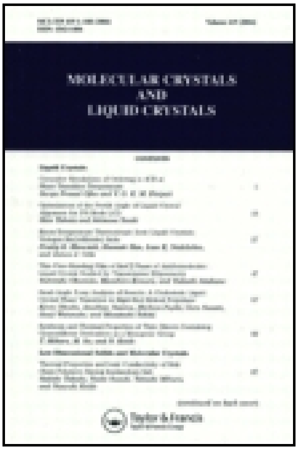

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Mary B. Atkinson [a] & Peter J. Collings [a]
[a] Department of Physics, Kenyon College, Gambier, Ohio, 43022

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Optical Rotatory Power in the Isotropic Phase of Four Cholesteryl Esters

MARY B. ATKINSON and PETER J. COLLINGS
Department of Physics, Kenyon College, Gambier, Ohio 43022

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Recent theoretical work by numerous authors has indicated that pretransitional properties of the isotropic phase are highly dependent on the chirality of the nearby ordered phase. To test this aspect of the theories, we present results on the optical rotatory power in the isotropic phase for a series of four cholesteryl esters of varying chirality. The most important finding is that the separation between the first and second order transition temperatures decreases with an increase in chirality. However, the results of a recent experiment which claimed to present evidence for strong coupling between the structural modes of the ordered phase are not substantiated by the new measurements reported here.

Keywords: cholesteric liquid crystal, optical rotatory power

INTRODUCTION

Recent theoretical and experimental work in liquid crystalline systems of high chirality has revealed that the transition from the isotropic phase to an ordered chiral phase is significantly different due to the presence of chirality. For example, the presence of the so-called blue phases found only in chiral systems testifies to the fact that the chiral symmetry of the ordered phase has an important effect on the free energy of such phases. Although these blue phases have been the subject of significant theoretical and experimental work,[1-7] much less attention has been paid to the transition from the isotropic phase to the ordered phase itself. Yet a number of theoretical investigations indicate that this transition is significantly altered by the chiral symmetry. To be specific, work by three theoretical groups predict that the chiral structure of the ordered phase can be represented by combinations of five basic modes, each of which has a different second order transition temperature.[8-10] Physical properties of the isotropic phase depend on the fluctuations in these five modes in different ways, indicating that the pretransitional phenomena in these systems should be very different, depending on which experimental property is being probed. In the one theoretical calculation where coupling between these modes was considered, even more exotic behavior was predicted for the pretransitional optical rotatory power.[11] Experimental evidence for such behavior was reported recently for one chiral system.[12]

A systematic investigation of a pretransitional property is certainly needed. For this reason, we examined the pretransitional optical rotatory power in the series of cholesteryl esters, in an attempt to investigate the dependence of this property on the chirality of the ordered phase. This series has been the subject of numerous studies so it has been well-characterized. In addition, the one reported piece of experimental evidence for the effect of mode coupling is in one of these cholesteryl esters, so such an investigation would also help to confirm or question this single finding. In this report, we present data on the pretransitional optical rotatory power in four cholesteryl esters of varying chirality. The experimental data are in good agreement with certain qualitative and quantitative predictions of the theory, but evidence for the importance of mode coupling in these esters is absent.

THEORY

All recent theoretical work is based on representing the long-range orientational order by the anisotropic part of the local dielectric tensor. Optical rotatory power results whenever this tensor lacks inversion symmetry. This tensor is zero in the isotropic phase, but short-range order over some correlation radius can result in a nonzero, fluctuating average over a small volume element. Near the transition to the ordered phase, the correlation radius grows and causes an increase in the small amount of optical rotatory power present due to the short-range order. Since the anisotropic local dielectric constant is a symmetric tensor with zero trace, it can be represented in terms of five independent modes. Using the notation of Ref. 10, $m = 2$ represents a planar spiral mode where two local principal axes rotate around the third, remaining perpendicular to each other and the spiral axis. The $m = 1$ mode represents a conical spiral mode where two local principal axes rotate around a spiral axis, but each makes an angle of 45 degrees with this axis. Finally, the $m = 0$ mode represents a non-chiral, nematic-like mode. The $m = -2$ and $m = -1$ modes are similar to the $m = 2$ and $m = 1$ modes respectively, but rotate in the opposite sense. All structures with long-range orientational order can be represented by a linear combination of these five modes; for example, the structure of the cholesteric phase with a right-handed helix can be represented by the proper combination of the $m = 0$ and $m = 2$ modes.

The theories start with the Landau-deGennes free energy for a cholesteric liquid crystal correct to fourth order in the fluctuations. The coefficients in front of the four quadratic terms are given the symbols a, b, c, and d, with $a = a_0(T-T^*)$, where T^* is the second order transition temperature for a racemic mixture. The coefficients for the third and fourth order terms are given the symbols μ and λ respectively. Expressing the anisotropic local dielectric tensor in terms of the five modes and retaining terms up to second order gives the following expression for the free energy:

$$F - F_0 = \frac{1}{2}\sum_m \int d^3q \left[a - mdq + \left\{ b + \frac{c}{6}(4 - m^2) \right\} q^2 \right] \left| \epsilon_m(q) \right|^2 , \qquad (1)$$

where m is the label for the mode, q is the wavevector, and $\epsilon_m(q)$ is the amplitude of the mode. Substituting into this equation the expression for the coefficient a allows one to solve for the temperature at which the free energy associated with each mode vanishes, *i.e.*, the temperature at which the correlation radius for each mode diverges. Again using the notation of Ref. 10, these temperatures can be written:

$$T^*_{\pm 2} = T^* \pm \frac{bq_0^2}{a_0} \qquad (2a)$$

$$T^*_{\pm 1} = T^* \pm \frac{1}{4\left(1 + \dfrac{c}{2b}\right)} \frac{bq_0^2}{a_0} \qquad (2b)$$

$$T^*_0 = T^* ,$$

where q_0 represents the chirality of the system, $q_0 = d/b = 4\pi/P$. P is simply the pitch of the system. Of course, the first-order transition to the ordered phase occurs at a temperature T_c, which is greater than the five T^* temperatures.

If each mode is assumed to contribute independently to the pretransitional optical rotatory power (no coupling between the modes), only the $m = 1$ and $m = -1$ modes need be considered.[8] This property will therefore tend to diverge at a temperature equal to T_1^*. If one expresses the Landau optical activity tensor in terms of these two modes, then applies the equipartition theorem to determine the amplitude of the fluctuations in each mode, and finally integrates over all wavevectors, one obtains a result for the pretransitional optical rotatory power

$$\phi = \frac{k_B k_0^2 q_0}{48\pi\bar{\epsilon}\sqrt{a_0 b}}\left[1 + \frac{c}{2b}\right]^{-3/2} \frac{T}{(T - T_1^*)^{1/2}} + \phi_0 , \tag{3}$$

where k_B is Boltzmann's constant, k_0 is the wavevector of the light, $\bar{\epsilon}$ is the average dielectric constant, and ϕ_0 is the molecular optical rotatory power. Of course the actual (first-order) transition to the ordered phase occurs at T_C, which is higher than T_1^*. All of the results of this section are only valid for temperatures above T_C.

It is useful to compare the actual transition temperature to the temperatures at which fluctuations in the various modes diverge. Unfortunately in highly chiral systems, this first-order transition can occur between the isotropic phase and one of the three blue phases or between the isotropic phase and the cholesteric phase. The result for the latter transition has been worked out by equating the free energies (correct to fourth order) of the isotropic and cholesteric phases,[10]

$$T_C = T^* + \frac{\mu^2}{27\lambda a_0} + \frac{3}{4}\frac{bq_0^2}{a_0} . \tag{4}$$

This transition temperature can be rewritten in terms of T_2^* and T_1^*, the two highest of the five second-order transition temperatures:

$$T_C = T_2^* + \left[\frac{\mu^2}{27\lambda a_0} - \frac{1}{4}\frac{bq_0^2}{a_0}\right] \tag{5a}$$

$$T_C = T_1^* + \left[\frac{\mu^2}{27\lambda a_0} + \frac{1}{4}\left(\frac{2 + \frac{3c}{2b}}{1 + \frac{c}{2b}} \right) \frac{bq_0^2}{a_0} \right], \qquad (5b)$$

with the stipulation, of course, that T_C is greater than T_2^*. According to the theory, therefore, an increase in the chirality (decrease in the pitch) with the Landau-deGennes free energy coefficients remaining constant will cause the transition to occur closer to T_2^* and farther from T_1^*. Of course highly chiral samples have the first-order transition between the isotropic phase and one of the blue phases, but since the free energies of the cholesteric and blue phases are so similar (relative to the isotropic phase), one might expect this dependence on chirality to still manifest itself.

Filev has worked out the effect of mode coupling on the pretransitional optical rotatory power.[11] Since T_2^* is higher than T_1^*, it might be possible in a highly chiral system for T_C to be very close to T_2^* without it being extremely close to T_1^*. In this case coupling between the $m = 2$ and $m = 1$ mode will be large. Filev calculates that this contribution will cause rotation in the opposite sense from the normal $m = 1$ mode contribution, so one would expect to see a non-monotonically increasing optical rotation just before the transition. Figure 1 illustrates this result by graphing the theoretical curves for the pretransitional optical rotatory power with and without taking coupling between the modes into account. Whereas numerous experiments have verified Eq. (3) in isolated chiral systems,[9,13] an experiment by Demikhov and Dolganov[12] reported that the pretransitional optical rotatory power of cholesteryl nonanoate deviated from Eq. (3) near the transition, qualitatively exhibiting the behavior predicted by Filev.

EXPERIMENT

The magnitude of the pretransitional optical rotatory power in the cholesteryl esters is extremely small; a rotation measurement system of high precision is therefore required. Our system utilized a rotating analyzer[14,15] and was capable of measuring rotation angles to ±0.01°. Light from a He–Ne laser was slit into two beams, both of which

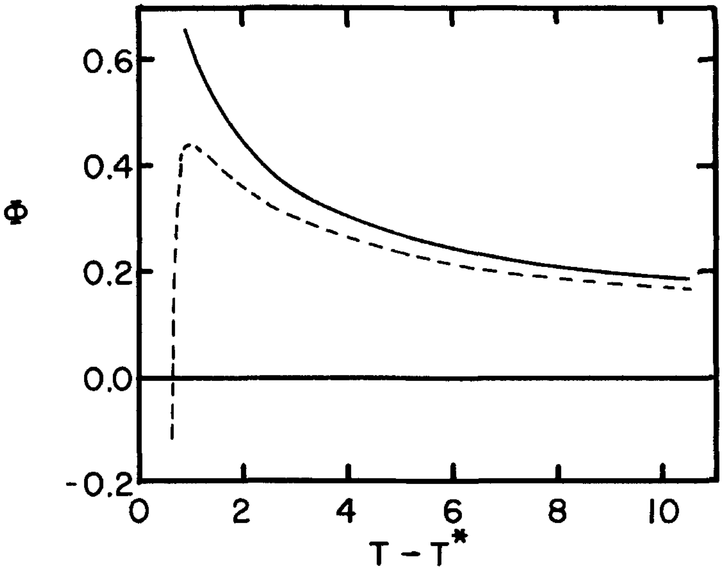

FIGURE 1 Theoretical dependence of the pretransitional optical rotatory power on temperature. The units of both axes are arbitrary. Solid curve: according to Refs. 9, 10, and 13. Dashed curve: according to Ref. 11.

passed through the same linear polarizer. One beam then passed through the sample while the other did not. Both beams then passed through the linear analyzer, which rotated with a frequency of about 13 Hz. Each beam was detected by a silicon photodiode detector and both outputs were fed to a computer. The computer sampled two periods of each output simultaneously, measuring the period and phase shift between the two waveforms. The optical rotation angle was calculated from these two measurements. This procedure was in fact performed repeatedly by the computer and averaged, easily achieving the desired measurement precision.

The cholesteryl esters were purchased from either Kodak or Frinton Laboratories; the compounds from Kodak were recrystallized several times while the others were used without performing additional purification procedures. The sample was contained in a glass spectrophotometer cell (1 cm path length), which was placed in a thermostatically controlled oven. We estimate the temperature homogeneity in the sample to be around 50 mK, since transitions detected by this apparatus possessed a width of this amount.

Measurements of the pretransitional optical rotatory power were taken with increasing temperature, starting at a temperature in the ordered phase. Although the intensity of the transmitted beam was large in both the blue phases and the isotropic phase, the presence of a two phase region was easily detected by a reduction in the intensity of the beam. This phenomena is in fact what one would expect considering the long path length in the sample (1 cm) and the scattering of light by droplets of one phase in another. In selecting those data points which represented measurements in the isotropic phase, we chose only those points which possessed the full intensity. This procedure insured that the data did not include measurements which were influenced by the much larger optical rotatory power of the ordered phase. The results of such a procedure are shown in Figure 2 for cholesteryl nonanoate. To see whether this data conforms to Eq. (3), the data was fit to the theoretical expression, generating values for T_1^*, the molecular optical rotatory power ϕ_0, and the coefficient in front of the temperature expression. This fit is most easily evaluated by plotting the data as shown in Figure 3. The linear relationship for all of the data (except for a few points very far from the transition) agrees with both the results using other compounds,[9,13]

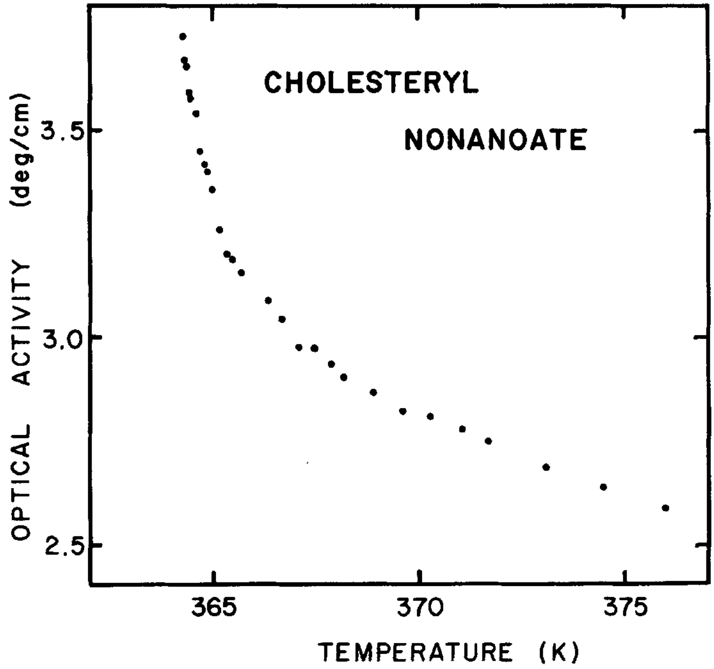

FIGURE 2 Pretransitional optical rotatory power in cholesteryl nonanoate. Wavelength of light is 633 nm.

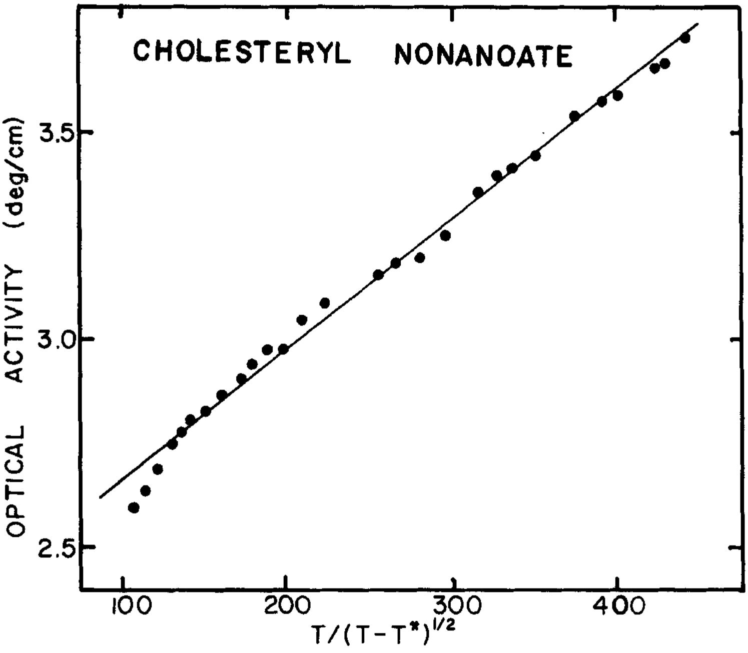

FIGURE 3 Pretransitional optical rotatory power in cholesteryl nonanoate. The straight line is the best fit to Eq. (3) using all but the five points farthest from the transition. Wavelength of light is 633 nm.

and with the data for cholesteryl nonanoate reported in Ref. 12 (ignoring the data within 300 mK of the transition).

Similar results were obtained in cholesteryl myristate, pentanoate, and proprionate. There was no evidence for any deviation from Eq. (3) near the transition and in each case the data could be fit very well to this function. Since each of these compounds possesses a different chirality, a graph of $T_c - T_1^*$ should reveal the dependence of this quantity on chirality. This is shown in Figure 4, where the blue phase stability regions are also included.[16] The spacing between the transition temperature and the $m = 1$ second-order transition temperature clearly becomes smaller as the chirality is increased.

DISCUSSION

These results bring into question whether the chirality of cholesteryl nonanoate is high enough to see the effect of mode coupling. The temperature region in which Demikhov and Dolganov saw the effect was six times our temperature homogeneity, implying that we should have easily detected such behavior. In fact, our data did show such an effect, but only in the 50 mK region where the intensity of the beam was significantly diminished. We are convinced that this is the transition region to the blue phase, since it occurs at a temperature above the BP I–BP II transition which agrees with previous data on these phases.[16] The BP III is only 70 mK wide in this compound, so it can not be observed due to our 50 mK temperature inhomogeneity. The important point is that if such a mode coupling effect occurs in cholesteryl nonanoate, based on our measurements it must take place within 50 mK of the transition, a region considerably smaller than the 300 mK region reported by Demikhov and Dolganov. Since the optical rotatory power of the ordered phase is much larger than in the isotropic phase and in the opposite sense, the presence of even a small amount of the ordered phase will in fact cause an effect similar to the predicted mode coupling effect. The question of whether cholesteryl nonanoate shows mode coupling behavior is therefore a delicate experimental problem which demands more work.

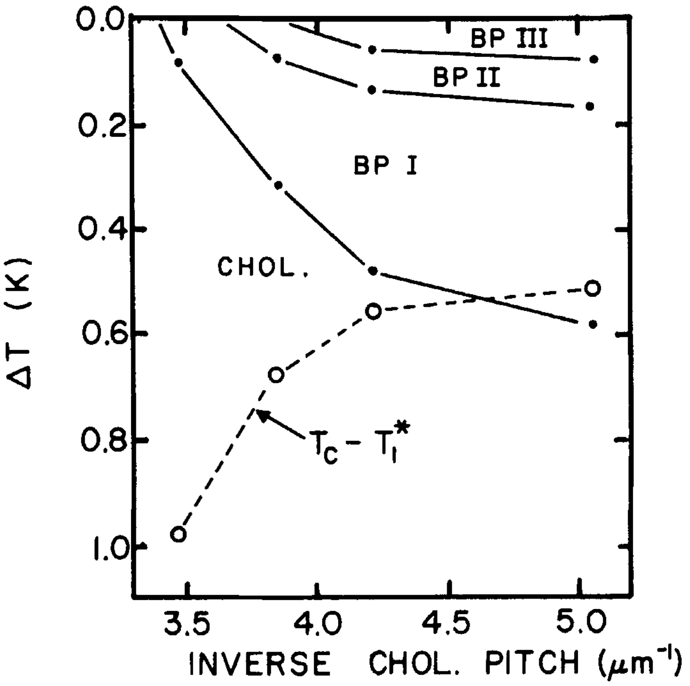

FIGURE 4 Relationship between the transition temperature T_C and the second-order $m = 1$ mode transition temperature T_1^* for four cholesteryl esters. The data on the blue phases are taken from Ref. 16.

An interesting observation from Figure 4 is that the closeness of the transition temperature to these second-order transition temperatures is correlated with the stability of the blue phases. This is of course contained within the theory, but perhaps not given proper weight in investigations thus far. Recent light scattering and Kerr effect experiments in the isotropic phase which are capable of measuring both $T^*_{\pm 2}$ and T^*_0 also point out this same correlation for these compounds.[17] The measured decrease in $T_C - T^*_1$ with increasing chirality is opposite to the theoretical dependence of Eq. (5b). This is not surprising, since the experimental T_C is not the transition to the cholesteric phase, and since the free energy coefficients probably are not constant for this system. Additional work on other systems (especially chiral-racemic mixtures) is called for to ascertain if this is in fact a general result.

CONCLUSION

The question of whether the cholesteryl esters show the effect of mode coupling remains open. Efforts are underway in our laboratory to increase the temperature homogeneity of our apparatus to 10 mK and repeat the cholesteryl nonanoate experiment. However, this system is clearly a marginal case at best; we therefore plan to conduct experiments in systems with a chirality higher than possible with the cholesteryl structure. Such an investigation should provide a good test for the prediction of Filev.

If a system where T_C is extremely close to T^*_2 is found, the optical rotatory power should not be the only property affected by mode coupling. In fact, all properties should be influenced, resulting in a transition of quite a different type. Theoretical work in this realm of chirality will also be needed to properly interpret such experimental results.

Acknowledgment

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