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Pretransitional Optical Rotation in the Isotropic Phase of Cholesteric Liquid Crystals*

Julian Cheng and Robert B. Meyer
Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts 02138

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A sharp increase of the rotatory power in the isotropic phase of cholesteric liquid crystals is observed near the isotropic-cholesteric liquid transition. This is interpreted as a manifestation of short-range chiral orientational order in the isotropic liquid. An application of the Landau–de Gennes theory predicts a $(T-T^*)^{-1/2}$ temperature dependence, in agreement with measured data in the immediate pretransition region.

The existence of short-range orientational order in the isotropic liquid phase of nematic liquid crystals is firmly established,[1,2] and the experimental observations are well explained by a phenomenological mean-field theory for nearly second-order phase transitions.[3,4] de Gennes's extension of this theory to cholesteric liquid crystals[4] was recently tested by Rayleigh-light-scattering experiments in the isotropic phase of a cholesteric system,[5] which showed that chirality plays a negligible role in Rayleigh scattering except for a narrow temperature range 0.68°C above T^*, the second-order transition temperature. In this region, the experimental data could not be explained by the de Gennes theory. In this Letter, we report the first experimental evidence for the existence of chiral short-range order in the liquid phase: the critical enhancement of optical rotatory power in the isotropic phase of cholesteric liquid crystals.

It is well known that the long-range spiral molecular orientational order of the cholesteric phase gives rise to optical rotatory powers as high as 10^4 deg/mm.[6] Substances possessing a cholesteric mesophase are also known to exhibit molecular optical activity. The chiral ordering dominates the optical activity of the ordered phase. In the absence of any orientational order, the isotropic liquid would exhibit only the molecular optical activity, which is very weakly dependent on temperature. If chiral short-range order exists in the isotropic phase, then the orientations of different molecules may be coupled in a manner preserving a local spiral conformation over a small correlation distance, which should strongly enhance the optical rotatory power of the liquid. This enhancement is a direct measure of the degree of chiral short-range order.

Experimental analysis is complicated by the fact that the rotatory power of the helical conformation, φ_C (φ_{chiral}), and the molecular optical activity φ_0 both depend on the local molecular environment and may become temperature dependent as the local order builds up near the phase transition. Since both contribute to the observed rotations, any scheme for extracting the temperature dependence of φ_C from the data requires justification. This can be circumvented if φ_C predominates. Since this effect should vary quadratically with dielectric anisotropy $\Delta\epsilon$, we chose to study materials for which $\Delta\epsilon$ is large and whose molecular optical activity is small. Esters of cholesterol were found to be unsuitable, since they give rise to $\varphi_C < 1°$/cm at 6328 Å, while φ_0 is 2.5 to 4.0°/cm. Thus we turned to chiral molecules with a structure similar to that of typical nematics ($\Delta\epsilon = 0.7$ or more), for which φ_C should be more than 2 orders of magnitude larger than for the cholesterol esters, while φ_0 should remain small.

With this as motivation, Dr. D. Dolphin and Dr. Z. Muljiani prepared several "chiral nematic" compounds by making Schiff's bases containing optically active and racemic β-methlbutylaniline. The optically active compounds p-alkoxybenzal-p'-(β-methylbutyl)aniline form a right-handed cholesteric mesophase, while their racemic counterparts form a nematic mesophase with identical physical and thermodynamic properties (phase diagrams, transition enthalpies, birefringence, etc.) Mixtures of active and racemic forms of a given compound produce a chiral nematic phase in which the torsion q_0 ($=2\pi$/pitch) varies linearly with composition, while other thermodynamic properties are independent of composition. Such mixtures may then be treated as one-component systems.[7]

We have measured the optical rotatory power in the isotropic phase of (I) (+)-p-ethoxybenzal-p'-(β-methylbutyl)aniline (EBMBA), and (II) a 30.15% dextro-EBMBA + 69.85% racemic EBMBA mixture, with pitches of 2180 and 7280 Å, respectively, in the ordered phase. Samples were carefully purified and protected against decomposition in cells 5 cm long, and the temperature was stabilized to 0.001°C. The polarimetry was accurate to 0.02° arc, and the source was a He-Ne laser (6328 Å).

The temperature dependences of the rotatory power of both samples are shown in Fig. 1, in which we have divided the rotation scale of sample II by 0.3015, the concentration of active EBMBA in the mixture, and shifted its temperature scale by 0.15°C to compensate for a small difference between the second-order transition temperatures T^* of the two samples (probably due to a small difference in purity of the two samples). The two curves are identical, which, in view of the linear dependence of inverse helix pitch on concentration, suggests the following: (1) The chiral parameter q_0 of the isotropic phase, which we interpret as the effective torsion of the short-range order, has no effect on the temperature dependence of the rotatory power. (2) The size of the rotatory power is linearly dependent on the concentration of active EBMBA, and therefore on q_0. (3) The sense of the rotation is independent of the ratio of the wavelength of light to the helix pitch, in marked contrast to the optical rotatory dispersion of the ordered phase. The rotatory power varies significantly over a large temperature range, becoming singular as $T \rightarrow T^*$, but the singular behavior is cut off at a temperature T_c by the first-order phase transition. ($T_c = 60.565°$ C for I and 60.75°C for II.)

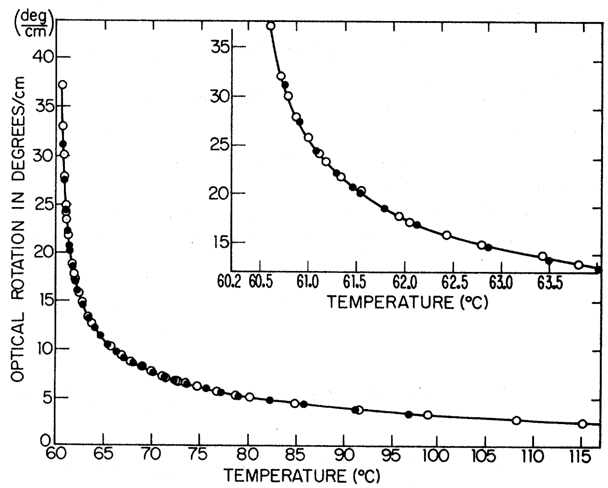

FIG. 1. Open circles, optical rotation of sample I; closed circles, sample II as a function of temperature in the isotropic phase. The rotations of II have been divided by 0.3015 and its temperature scale shifted by 0.15°C. The inset gives a magnified view of the pretransition region ($\lambda_0 = 6328$ Å).

The value of the molecular optical activity in the absence of local order effects is approximated by measuring the rotatory power of dilute solutions of dextro-rotatory EBMBA in benzene and CCl_4, at concentrations of 2%, 5%, and 10%. Extrapolation to 100% EBMBA for each solution, taking into account the Lorentz factors $(n^2+2)/3$, gives values of 0.98°/cm in benzene and 1.028°/cm in CCl_4, with a spread of 0.03 for different solutions. This is quite small compared to the peak rotation observed in pure EBMBA of 37°/cm, so that the rotation due to chiral ordering is clearly the dominating effect.

We interpret the effect in terms of de Gennes's phenomenological theory. Only a qualitative description will be presented here.[8] The free energy F is expanded to second order in a tensorial order parameter $Q_{\alpha\beta}$, which is defined in terms of the local dielectric susceptibility tensor $\chi_{\alpha\beta}$:

$$Q_{\alpha\beta} = \frac{6\pi}{\Delta\epsilon}\left[\chi_{\alpha\beta}(r) - \tfrac{1}{3}\delta_{\alpha\beta}\chi_{\gamma\gamma}\right] = \frac{6\pi}{\Delta\epsilon}\chi_{\alpha\beta}{}^{a}(r), \qquad (1)$$

$$F = F_0 + \tfrac{1}{2}AQ_{\alpha\beta}Q_{\beta\alpha} + \tfrac{1}{2}L_1\partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma} + \tfrac{1}{2}L_2\partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} + q_0 L_1 \epsilon_{\alpha\beta\gamma}Q_{\alpha\mu}\partial_\gamma Q_{\beta\mu}. \qquad (2)$$

In the absence of the last term, F has the same form as for a nematic, and has a fluctuation spectrum in which different components of $Q_{\alpha\beta}$ are uncorrelated. The last term, the lowest-order chiral term for a cholesteric, couples different components of $Q_{\alpha\beta}$, thereby coupling the orientational order in different directions in a way which destroys local inversion symmetry. These correlations persist only over a short coherence length $\xi = (L_1/A)^{1/2} \propto (T-T^*)^{-1/2}$ according to mean-field theory. They contribute to the macroscopic properties of the medium by altering the dielectric susceptibility, giving it a spatially dependent character responsible for optical activity. This effect is calculated via a model outlined by de Gennes in which we picture each molecule to be polarized by an effective local electric field containing the phase-shifted dipole fields of all other molecules. The average polarization is given by

$$\begin{aligned}\langle P_\alpha(k)\rangle &\cong \int d^3r\, V^{-1}\langle \chi_{\alpha\beta}(\vec{r})\{E_\beta{}^0 + \int T_{\beta\gamma}(\vec{r}-\vec{r}\,')\chi_{\gamma\mu}(\vec{r}\,')E_\mu{}^0 \exp[i\vec{k}\cdot(\vec{r}-\vec{r}\,')]d^3r'\}\rangle \\ &= [\chi^0\delta_{\alpha\beta} + V^2\int d^3q\,(2\pi)^{-3}\langle\tilde{\chi}_{\alpha\mu}{}^a(\vec{q})\tilde{\chi}_{\nu\beta}{}^{a}{}^*(\vec{q})\rangle\tilde{T}_{\mu\nu}(\vec{k}-\vec{q})]E_\beta{}^0, \qquad (3)\end{aligned}$$

where $T_{\mu\nu}(\vec{R}) = (3R_\mu R_\nu - \delta_{\mu\nu}R^2)/R^5$ and $\tilde{T}_{\mu\nu}(\vec{q})$ is its Fourier transform, χ^0 is the mean susceptibility, V is the volume, $\vec{k} = n\vec{k}_0$ is the optical wave vector in the medium, and $\vec{E}^0$ is the incident field. The calculated rotatory power, to the lowest order in $k\xi$,[9] is given by

$$\varphi_C = \frac{k_BT}{L_1}\frac{(\Delta\epsilon)^2}{90\pi}k_0{}^2q_0\xi. \qquad (4)$$

Higher orders in $k\xi$ add negligible corrections.

An order-of-magnitude check can be performed to test the plausibility of this result. Using the known parameters of the chemically similar p-methoxy-benzylidine, p-n butyl-aniline in (4), $L_1 = 1.0\times10^{-6}$ erg/cm, $\xi = 145$ Å at $T^* + 1$°C,[1,2] and the measured $q_0(T_0) = 2.85\times10^5$ cm^{-1}, $T^* = 332.4$° K, and the extrapolation $\Delta\epsilon = 0.66$,[7] we obtain $\varphi = 0.32$ rad/cm $= 18$°/cm, compared with the observed value of 22°/cm at $T^* + 1$°C. The difference is easily accounted for by slightly different values of L_1 and ξ for our sample of EBMBA.

We tried to fit the data of sample I by the form

$$\varphi = \varphi_O + \text{const}\times T(T-T^*)^{-\gamma}, \qquad (5)$$

where φ_O is the molecular optical activity. The parameters T^*, φ_O, and γ are to be determined. Our procedure assumed $\gamma = 0.50$ as predicted by mean-field theory, and varied φ_O to obtain the best linear fit to $T^2/(\varphi-\varphi_O)^2$. In practice, no value of φ_O gives a linear fit over the entire 55°C range measured, but for $\varphi_O = 1.00$°/cm, an excellent fit obtains over a region within 6°C of T^*. For other values of φ_O, the linear region shifts away from T^*. No other value of γ gives a linear fit to $[T/(\varphi-\varphi_O)]^{1/\gamma}$ in the pretransition region. For the reasons that (1) the molecular optical activity in dilute solution is 1.00°/cm, and (2) this value gives the best linear fit in the pretransition region, in which the largest and most meaningful effects are observed, we set $\varphi_O = 1.00$°/cm, which leads to the value $T^* = 60.25$°C. To demonstrate the temperature dependence of this fit, we plotted $\log(\varphi-\varphi_O)$ versus $\log(T-T^*)$ in Fig. 2, which shows an excellent linear fit in the pretransition region with a slope of -0.49. Finally, we note that $T_c = T^* + 0.31$°C, so that using the previous estimates we obtain $\xi(T_c) = 250$ Å and $q_0\xi(T_c) = 0.71$. This is consistent with the de Gennes prediction that the first-order transition must occur before the isotropic phase becomes absolutely unstable at $q_0\xi = 1$.

We propose the following explanations for the discrepancy between the mean-field prediction and observed data at higher temperatures:

(i) The mean field holds only in the vicinity of the transition, where the coefficients of the Landau expansion are independent of temperature. Far from T^*, this assumption fails and the temperature dependence of all coefficients must be considered. In particular, the parameter q_O describing the strength of the chiral coupling in the

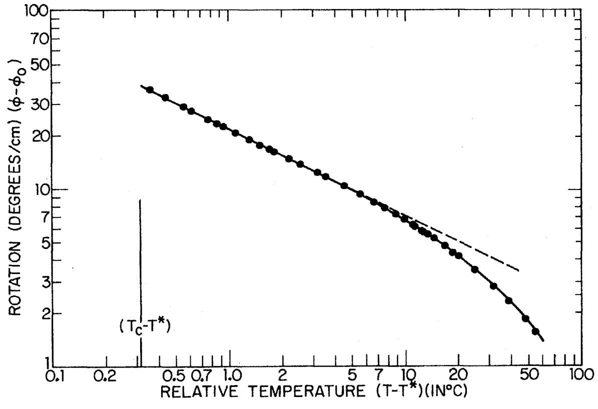

FIG. 2. $\log(\varphi-\varphi_O)$ as a function of $\log(T-T^*)$, showing the -0.50 exponent in the pretransition region. The sample is I, pure dextro-EBMBA, and $\lambda_0 = 6328$ Å.

liquid may decrease at higher temperatures, where thermal fluctuations have destroyed the local orientational order sufficiently to decrease the effectiveness of the shorter-range chiral perturbations[10] in producing twisted structures. L_1 and L_2 may also become temperature dependent (probably much less so than q_0, as suggested by some preliminary measurements on ξ). One may adopt the viewpoint that mean-field theory is correct and let the discrepancy define the temperature dependence of q_0.

(ii) Treating φ_0 as a constant assumes it is not coupled to the local order. While this can be justified by order-of-magnitude arguments on the orientational-order's contribution to the Lorentz local field, the theories of optical activity[11] are suspect in their applicability to anisotropic, orientationally correlated molecules. An enhancement of φ_0 near T^*, where there is a large degree of local order, may partially explain the discrepancy.

Finally, a few remarks on the different behavior of optical rotation in the ordered and liquid phases. According to de Vries[6] rotation in the ordered phase is proportional to $q_0(1-\lambda^2)$, where λ is the ratio of optical wavelength in the medium to the pitch. Thus the sense of the rotation depends on λ as well as q_0. Our samples I and II correspond to $\lambda = 1.79$ and 0.54, respectively, and the fact that their rotatory powers in the isotropic phase are not of opposite signs is indicative of the absence of the long-range order which produces the factor $1-\lambda^2$. Following the rotatory power across the transition into the ordered phase, there will be a sign change for samples with $\lambda > 1$, as was indeed observed in cholesteryl nonanoate ($\lambda \cong 1.8$).

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Photoemission Verification of the Resonance Formulation of *d*-Band Metals

Neville V. Smith and Morton M. Traum
Bell Laboratories, Murray Hill, New Jersey 07974

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Photoelectron energy spectra have been measured on clean and cesiated samples of the fcc metals Rh, Ir, Pd, Pt, Cu, Ag, and Au. The behavior of structure on varying the photon energy shows a consistent pattern across the series in agreement with the resonance picture. The data are used to construct empirical band structures.

The resonance picture[1-3] of the noble and transition metals has provided valuable insight into the nature of their band structures. The *d* bands are considered to arise through a singularity, or resonance, in the tangent of the $l = 2$ phase shift. As a consequence, once the position and width of the resonance have been specified, the internal features of the *d* bands, although complicated, are almost completely determined and, apart from a scaling, should be the same for metals of the same crystal structure. We will refer to this as the principal result of the resonance formulation. The result can be verified quite readily from a *theoretical* point of view by