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T. Harada [a] & P. Crooker [a]

[a] Department of Physics and Astronomy, University of Hawaii, Honolulu, Hawaii, 96822

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The Temperature Dependence of the Pitch of CEEC

T. HARADA and P. CROOKER

Department of Physics and Astronomy, University of Hawaii, Honolulu, Hawaii 96822

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The pitch of cholesteryl 2-(2-ethoxyethoxy) ethyl carbonate (CEEC) is measured as a function of temperature and is shown to increase with increasing temperature, unlike the behavior of other single component cholesteric liquid crystals. We find that improved sample purification shifts the pitch horizontally on the temperature axis, while sample aging causes an increased disorientation of the sample domains themselves.

INTRODUCTION

In 1967, Durand[1] reported that the sense of the pitch helix of cholesteryl 2-(2-ethoxyethoxy) ethyl carbonate (CEEC) is right handed below 30°C, inverting and becoming left handed as the temperature is raised above 30°C. This behavior had not been previously observed in any single component cholesteric liquid crystal, although similar effects had been observed in mixtures of liquid crystals of opposite handedness.[5]

In 1970, Leder[2] and Baessler, *et al.*[3] studied carefully purified CEEC and demonstrated that the pitch inversion seen by Durand was in fact caused by the presence of impurities. Leder[2] purified CEEC using standard chemical separation techniques and measured the wavelength of maximum reflection in a variety of mixtures of CEEC with cholesteryl chloride (right handed) and cholesteryl *n*-propyl carbonate (left handed). By extrapolating his results to zero mixing ratio, he obtained the wavelength of maximum reflection nP_0 (n = mean refractive index and P_0 = full pitch of the helix) of CEEC itself. According to Leder, CEEC is cholesteric up to 32°C and the value of nP_0 is about 2.5 μm at room temperature.

Baessler, *et al.*,[3] on the other hand, measured the optical rotatory power of CEEC which had been purified by column chromatography. Their results indicate that CEEC is cholesteric between 15°C and 31°C and that the value nP_0 is 0.9 μm at room temperature. Although the two authors explained Durand's observations, the disagreement between their room temperature values of nP_0 is too large to be overlooked. Furthermore there has as yet appeared no systematic measurement of the behavior of pitch with temperature in CEEC despite the fact that CEEC has been used widely in other experiments on cholesteric liquid crystals, some of them conflicting.[6] In order to make the situation clearer, we have repeated the measurements of Durand using carefully purified CEEC samples. In the presentation of our results, the effect of sample purity on pitch behavior and on the cholesteric-isotropic transition temperature is shown. Finally, we are able to provide insight, in a qualitative way, on the aging process in prepared CEEC samples.

EXPERIMENTAL METHOD

The method used in our measurements is essentially the same Bragg scattering technique used by Durand.[1] If a beam of laser light is passed perpendicularly through a thin sample of liquid crystal, the scattered light is observed to lie on a cone about the axis of the unscattered laser beam. The angular location of this cone in the sample is given by the wavevector conservation equation $\mathbf{k} - \mathbf{k}' = 2\mathbf{q}_0$, where $\mathbf{k}$ and $\mathbf{k}'$ are the wavevectors in the sample of the incident and scattered light, and $\mathbf{q}_0 = 2\pi/P_0$ in the direction of the pitch axis. In order to experimentally determine the pitch, the scattering angle θ in the sample is measured. The above equation then yields the "optical pitch" $nP_0 = \lambda/\sin(\theta/2)$ where λ = laser wavelength in air and n is the mean index of refraction of the sample. Since the index of refraction n in CEEC depends only weakly on temperature,[7] the behavior of the "optical pitch" with temperature is proportional to the behavior of the pitch itself. In most applications, nP_0 is a more useful quantity than the true pitch, and in what follows, we shall use the word pitch to denote nP_0 without ambiguity.

In Figure 1, we show the experimental apparatus. The CEEC sample was sandwiched between a microscope slide and a cover slip held 0.25 mm apart by a glass spacer. Samples were prepared in a dry nitrogen atmosphere to protect against oxidation and possible contamination by water vapor, and sealed hermetically with vacuum grease. The sample cell was contained in a massive brass block whose temperature was controlled to within ±0.05°C by a water circulator. The temperature was measured by a thermistor calibrated to an accuracy of ±0.05°C. Unpolarized light from a 1 mw He—Ne laser was directed onto the sample through a tunnel in the brass

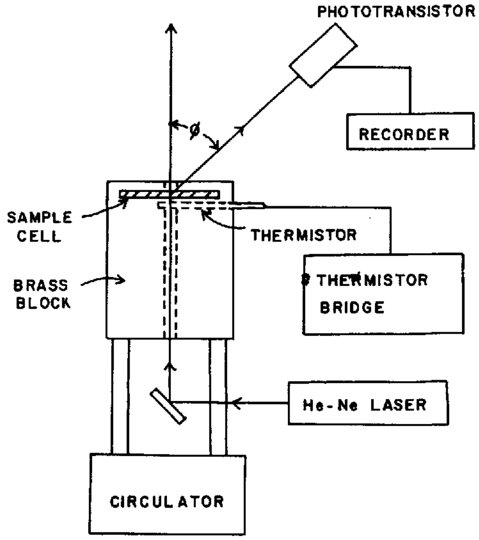

FIGURE 1 Experimental apparatus used to measure the pitch of CEEC by Bragg diffraction.

block and the intensity of the scattered light detected by a motor driven phototransistor operated in its linear region. Measurements were made by sweeping the detector at constant speed in an arc about the center of the sample cell, with the position and output of the phototransistor being read out directly on an x-y recorder.

Our samples were obtained from Eastman Kodak, as were those of Leder[2] and Baessler, *et al.*[3] Inspection of the CEEC in one bottle showed the presence of solid impurities which were removed by centrifugation; data taken from this sample were labeled CP in Figure 2. The contents of a second bottle appeared much cleaner and we measured the pitch without further purification (labeled NU). We then purified the same sample according to the method of Leder (labeled NPL), but found we could not get a pure sample by this method alone: using thin layer chromatography, we found several impurities, the most abundant being cholesterol. For our tests we used Silica Gel HF-254: Kieselguhn (1:1 mixture) as the sorbent layer and benzene with a few mole percent methanol as the solvent. We then went on to purify our NPL sample with preparatory thin layer chromatography (labeled TLCP); samples prepared in this fashion showed no impurities using the same thin layer chromatography as above.

In attempting to determine the purity of our samples, we also resorted to infrared spectra and were able to obtain the same spectrum obtained by Baessler, *et al.*, for their purest samples. The infrared spectrum is not of itself a decisive test of purity, however, for both the impure NPL sample

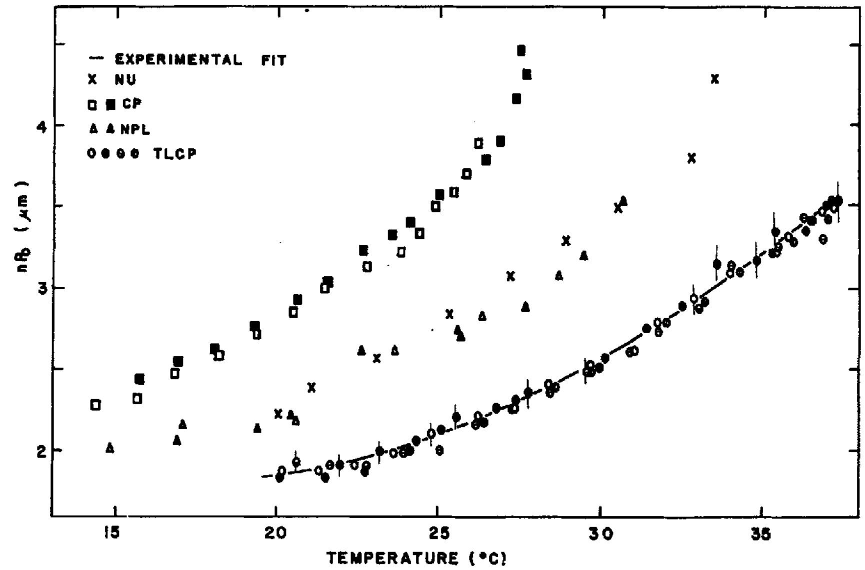

FIGURE 2 Optical pitch nP_0 of CEEC as a function of temperature. NU refers to a new, unpurified sample; CP is a different centrifugally purified sample; NPL is a sample purified by the method of Leder; and TLCP refers to various samples purified by preparatory thin layer chromatography. All data may be fit by shifting the experimental curve horizontally on the temperature axis.

and the purer TLCP samples had identical spectra. We also used mass spectroscopy as a test for purity, but the CEEC molecule seems to be quite fragile and the results proved inconclusive.

Once prepared, samples were kept stored in dry nitrogen and rechecked for purity after our measurements using thin layer chromatography.

RESULTS AND DISCUSSION

Our experimental results are exhibited in Figures 2, 3, and 4. Figure 2 shows the pitch nP_0 of CEEC as a function of temperature for several sample purification techniques. A unique feature of this liquid crystal is that the pitch *increases* with increasing temperature while, to the best of our knowledge, the pitch of other pure, single-component cholesteric liquid crystals *decreases* with increasing temperature. Also, the cholesteric-isotropic transition temperature of CEEC appears to be a strong function of purity, generally increasing as the purity of the samples improved. The increase of transition temperature with purity may not hold in all cases, however:

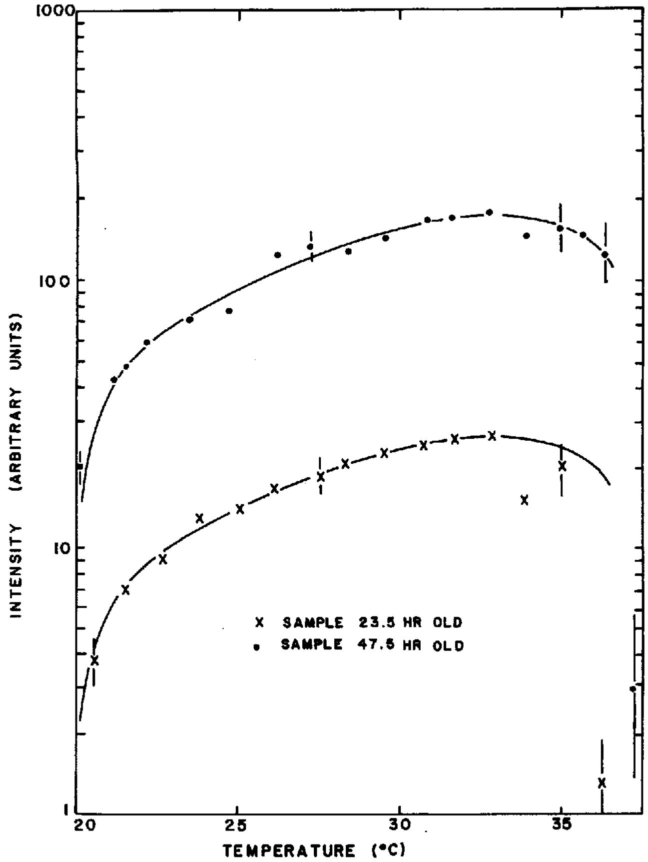

FIGURE 3 Intensity of the scattered light in the sample as a function of temperature for the same sample at two different times. Experimental fit (solid line) is the same for both sets of data.

Durand's impure samples had a transition temperature of 48.5°C, much higher than the value of 37.5°C we obtained in our purest samples. For our NPL samples, purified by Leder's method, we measured a temperature of 31°C which agrees favorably with the 32°C temperature measured by Leder.

As far as the behavior of pitch with temperature is concerned, the data for the various samples in Figure 2 can all be made to coincide merely by uniformly shifting the points along the temperature axis. Therefore, as long as the amount of impurity is not too great, we would conclude that the effect of impurities on the functional form of the pitch is small as long as temperatures are measured relative to the cholesteric-isotropic transition temperature.

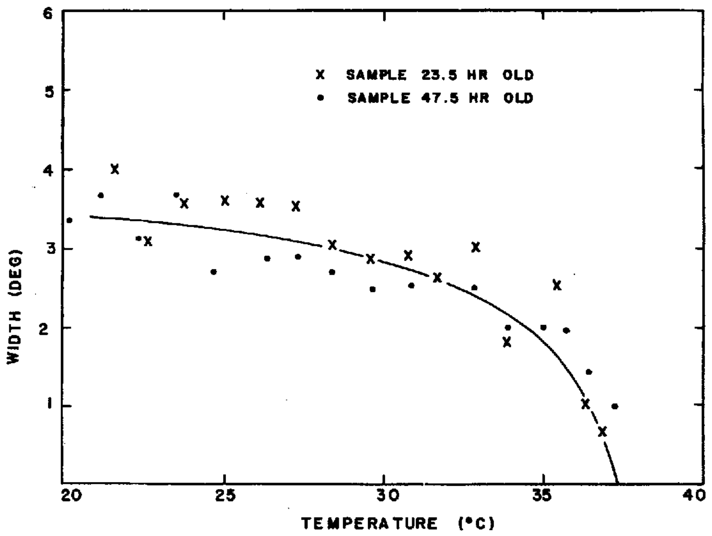

FIGURE 4 Width (full width at half max) of the scattering cone in the sample as a function of temperature for the same two runs shown in Figure 3. Solid line is experimental fit.

This effect allows a comparison between our room temperature value of pitch and that of Leder.[2] Taking room temperature to be 22°C and adjusting our transition temperature to coincide with that of Leder, we obtain a value of 2.3 μm for the pitch. This is in substantial agreement with the 2.5 μm value of Leder and in disagreement with the 0.9 μm value of Baessler, *et al.*[3]

For cholesteric liquid crystals having no smectic phase, there is as yet no theory explaining the temperature dependence of the pitch. We have, however, attempted to construct such a theory by modifying a temperature independent model of Goossens.[4] In Goossens' model, the pitch is attributed to a competition between intermolecular dipole-dipole forces, which tend to align neighboring molecules, and dipole-quadrupole forces, which tend to misalign them. Our modification allows the molecules to deviate from the fixed orientations of Goossens, and to rotate about their respective long axes. Averaging over these motions, we obtain the pitch in terms of the usual order parameter $S = \langle 3 \cos^2 \theta - 1 \rangle /2$, which in turn is a function of temperature. Although in principle the model contains the essential features required to explain the temperature dependence of the pitch, the presence of the dipole and quadrupole matrix elements of the molecules, which are not known, makes the model difficult to apply in any given situation. We therefore consider the model untested and omit the details from the present paper.

Figures 3 and 4 show some additional characteristics of the scattering process in CEEC. In Figure 3, we have corrected the observed scattering intensity for refraction effects, and have plotted integrated scattering intensity, in the sample, as a function of temperature. Two TLCP sample runs are presented: one for a sample 23.5 hours after preparation, and one for the same sample 47.5 hours after preparation. In Figure 4, the observed angular width (full width at half maximum) of the scattering cone has been corrected for index of refraction effects and the cone width in the sample has been plotted versus temperature for the same two samples as in Figure 3.

These curves show the effects of aging on samples of CEEC. Although the scattering intensity from the older sample has increased by a factor of ten, a comparison of the temperature dependence of the two curves show that they differ over the whole temperature range by only a constant factor. The solid line experimental fit to the two curves in Figure 3 is, in fact, the same curve shifted upwards. This change in the intensity with aging does not, however, alter the linewidth of Figure 4, nor does it seem to affect the pitch (these sample runs are represented in the TLCP data of Figure 2).

We attribute the intensity difference in Figure 3 to the tendency of the sample to form domains, so that the scattering intensity is proportional to the number of domains in the scattering volume which have an orientation satisfying the Bragg condition. When the sample is freshly made, the domains are fairly well oriented by the sample boundaries and the scattering intensity is, as we have observed qualitatively, quite weak. With aging, the domains become more and more disoriented and the Bragg intensity increases. The characteristics of the domains themselves do not change with age, however, for this would change either the width of the scattered cone (which is inversely proportional to domain size[8]) or the pitch. We have observed the domain structure microscopically in CEEC samples and while the domains *do* become better defined with age, the domain size does not change with time.

An explanation of the functional form of the intensity curves of Figure 3 is difficult to formulate since our samples are not oriented. Simple considerations show that, in addition to depending on the number of properly aligned domains, the scattering intensity is also proportional to S^2, where S is the order parameter, and some angular factor depending on the alignment of the sample and the polarization of the incident and scattered light.

The nature of the domains causing the width of the scattered light is still unclear. A calculation of domain size from the scattering widths[8] results in domains about 8 μm in diameter below 30°C which increase in size as the cholesteric-isotropic phase transition is approached. Observations made with a polarizing microscope, however, reveals domain-like structures of about 80 μm in diameter below 30°C which *decrease* in size near the phase transition. These "domains", however, are not optically uniform inside.

Probably the length associated with the scattering width is not the domain seen in the microscope, but rather some smaller region perhaps not very well defined or too small to be identified by our microscope.

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