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Optical activity in the smectic-A phase of a highly chiral liquid crystal

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Optical-activity measurements in the smectic-A phase of various chiral-racemic mixtures of S-4-(2′-methylbutyl)phenyl-4′-n-octylbiphenyl-4-carboxylate (CE8) demonstrate that contributions from fluctuations in more than one chiral structural mode are important near the transition to the smectic-C^* phase. Although these results are similar to earlier measurements in the isotropic phase of highly chiral liquid crystals, previous theoretical work points out that the nature of these fluctuations and the reason for the importance of the second structural mode are very different. Because the present measurements are reported on mixtures of varying chirality, they provide a stringent test of the theory. Agreement between theory and experiment is good.

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INTRODUCTION

There has been a significant amount of theoretical and experimental work on the optical activity caused by fluctuations in the isotropic phase of highly chiral liquid crystals. The picture which emerges from these efforts is that the short-range order due to fluctuations can be described successfully by a Landau–deGennes free energy, in which the orientational order is represented by a linear combination of five structural modes. These five structural modes are two planar spiral modes (one right-handed, one left-handed), two conical spiral modes (one right-handed, one left-handed), and one achiral nematic-like mode. See Ref. [1] for a recent review of this work. If the chirality is not too high, fluctuations in only the conical spiral mode contribute to the optical activity and the result is a simple $(T-T^*)^{-0.5}$ temperature dependence, where T^* is a temperature slightly below the transition to the liquid-crystal phase. This optical activity is positive in the isotropic phase of a right-handed liquid crystal and negative in a left-handed liquid crystal, regardless of whether the wavelength of light in the liquid crystal is less than or greater than the pitch of the liquid-crystal phase. In highly chiral systems, however, the optical activity near the liquid crystal transition also depends on fluctuations in the planar spiral mode, so the situation is more complicated. This was first predicted by Filev [2], and his ideas recently have been embellished by Demikhov and Dolganov [3]. The planar spiral mode is the only chiral structural mode of the chiral nematic phase and the dominant mode in the blue phases [4], so just as in these phases the sign of this contribution to the optical activity can be either positive or negative depending on the relationship between the wavelength of light and the pitch. Since this contribution is only significant in highly chiral systems, the pitch is much shorter than the wavelength of light and the optical activity is negative for right-handed systems and positive for left-handed systems. The difference of sign in the two contributions in highly chiral liquid crystals causes a nonmonotonically increasing temperature dependence in the vicinity of the phase transition. According to these latest theoretical investigations [3,5], the simple $(T-T^*)^{-0.5}$ temperature dependence enters due to the conical spiral mode in second order of k/q_0, where k is the wave vector of the light in the material and $q_0=4\pi/P$ (where P is the pitch) is the chirality of the material. Contributions to the optical activity in fourth order of k/q_0 enter from both the conical and planar spiral modes with a $(T-T^*)^{-1.5}$ temperature dependence. Although these most recent ideas have not been fully tested by experiment, they do agree with the experimental finding that the second-order term contains a contribution from only the conical spiral mode, while the fourth-order term contains contributions from both the conical and planar spiral modes [6].

Fluctuations in the smectic-A phase also produce optical activity near the transition to the smectic-C^* phase [7,8]. Again, if the chirality is not too high, only the conical spiral mode contributes to the optical activity. However, the nature of the fluctuations in the smectic-A phase is very different from the fluctuations in the isotropic phase. In the isotropic phase, the spiral axis of a structural mode can make any angle with the light propagation direction, so the optical activity is due to an "average" over all directions. For light propagating along the director of the smectic-A phase (perpendicular to the smectic layers), the spiral axis of a structural mode is restricted to be close to the light propagation direction. Although the result is again the simple $(T-T^*)^{-0.5}$ temperature dependence, this very different "average" produces optical activity of the opposite sign from the isotropic phase (negative for a right-handed system and positive for a left-handed system). The sign and temperature dependence have been verified by experiments using a single liquid-crystal compound of moderate chirality [7,8]. However, Filev again predicts the fluctuations in the planar spiral mode are important at high chirality near the transition to the smectic-C phase [2]. This structural mode is not necessarily the dominant mode of the smectic-C^* phase (it depends on the value of the tilt angle), but it is the sole contribution to the optical activity for light propagating perpendicular to the smectic layers.

This contribution to the optical activity in the smectic-A phase therefore can have either sign, depending on the values of the wavelength of light and the pitch. If the pitch of the smectic-C^* phase is greater than the wavelength of light in the material, the contribution of the planar spiral mode is opposite from the conical spiral mode, so again it is possible that the optical activity has a nonmonotonically increasing temperature dependence in the smectic-A phase near the transition to the smectic-C^* phase. In order to fully test the predictions for both the conical and planar spiral contributions, experiments must be performed (1) in a highly chiral system, and (2) in a system where the chirality can be varied.

We report the results of optical activity measurements in the smectic-A phase in several chiral-racemic mixtures of S-4-(2′-methylbutyl)phenyl-4′-n-octylbiphenyl-4-carboxylate (CE8). The presence of a nonmonotonically increasing temperature dependence verifies that the contribution of the planar spiral mode is important at high chirality. By studying mixtures of varying chirality, it is shown that both the strength of the conical spiral mode contribution and the temperature interval over which the planar spiral mode contributes significantly increase with chirality just as predicted by the theory.

THEORY

Demikhov, Dolganov, and Filev calculate the optical activity due to fluctuations in the smectic-A phase in much the same way as in the isotropic phase [7]. The Landau-deGennes free-energy functional is written for the smectic-A to smectic-C^* transition in terms of the order parameter for that transition. Instead of the tensor order parameter appropriate for the isotropic phase, a vector order parameter is used, $\boldsymbol{\beta}=(\beta_1,\beta_2,0)$, which denotes the position of the axis of orientational order relative to the normal to the smectic planes $\mathbf{n}=(0,0,1)$. The free-energy functional is thus

$$(F-F_0)/T=\tfrac{1}{2}\int d\mathbf{r}\{a\beta_\alpha^2+b(\partial_\alpha\beta_\gamma)^2 +2bq_c e_{\alpha\gamma\mu}\beta_\gamma(\partial_\mu\beta_\alpha)+\lambda\beta_\alpha^2\beta_\gamma^2\}\ , \quad (1)$$

where a, b, and λ are coefficients in the expansion $[a=a_0(T-T^*)]$, and $q_c=2\pi/P$, where P is the pitch of the smectic-C^* phase. The anisotropic part of the dielectric tensor deviates from its value in the smectic-A phase due to fluctuations in $\boldsymbol{\beta}$

$$\epsilon_{\alpha\gamma}(\mathbf{q})=\Delta\epsilon[\beta_\alpha(\mathbf{q})n_\gamma+n_\alpha\beta_\gamma(\mathbf{q})],\quad |\beta_\alpha|\ll 1\ , \quad (2)$$

where $\Delta\epsilon$ is the dielectric anisotropy, and from this the optical activity can be calculated for light propagating along the z axis. For temperatures far from the transition, only the conical spiral mode contributes, giving the result

$$\phi=-A(T-T^*)^{-0.5}+\phi_0\ , \quad (3)$$

where A is a proportionality constant which depends linearly on k and q_c and quadratically on $\Delta\epsilon$, and ϕ_0 is the optical activity in the absence of fluctuations. Perhaps the most important aspect of this result is that the sign of the optical activity is opposite to the optical activity caused by fluctuations in the isotropic phase. Again, the reason for this is that the light is propagating along the director in the smectic-A phase, with fluctuations creating a spiral axis which deviates only slightly from the direction of light propagation. The situation is much different in the isotropic phase, where fluctuations produce small regions of orientational order which have spiral axes pointing in all directions. Another prediction of this calculation is that the coefficient A should increase linearly with the chirality if all other parameters are kept constant.

Filev further argues that because the optical activity for light propagating along the spiral axis is zero for the conical spiral mode but nonzero for the planar spiral mode, the optical activity very close to the smectic-C^* transition may also show a nonmonotonically increasing temperature dependence [2]. As the transition temperature is approached, the contribution to the optical activity from the conical mode decreases as the spiral axis is increasingly restricted to lie parallel to the light propagation direction. The contribution from the planar spiral mode is not similarly affected, so it continues to increase (although it does not show singular behavior as in the isotropic phase). Since these contributions have opposite signs, the optical activity reaches a maximum near the transition and then decreases.

The temperature interval near the transition where the contribution from the planar spiral mode is important depends on the relationship between the bare correlation length ξ_A and the product of k and q_c,

$$[(T-T^*)/T^*]\xi_A^{-2}<2kq_c\ . \quad (4)$$

Thus this temperature interval should increase linearly as the chirality is increased if all other parameters remain constant.

It is important to note that the reason for the complicated behavior is very different in the isotropic and smectic-A phases. In the isotropic phase, the fact that the T^* temperature for the planar spiral mode is higher than for the conical spiral mode is the reason that near the transition the contribution from the planar spiral mode becomes significant. In the smectic-A phase, the fact that the light is propagating along the spiral axis causes the optical activity from the conical spiral mode to decrease, and thus allows the contribution from the planar spiral mode to become important.

EXPERIMENT

The sample of CE8 was contained between two pieces of glass which had been coated with octadecyltriethoxysilane to produce homeotropic alignment. The thickness of the cell was 100 μm. Uniform textures of the smectic-A phase were obtained by cooling from the chiral nematic phase to the smectic-A phase (transition temperature $\sim$135 °C). Measurements of the optical activity were taken upon cooling starting at 105 °C and ending at the transition between the smectic-A and smectic-C^* phases which occurred between 84.8 and 84.9 °C. Three chiral-racemic mixtures were studied: 50% optically active

TABLE I. Least-squares-fitted values for the optical activity of the three CE8 mixtures using Eq. (3).

Chiral fraction	A (deg $K^{1/2}$)	T^* (°C)	ϕ_0 (deg)
0.50	0.0478±0.0050	84.43±0.14	−0.0610±0.0019
0.75	0.0927±0.0131	83.13±0.40	−0.0397±0.0037
1.00	0.1056±0.0160	83.65±0.40	0.0176±0.0047

CE8 (CE8*) and 50% racemic CE8 (CE8*R*), 75% CE8* and 25% CE8*R*, and 100% CE8*. The transition from the smectic-A to smectic-C^* phase was visible under the microscope in the 50% and 75% CE8* mixtures, since pitch bands were visible in the smectic-C^* phase. This transition was visible under the microscope for 100% CE8*, but only in a wedge-shaped sample where Cano lines were visible in the smectic-C^* phase. Determination of this transition temperature was crucial to ensure that data could be obtained close to the transition, but always in the smectic-A phase.

The sample was contained in an Instec HS-1 hot stage, the temperature of which was maintained to within 0.001 K. The temperature inhomogeneity across the illuminated part of the sample was less than 0.01 K. The sample thickness was maintained by a 100-μm spacer.

The optical-activity measurement system consisted of an argon-ion laser operating at 488 nm, two Glan-Thompson cube polarizers, a Faraday-effect modulator, and a silicon diode detector. Light from the laser passed through the first polarizer, was modulated by a fraction of a degree by the Faraday-effect modulator, and then passed through the sample. The light then passed through a polarizer mounted in a computer-controlled rotation stage before striking the detector. The output from the detector went to a lock-in amplifier. The reference signal for the lock-in amplifier was the alternating voltage driving the modulator. The computer rotated the second polarizer in steps of 0.01° and recorded the output of the lock-in amplifier at each step. Linear interpolation of the data determined the angle at which the lock-in output crossed zero, which was a measurement of the amount of optical rotation introduced by the sample. The typical standard deviation for such a measurement in the smectic-A phase was about 0.003°.

The results for the 50%, 75%, and 100% CE8* mixtures are shown in Figs. 1–3. The inset in each graph contains the data very close to the transition to the smectic-C^* phase. Notice that in all three mixtures, the optical activity is negative (CE8 is a right-handed system) and a nonmonotonically increasing function of temperature, but that the effect increases as the chirality increases. To illustrate this more clearly, least-squares fits of the data to Eq. (3) were generated, dropping off the lowest temperature point one at a time until the fit with the lowest χ^2 per data point was obtained. This fit is shown in the figures for each of the three mixtures and the values of the fitting parameters are contained in Table I.

DISCUSSION

The fitting parameter values can be used to check quantitatively the theory concerning the contribution from the conical spiral mode. The coefficient A is supposed to be linear with the chirality. As Fig. 4 demonstrates, the data are consistent with a straight line through the origin. The theory does not predict much concerning the value of T^*. Because the free-energy functional depends on q_c, the temperature dependence of

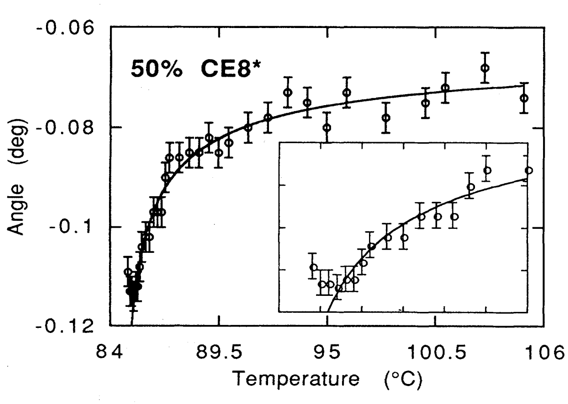

FIG. 1. Optical activity in the 50% mixture of CE8*. The inset shows the lowest temperature data; each horizontal division is 0.5 °C and each vertical division is 0.01°. The solid line is the least-squares fit using Eq. (3) with the three lowest temperature points omitted. The wavelength of the light is 488 nm and the sample thickness is 100 μm.

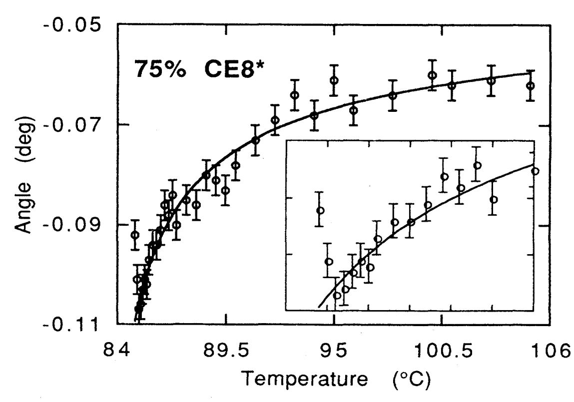

FIG. 2. Optical activity in the 75% mixture of CE8*. The inset shows the lowest temperature data; each horizontal division is 0.5 °C and each vertical division is 0.01°. The solid line is the least-squares fit using Eq. (3) with the two lowest temperature points omitted. The wavelength of the light is 488 nm and the sample thickness is 100 μm.

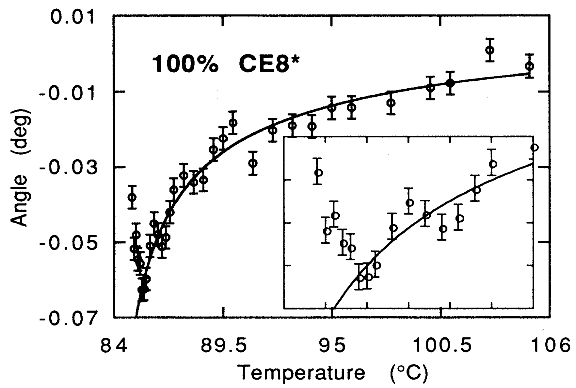

FIG. 3. Optical activity in the 100% mixture of CE8*. The inset shows the lowest temperature data; each horizontal division is 0.5 °C and each vertical division is 0.01°. The solid line is the least-squares fit using Eq. (3) with the five lowest temperature points omitted. The wavelength of the light is 488 nm and the sample thickness is 100 μm.

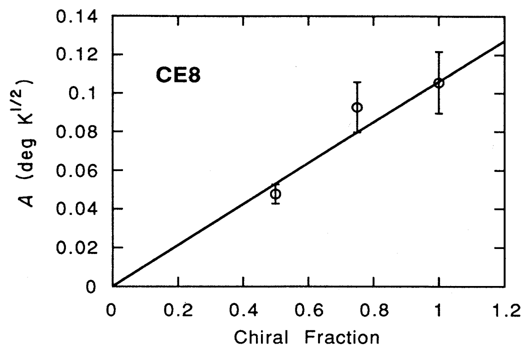

FIG. 4. Dependence of the parameter A in Eq. (3) on chirality. The straight line through the origin has been drawn to aid the eye.

the fluctuations should depend on chirality, although without firm knowledge of the free-energy coefficients it is difficult to determine how large this effect is. As can be seen from Table I, the results reported here do not allow for a strong conclusion, although there is some indication that T^* decreases with increasing chirality as is the case for the isotropic phase [9]. The values for ϕ_0 are also interesting. They represent the intrinsic optical activity of the molecules themselves (which is positive in CE8), and the optical activity of the smectic phase due to the correlations which result from interactions between the chiral molecules. This latter effect has been investigated by Osipov using the molecular field approximation [10]. Unfortunately, even the sign, not to mention the magnitude, of the optical activity depends on molecular parameters which are not known for CE8.

As predicted, the temperature interval over which the contribution of the planar spiral mode is important definitely increases with chirality. It is worthwhile to determine if the theory is also quantitatively correct. Equation (4) can be used to estimate this temperature interval in CE8*, since the wavelength of the light in CE8* (0.30 μm) and the pitch of CE8* (0.40 μm) are known [11]. The bare correlation length can also be estimated from relaxation-time measurements in the smectic-A phase of CE8* just above the smectic-C^* transition (1.6 nm) [11]. These numbers give temperature intervals of 0.31, 0.46, and 0.61 K for the 50%, 75%, and 100% mixtures, respectively, which agree nicely with the data.

One last interesting feature of the data is that the optical activity decreases rapidly but is still negative after entering the smectic-C^* phase. It crosses zero about 0.4 K below the transition. This indicates that the fluctuations in the smectic-C^* phase include a contribution from the conical spiral structural mode, since this is the mode with negative optical activity. This is similar to what occurs just below the isotropic to blue phase transition, where the optical activity crosses zero just below the transition, as the planar spiral mode which dominates the blue phase contributes more to the optical activity than the conical spiral mode which dominates the optical activity of the isotropic phase [12]. In the rest of the smectic-C^* phase, the optical activity is positive and increases linearly with decreasing temperature as has been reported previously [13].

CONCLUSION

By using mixtures of a highly chiral liquid crystal and its racemate, a strong experimental test of the theory for the optical activity produced by fluctuations in the smectic-A phase has been performed. The dependence of the optical activity on chirality, the nonmonotonically increasing temperature dependence of the optical activity in the vicinity of the transition to the smectic-C^* phase, and the temperature interval over which the planar spiral mode is important all show quantitative agreement with the theory.

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