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MAGNETICALLY INDUCED CHOLESTERIC-TO-NEMATIC PHASE TRANSITION IN LIQUID CRYSTALS*

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We optically observe the untwisting and alignment, along an applied magnetic field, of high-pitch cholesteric liquid crystals, mixtures of para-azoxyanisole and cholesteryl esters. The results agree quantitatively with de Gennes's predictions and allow a determination of the twist elastic constant of pure para-azoxyanisole.

The influence of a magnetic field on a nematic liquid crystal (LC) composed of diamagnetic anisotropic molecules is well known since the experiments of Mauguin[1] and, later, Freedericksz.[2] The effect of a magnetic field on cholesteric liquid crystals has recently been observed by Sackmann, Meiboom, and Snyder,[3] using an indirect NMR technique; beyond a critical value H_c, the magnetic field can untwist the cholesteric texture and locally align the rodlike molecules. In this Letter, we present what we believe to be the first direct optical observation of such a cholesteric-to-nematic phase transition, induced by the application of a static magnetic field on cholesteric liquid crystals.

This effect has recently been computed by de Gennes[4] using the Frank description[5] for the elastic free energy of the cholesteric liquid crystal. If we call K_{22} the "twist" elastic constant of the material, $\chi=\chi_{\|}-\chi_{\perp}$ $(\chi>0)$ the anisotropic part of its diamagnetic susceptibility, and p_0 the pitch of the undisturbed cholesteric texture, then the critical field condition is

$$H_c p_0=\pi^2(K_{22}/\chi)^{1/2}.$$

On increasing the magnetic field H, applied perpendicular to the cholesteric screw axis, the pitch p should first increase very slowly, and then diverge logarithmically for $H=H_c$; beyond H_c, the liquid crystal should be nematic.

The optical observation of this transition on pure liquid crystals is generally difficult if not impossible; for instance, for the well-known cholesteryl esters, p_0 and χ are comparatively small, resulting in a very large expected critical field ($H_c\sim100$ kG); moreover, they may well have a negative χ as in the few reported cases,[6] and would obviously not align along the magnetic field. In order to perform our experiment, we have used a cholesteric liquid crystal which is a mixture of an ordinary nematic compound, mainly the para-azoxyanisole (PAA), and a small fraction of an optically active material [cholesteryl chloride (CC), acetate (CA), nonanoate (CN), palmitate (CP), or decanoate (CD)]. By adjusting the mass concentration C of these asymmetric molecules, one obtains a cholesteric texture of variable pitch as formerly pointed out by Friedel[7]; at low C (~1%), the resulting pitch may be quite large (10-50μ) and χ is dominated by the large and positive value (~10^{-7} cgs) of the nematic PAA, both properties leading to a reasonably low critical field.

Our experimental apparatus consists of the slide and watch glasses of Freedericksz,[2] containing a drop of cholesteric LC (Fig. 1), placed in an oven at constant temperature T. $\vec{H}$ is parallel to the slide glass. The glass surfaces are rubbed, according to the Châtelain technique,[8] so

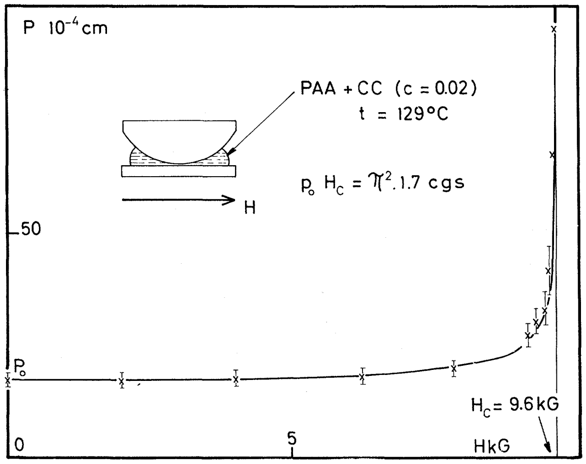

FIG. 1. Typical variation of the pitch p of the cholesteric LC versus the applied magnetic field H. The curve is drawn from de Gennes's (Ref. 4) theory.

that one can observe with a microscope the Frank-Cano disinclination[5,9] lines. The direction of rubbing is parallel to $\vec{H}$. For any value of H, one measures the pitch of the cholesteric LC from the distance between the disinclination lines in the variable thickness cell.

In the low-dilution regime $[0<C<0.1]$ the product p_0C is found constant as noted by Cano[10]; for instance, with the PAA + CC mixture, p_0C is equal to $0.34 \pm 0.03\,\mu$ at $T = 129°\mathrm{C}$.

On applying the magnetic field, one observes a radial expansion of the disinclination pattern, corresponding to the expected increase of the pitch; for a well-defined value H_C of H, the pattern moves off to infinity (p is infinite) and the sample is optically nematic; by decreasing H, the disinclination lines reappear, with some hysteresis, by nucleation on defects or dust. A typical plot of p vs H is given on Fig. 1 in good agreement with the de Gennes predicted curve. H_C is independent of the relative orientations of the rubbed surfaces and of the magnetic field. H_C is found to be a linear function of C as shown in Fig. 2, i.e., is inversely proportional to p_0, as expected.

From these results, one can derive the value of $(K_{22}/\chi)^{1/2} = 1.65 \pm 0.15$ cgs at $T = 129°\mathrm{C}$ for PAA; the main uncertainty is due to the observed hysteresis. Similar experiments with low-dilution CD, CN, CA, or CP in PAA give the same value for this constant, which appears as characteristic of the nematic PAA. The cholesteric-to-nematic transition has also been observed with the same features on mixtures of para-azoxyphenetole (PAP) + CC, with the $(K_{22}/\chi)^{1/2}$ value of 2.8 ± 0.3 cgs for PAP at 147°C. For PAA, our measurement of $(K_{22}/\chi)^{1/2}$ is slightly larger than the previous determination of Freedericksz[2] $[(K_{22}/\chi)^{1/2} = 1.50$ at 129°C$]$, using a completely different method based on the magnetic distortion of a nematic pure PAA sample; however, because of our present inaccuracy, this difference is not significant. For PAP, we are not aware of any independent measurement.

In conclusion, our experiments agree quantitatively with the cholesteric-to-nematic magnetic-field–induced transition theoretically described by de Gennes. This observation seems to us a good argument for supporting the commonly accepted model of the cholesteric texture, in the mixtures we used. We finally emphasize that this phase transition observation is a general experimental method for the determination of the "twist" elastic constant of all nematic materials.

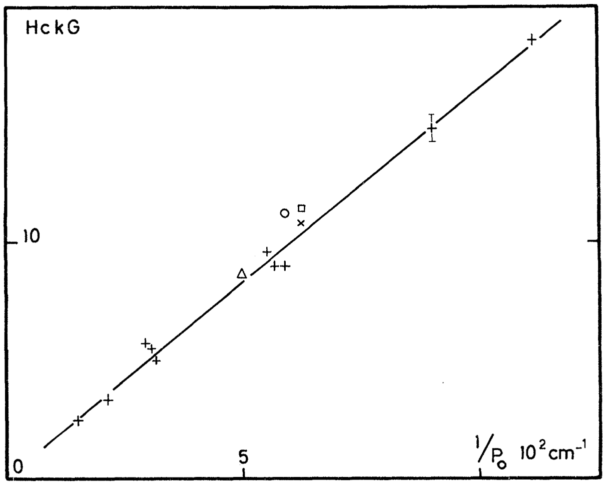

FIG. 2. Linear variation of H_C vs $1/p_0$ for various PAA cholesteric mixtures (+, CC; ○, CA; □, CD; ×, CN; △, CP). The low-concentration regime is close to the origin.

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