gives rise to only a small VCD signal in both conformers, even though it is experimentally observed as a major peak at 1700 cm^{-1}. To examine these two features, simulations were carried out using 18 conformations of a real molecule **1−6**. The results are shown in Figure S10 (Supporting Information). Although VCD spectra showing good agreement with the experimental one were not obtained, we found that a strong VCD signal due to the C═O stretching can be obtained by introducing gauche conformations in the end chain.

Competing chiral symmetry-breaking theories[26] all suggest that, unlike intermolecular interactions between chiral substances, the induced formation of chirality from achiral molecules is caused by a collective tilting from the molecular layer normal of the superstructure formed from dimerically interacting molecules.[27] Based on the results obtained in the current study, chiral dimeric (or bent) conformations appear to be an important feature that gives rise to the chiral properties of LCs. The molecules used to form LCs in the current investigation, although having rod structures, are bent at the ester carbonyl group. This gives rise to LCs that are similar to antiferroelectric liquid crystals.[28] In the higher-temperature, smectic phases (e.g., SmA) the system is uniaxial as a consequence of free rotation of molecules about their long axis. In lower-temperature smectic phases (e.g., SmB, SmE, SmX$_1$, and SmX$_2$) free rotation is slowed, so that the consequence of collective molecular tilting becomes observable. The tilting that takes place in the systems explored in this effort is driven by packing entropy which governs the formation of conformations in which the major molecular axis is perpendicular to the smectic layer and the bent arms of the molecules are oriented in the same direction. This conclusion is supported by the observation of a nonuniform, partially bright homeotropic texture at low temperatures (Figure S4 (third row) (Supporting Information)and Figure 4a.

Recently, Yan and his co-workers[29] succeeded in simulating the formation of self-assembled chiral superstructures by using rigid achiral molecules. In the systems probed in Yan's work, two rigid parts of the molecules are bent by ~150°. Energy minimization of these systems suggests that the molecules exist in a staggered alignment that gives rise to a chiral column phase and a chiral superstructure. The local molecular assemblies envisaged in Yan's systems are similar to the layer structures proposed to exist in the systems we have explored (i.e., one molecular arm is parallel to the layer normal and the other arm is tilted from the normal). It is important to emphasize that the molecules here take chiral conformations, although the rigid molecules in the simulation never become chiral on the microscopic scale. The scenario portrayed in Yan's system can be applied to our studies. Thus, relatively large CD signals are seen only when chiral superstructures are generated[11] from individual axially chiral molecules.

4. Conclusion

In summary, the results uncovered in this investigation provide unambiguous experimental proof that rod-shaped achiral molecules can undergo spontaneous enantiomer formation and resolution (deracemization) in their homeotropically aligned, highly ordered, smectic liquid crystalline phase. As with molecules that show unusual chiral phenomena, such as chiral segregation in bent-core mesogens[9] and enhanced twisting power by doping a cholesteric liquid crystal with achiral rodlike molecules,[20] the achiral rod-structured substances that contain ester moieties probed in the current effort undergo chiral induction and enantiomeric separation. Thus, the results of the investigation described above show that chiral segregation is not a phenomenon exclusively restricted to achiral bent-core mesogens but that it can take place even in LCs formed from rod-shaped achiral molecules that contain ester linkage(s).

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Supporting Information Available: (1) Synthesis route, (2) DSC of compounds **1−6** and **2**, (3) XRD of compounds **1−8** and **2**, (4) POM images of the compounds, (5) CD spectra in a twisted nematic cell with some rotation angles about the cell surface normal, (6) CD spectra of chiral dopant (**3**) and mixtures, (7) additional photograph of freestanding film and CD spectra with some rotation, (8) IR assignment of compound, (9) POM image and CD spectra of reference nonester compounds, (10) simulation result of VCD spectrum of a real molecule **1−6**, (11) experimental details, and (12) full citation of ref 25 This material available free of charge via the Internet at http://pubs.acs.org.

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