

Interlayer interactions in enantiomeric anticlinic liquid crystalline mixtures

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The interlayer interaction coefficient U in the anticlinic phase of enantiomeric binary mixtures was determined by measuring the threshold electric field for the onset of solitary waves. U was found to increase with decreasing temperature in the anticlinic phase for a given enantiomer excess X . The ratio $U(X, \theta)/U(X=1, \theta)$, where θ is the polar angle, was found to be significantly smaller for mixtures with low enantiomer excess than for the optically pure material. The observed behavior is analyzed using a mean-field model for dipole-dipole interactions in adjacent layers.

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The physics of anticlinic liquid crystals is extraordinarily rich [1–3]. In both the anticlinic and synclinic phases, the director \hat{n} tilts by polar angle θ with respect to the smectic layer normal (Fig. 1). In the synclinic phase the azimuthal angle φ is identical in every layer, aside from a spatially slow layer-to-layer rotation due to the helical nature of the chiral molecules [4]. On the other hand, in the anticlinic phase the azimuthal orientation alternates between $\varphi_i=0$ and $\varphi_{i+1}\approx\pi$ from layer to layer. If the molecules are chiral, φ_i and φ_{i+2} differ slightly, as there exists a pair of commensurate long wavelength helices, one associated with the odd layers and one with the even layers. Materials having an anticlinic phase exhibit tristable behavior [1], and can be switched from the anticlinic to synclinic configuration by a sufficiently large electric field. This switching, in fact, has been shown to occur via fingerlike solitary waves of the synclinic phase invading the anticlinic region [5], where the threshold field $E_{th}=2U/P$ for the onset of fingering. Here, P is the local component of polarization that lies perpendicular to the molecular tilt plane and U is the coefficient of the layer-layer interaction term in the free energy, viz., $f_i=(U/2)\{\cos(\varphi_{i+1}-\varphi_i)+\cos(\varphi_i-\varphi_{i-1})\}$, where f_i is the free-energy density of the i th smectic layer [6]. A positive coefficient U promotes the anticlinic phase, whereas a negative value of U promotes the synclinic phase. Using a perturbative scheme in which an optic mode was electrically excited in an unwound pitch-compensated mixture, Kimura *et al.* measured the coefficient U for small deviations from π of the quantity $\varphi_i-\varphi_{i-1}$. They showed that this value closely corresponds to the value obtained from solitary wave threshold field measurements, i.e., $U=\frac{1}{2}PE_{th}$ [6], where P is the polarization and E_{th} is the threshold field.

The phase diagram of enantiomeric mixtures of TFMHPOBC [4-(1-trifluoromethylhexyloxy-carbonyl) phenyl 4'-octyloxybiphenyl 4-carboxylate] is quite simple [7], exhibiting a direct transition from the smectic-A phase to the anticlinic smectic C_A^* phase at large enantiomeric excess $X>0.6$, where $X=|([R]-[S])/([R]+[S])|$, and $[S]$ and $[R]$ are the molar concentrations of *S*-TFMHPOBC and *R*-TFMHPOBC, respectively, and $||$ indicates the absolute value. For $X<0.6$, a tilted smectic phase exists between the smectic-A and smectic- C_A^* phases; this phase has been identified as the synclinic smectic- C^* phase [7], although there is

some controversy over its precise nature [8]. If the intervening phase is, indeed, synclinic, one would expect the coupling coefficient U to be positive *but small* just below the synclinic-anticlinic phase transition temperature (at small X), and considerably larger just below the smectic-A-anticlinic phase transition temperature close to $X=1$. In this paper, we report on measurements of the solitary wave threshold field E_{th} in the anticlinic phase as a function of temperature T and enantiomer excess. From the data we obtain the coupling coefficient U , and examine its evolution as a function of enantiomeric excess.

Binary mixtures of left- and right-handed enantiomers of TFMHPOBC were prepared by dissolving appropriate concentrations of the enantiomers in chloroform and evaporating the solvent at 40–50 °C for one day. Sample cells were constructed from two glass slides coated with indium tin oxide. The glass slides were washed in a detergent solution, distilled water, acetone, and finally, ethanol. After cleaning, the slides were spin coated with polyimide RN1266 (Nissan Chemical) and baked. The polyimide-coated surfaces were then uniformly rubbed using a dedicated rubbing machine, immersed in isopropyl alcohol, and sonicated. The slides were then dried and subjected to a deionizing air stream. Finally they were placed together, separated by Mylar spacers of thickness 5 μm , and cemented. For each mixture, the empty cell was mounted in a computer-controlled oven and filled with the liquid crystal in the isotropic phase. The temperature of the sample was then gradually lowered into the anticlinic phase.

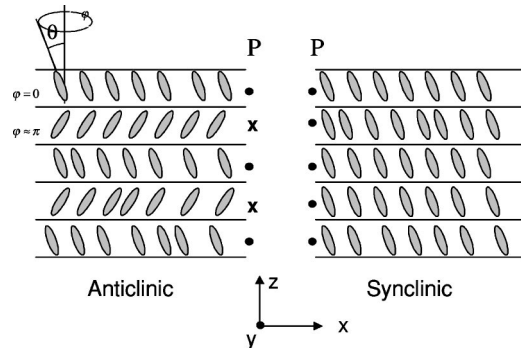
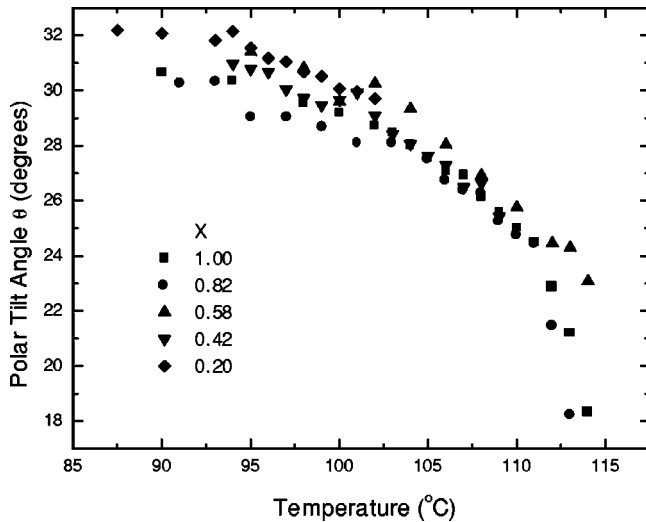
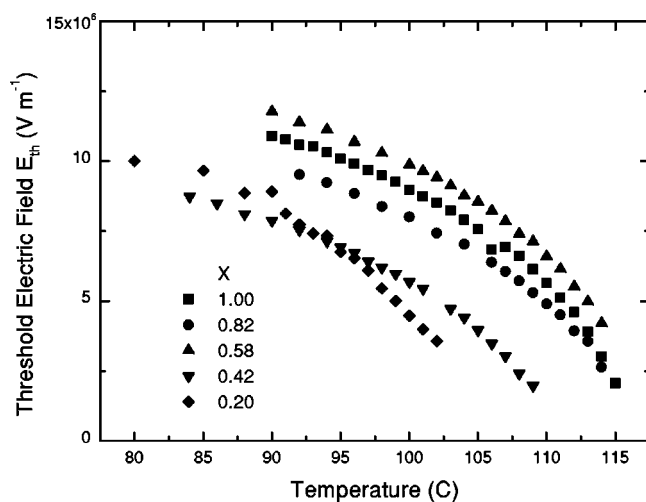
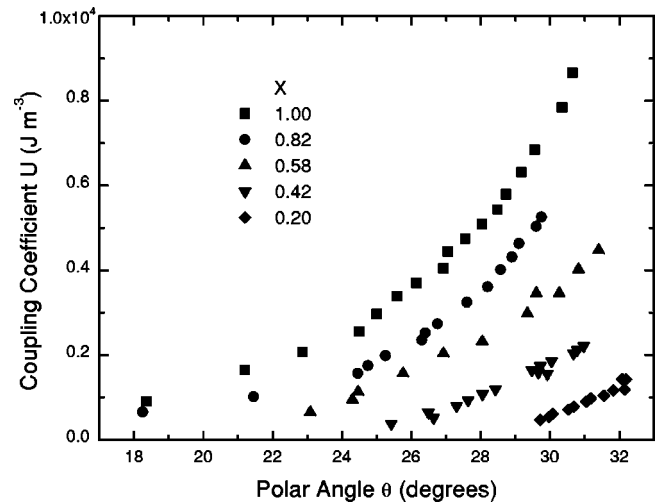


FIG. 1. Schematic representation of anticlinic and synclinic phases.

FIG. 2. Polar tilt angle θ vs temperature for different mixtures.

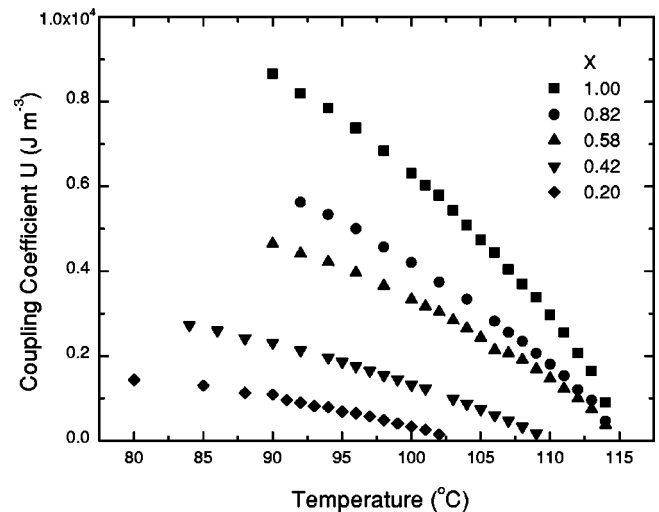
In order to measure the threshold field for the onset of solitary waves, light from an He-Ne laser passed consecutively through a polarizer oriented parallel to the smectic layer normal, a lens of focal length $f=85$ mm (to focus the beam to a spot size of ~ 0.5 mm at the sample), a recollimation lens, an analyzer, and a photodiode detector. A high-precision dc voltage source (Keithley 230) was used to generate a dc electric field E in the cell. The voltage was ramped in 200 mV increments from zero to a value above the solitary wave threshold at a rate of 2 V s^{-1} , and the detector output was computer recorded. The threshold field E_{th} , corresponding to V_{th}/d , where d is the cell thickness, was taken as the point where the detector output suddenly increased [5]. To ensure that E_{th} is independent of ramp rate, the measurement was performed at several different ramp rates down to 0.1 V s^{-1} , with no significant difference in results.

We now wish to relate E_{th} to the interaction coefficient U . Since a variety of physical quantities such as polarization are better parameterized by the polar tilt angle θ rather than temperature, it is necessary to measure θ in the anticlinic phase as a function of enantiomeric excess and temperature. The sample was placed under a polarizing microscope and a

FIG. 3. Threshold electric field E_{th} vs $T - T_c$ FIG. 4. Coupling coefficient U as a function of polar angle θ .

dc field higher than E_{th} was applied. The sample was then rotated so that the transmitted intensity was at a minimum, at which point the applied electric field was reversed. The microscope stage was rotated by an angle α to again minimize the transmitted intensity, and θ was taken to be $\alpha/2$. Figure 2 shows θ vs enantiomer excess X and temperature.

Figure 3 shows E_{th} vs $T - T_c$ for all mixtures, where T_c is the concentration-dependent transition temperature from anticlinic to either the synclinic ($X < 0.6$) or smectic-A ($X > 0.6$) phase. In order to extract $U(X, \theta)$ from the threshold field data, we assume that the polarization P is given by $P = XP_o$, where P_o [7] is the polarization of the optically pure material. The data for P_o vs temperature in Ref. [7] may be converted to P_o vs θ using our data for $\theta(X=1)$ vs T from Fig. 2. Note that we constructed smooth curves for each X . The interaction coefficient $U(X, \theta)$ is given by $\frac{1}{2}E_{th}(X, \theta)P(X, \theta)$ [5]. Figure 4 shows $U(X, \theta)$ as a function of polar tilt angle θ , and for completeness we show in Fig. 5 $U(X, T)$ vs temperature. Several features are clearly seen. First, U increases for all values of enantiomer excess with decreasing temperature. This is not surprising, as the anti-

FIG. 5. Coupling coefficient U as a function of temperature and enantiomer excess.

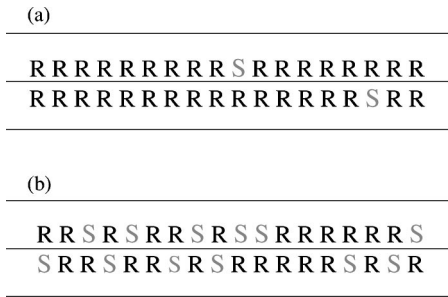


FIG. 6. Schematic representation of dipole-dipole pairing in two mixtures with high (a) and low (b) enantiomer excesses. *R* and *S* stand for right- and left-handed molecules, respectively.

clitic tendency is expected to increase deeper into the anticlinic phase. Additionally, we note that U is generally larger for the optically pure samples, and decreases as $X \rightarrow 0$. For the (nearly) optically pure material ($X=1$), the component of the molecular dipole perpendicular to the tilt plane may easily pair with an antiparallel dipole in the adjacent layer [9], as shown in Fig. 6(a). With decreasing X it becomes more likely for a dipole moment of an *R* molecule to be associated with a *parallel* dipole of an *S* molecule in the adjacent layer [Fig. 6(b)]. This is an energetically unfavorable situation, and will tend to destabilize the anticlinic phase in favor of the synclitic phase, in which the same azimuthal orientation of *R* and *S* molecules in adjacent layers is associated with *antiparallel* *R-S* dipole pairs. Thus, the anticlinic coefficient is maximum at $X=1$, and decreases with decreasing enantiomer excess. Interestingly, U does not necessarily need to vanish at $X=0$, although we are physically unable to measure the layer polarization for the racemic mixture. In principle, at $X=0$ one can have a small excess of *S-S* and *R-R* (compared to *S-R* and *R-S*) anticlinic pairings which, although entropically unfavorable, are nevertheless favored from the standpoint of the internal energy at sufficiently low temperature. At higher temperatures, where entropic effects become more important, *R-S* and *S-R* anticlinic pairings become nearly as likely as *R-R* and *S-S*, and the synclitic phase appears.

Before continuing, it is important to note that the coefficient U is deduced using the value of polarization obtained from a Tower-Sawyer experiment, in which the liquid crystal is electrically driven between the two synclitic states [10]. For the material MHPOBC it has been shown that the molecular dipole moments are oriented nearly perpendicular to the tilt plane in the synclitic phase, but make an angle of nearly 45° : with the tilt plane normal in the anticlinic phase [9]. Thus, a measurement of polarization between the two synclitic states may result in an overestimate of the effective polarization involved in the anticlinic coupling, resulting in an overestimate of U , possibly by as much as a factor of 2. Nevertheless, we believe that our discussions and conclusions about the normalized interaction coefficient are substantially unaffected by these differences.

Figure 7 shows the normalized coefficient $U_n(X, \theta)$, which is defined as

$$U_n(X, \theta) = \frac{U(X, \theta)}{U(X=1, \theta)}. \quad (1)$$

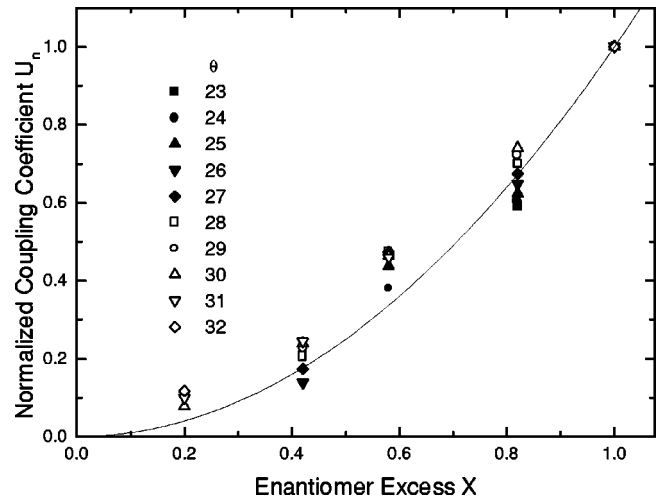


FIG. 7. Normalized coupling coefficient $U_n(X, \theta)$ as a function of enantiomer excess. Legend shows the polar tilt angles (in degrees). The line is the mean-field calculation.

It is interesting to note that, for a given enantiomer excess X , U_n is only slightly larger at a larger tilt angle (and thus at larger layer polarization). This would indicate that there is not a large excess of *S-S* and *R-R* pairings (which might be expected to occur at larger polarization), and that on average an *R* molecule has only a slightly higher propensity to form an anticlinic pair with another *R* as it does with an *S* molecule. Given this situation, we introduce a very simple mean-field model for adjacent layer dipolar pair interactions that neglects the small degree of *R-R* and *S-S* correlations. In our model, each smectic layer is represented by a two-dimensional lattice with N lattice sites, where N is equal to the number of molecules in the layer. We assume that each site is occupied by one and only one molecule. Since the mixtures contain *R* and *S* molecules, there are four possible configurations for an interlayer molecular pair (Fig. 8). Neglecting intralayer interactions, the *R-R* and *S-S* pairings in the anticlinic phase are energetically favorable, whereas the *R-S* and *S-R* pairings are (equally) energetically costly. As noted above, we neglect entropic effects and assume that the mean interaction $U \propto p_i p_{i+1}$ between two dipoles p_i and p_{i+1} in adjacent layers is equal to their interaction between the mean dipoles. If p is the dipole moment of *R* TFMHPOBC and $-p$ is the dipole moment of *S* TFMHPOBC in a given layer, the mean dipole p_{mean} is given by

$$p_{mean} = p \frac{[R]}{[R]+[S]} + (-p) \frac{[S]}{[R]+[S]} = pX. \quad (2)$$

For pairwise dipole interactions, the normalized interaction coefficient is thus given by

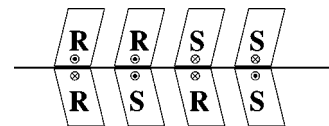


FIG. 8. Four possible pairings of two molecules in two adjacent layers.

$$U_n \equiv \frac{U(X, \theta)}{U(X=1, \theta)} = X^2. \quad (3)$$

The curve $U_n = X^2$ is shown in Fig. 7. This simple mean-field approach apparently provides reasonable agreement with the data; a model that includes R - R and S - S correlation is beyond the scope of this paper, however.

The results are important on several levels. First, the data represent the first quantitative measurement of the anticlinic interaction coefficient as a function of concentration for enantiomeric mixtures, and show a tendency for (i) stronger anticlinic interactions at decreasing temperatures and (ii)

weaker anticlinic interactions for less optically pure mixtures. The second result is consistent with the incursion of a synclinc phase between the smectic-A and anticlinic phases in regions of small enantiomer excess. Additionally, the data strongly suggest that R - R and S - S correlation effects are weak, and that mean-field theory is a viable approach to understanding the data. Finally, we note that comparisons of data at different temperatures and enantiomer excesses are appropriate as long as the polar tilt angles are the same.

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- [1] A. D. L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys., Part 2* **27**, L729 (1988).
- [2] A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, *J. Mater. Chem.* **4**, 997 (1994).
- [3] S. T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals* (Wiley-VCH, Weinheim, 1999).
- [4] Y. P. Panarin, O. Kalinovskaya, and J. K. Vij, *Liq. Cryst.* **25**, 241 (1998).
- [5] J. F. Li, X. Y. Wang, E. Kangas, P. L. Taylor, C. Rosenblatt, Y. Suzuki, and P. E. Cladis, *Phys. Rev. B* **52**, 13 075 (1995).
- [6] M. Kimura, D. S. Kang, and C. Rosenblatt, *Phys. Rev. E* **60**, 1867 (1999).
- [7] Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe, and A. Fukuda, *Liq. Cryst.* **6**, 167 (1989).
- [8] J. F. Li, J. J. Stott, E. A. Shack, X. Y. Wang, R. G. Petschek, C. Rosenblatt, and Y. Suzuki, *Liq. Cryst.* **23**, 255 (1997).
- [9] T. Matsumoto, A. Fukuda, M. Johnno, Y. Motoyama, T. Yui, S.-S. Seomun, and M. Yamashita, *J. Mater. Chem.* **9**, 2051 (1999).
- [10] P. Martinot-Lagarde, *J. Phys. (France) Lett.* **38**, L-17 (1977).