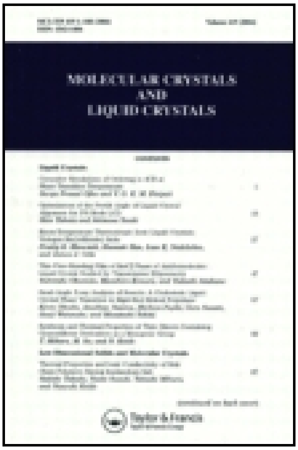

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 14 Oct 2011.

To cite this article: Khoon-Cheng Lim & John T. Ho (1981): Cholesteric Pitch Near the Smectic-C Phase, Molecular Crystals and Liquid Crystals, 67:1, 199-204

To link to this article: http://dx.doi.org/10.1080/00268948108070888

*Mol. Cryst. Liq. Cryst.*, 1981, Vol. 67, pp. 199–204
0026–8941/81/6704–0199$06.50/0

Printed in the U.S.A.

# Cholesteric Pitch Near the Smectic-C Phase†

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(*Received July 28, 1980*)

The temperature dependence of the cholesteric pitch of the chiral ester 4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)biphenyl-4-carboxylate has been measured in detail using the method of selective reflection. This compound has a cholesteric to smectic-C transition at 79°C. Because of the first-order nature of the transition, the pretransitional unwinding of the pitch is considerably less pronounced than that in cholesteryl esters near the smectic-A transition. The wavelength of maximum reflection increases from 440 nm at 110°C to 560 nm at the transition. When fitted to a power-law temperature dependence, the data imply an exponent of 0.82 ± 0.15, which is consistent with de Gennes' theory in the meanfield approximation.

## INTRODUCTION

While there is general agreement on the molecular order in the smectic-A phase, the nature of the smectic-C phase is still unclear. Several theories have been proposed involving a tilt-angle order parameter,[1] transverse dipoles,[2,3] or steric interactions.[4,5] In a nematic or cholesteric liquid crystal near the smectic-C phase, all three Frank elastic constants are expected to diverge.[1] This has only been observed qualitatively.[6] The nematic or cholesteric to smectic-C transition is interesting because different theoretical approaches produce quite different predictions on the temperature dependence of the Frank elastic constants. The theory of de Gennes[1] predicts that the three Frank elastic constants diverge as $\xi^{3/2}$, where $\xi$ is the smectic-C

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† Paper presented at 8th International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

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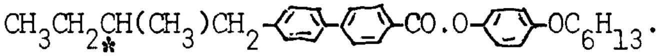
correlation length. The theory of Chen and Lubensky[7] predicts a $\xi^2$ dependence. The theory of Chu and McMillan[8] predicts a divergence proportional to $\xi$.

One way to monitor the behavior of the twist elastic constant $K_{22}$ near a smectic transition is to measure the cholesteric pitch $p$ of a chiral system. The stiffening of $K_{22}$ near the transition leads to an unwinding of $p$. It is expected that the pretransitional increase $\delta p$ of $p$ is directly proportional to the increase $\delta K_{22}$ of $K_{22}$.[1, 9] The pitch can be conveniently and accurately measured by studying the peak wavelength of Bragg-like reflection of light.[10] We have previously applied this technique to study the cholesteric to smectic-A transition in cholesteryl esters. Those results imply a correlation-length critical exponent $\nu$ of 0.67, analogous to that of the superfluid transition.[11, 12] We report here the first detailed measurement of the temperature dependence of the cholesteric pitch near the smectic-C transition. Our objective is to differentiate among the various predictions of the behavior of the twist elastic constant.

## EXPERIMENTAL

The compound studied in the chiral ester 4-*n*-hexyloxyphenyl-4′-(2″-methylbutyl)biphenyl-4-carboxylate (CE3):[13]



Its transition temperatures are: crystal to smectic-C, 65°C; smectic-C to cholesteric, 79°C; cholesteric to isotropic, 162°C. The cholesteric to smectic-C transition entropy is 0.40 $R_0$.[14] For comparison, the cholesteric to smectic-A transition entropy in cholesteryl nonanoate is 0.05 $R_0$.[11] The first-order nature of the cholesteric to smectic-C transition in CE3 is consistent with theoretical considerations which take into account of fluctuations.[15–17]

Our samples of CE3 were supplied to us by Professor G. W. Gray and Dr. D. G. McDonnell. Planar samples were formed between glass slides separated by a 27 $\mu$m Mylar spacer. The temperature of the sample was controlled to a stability of 1 mK. The temperature gradient across the illuminated part of the sample was estimated to be less than 10 mK. The standard selective reflection method was used to measure the cholesteric pitch. The apparatus included a halogen–tungsten light source, a Jarrell-Ash 82–410 monochromator driven by a stepping motor, and a Hamamatsu R955 photomultiplier tube. The experimental arrangement was similar to that described previously.[11] The peak reflection wavelength $\lambda_p$ is a measure of the optical pitch $np$, where $n = (n_e + n_0)/2$ is the average refractive index.

The location of $\lambda_p$ was determined with an accuracy of 2 nm. The half-width $\Delta\lambda$ of the reflection peak is typically about 50 nm, which is considerably larger than that found in cholesteryl esters. This is because $\Delta\lambda = p(n_e - n_0)$ and the birefringence is larger in CE3, which is non-sterol, than in cholesteryl esters.

## RESULTS AND ANALYSIS

The temperature dependence of the peak reflection wavelength $\lambda_p$ in two samples of CE3 is shown in Figure 1. The value of $\lambda_p$ increases as the smectic-C transition is approached, reaches a maximum at the transition, and decreases as the temperature is reduced in the smectic-C phase. The overall change of $\lambda_p$ with temperature in the cholesteric phase is considerably larger than that in cholesterics that do not have a smectic transition, and clearly shows a pretransitional effect. However, the extent of the pretransitional increase of $\lambda_p$ in CE3 is small compared with that in cholesteryl esters that undergo a nearly second-order transition to a smectic-A phase. Specifically, $\lambda_p$ increases from 370 nm to 690 nm in the last 10 K close to the cholesteric to smectic-A transition in cholesteryl nonanoate,[11] while $\lambda_p$ increases only from 480 nm

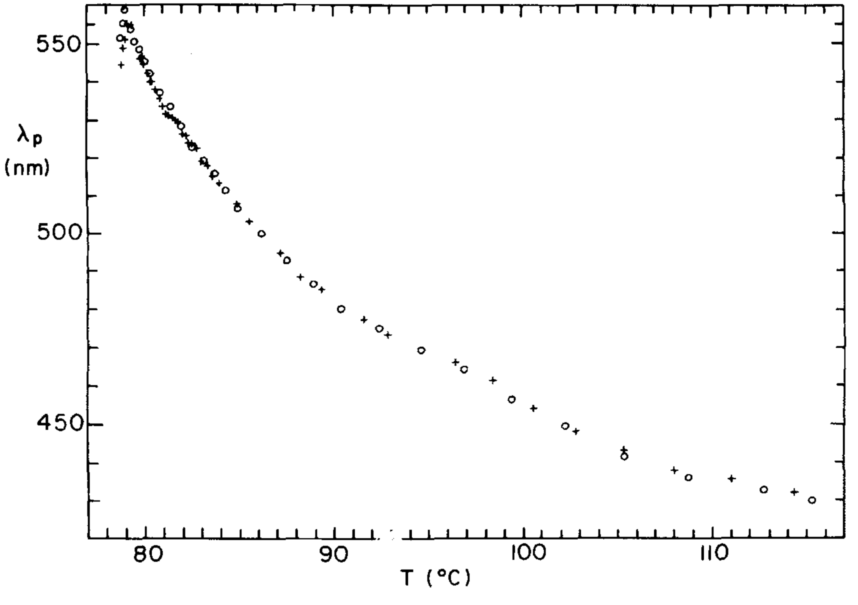


FIGURE 1 Temperature dependence of peak reflection wavelength $\lambda_p$ of CE3. The two different symbols refer to two separate experimental runs.

to 570 nm in a similar temperature range near the cholesteric to smectic-C transition in CE3. The weak divergence of $\lambda_p$ in CE3 is consistent with the comparatively large latent heat of this first-order transition.

Because of the decidedly first-order nature of the transition, the data analysis has been performed with the assumption that meanfield theory holds in this case. Within the context of the meanfield approximation, the smectic-C correlation length $\xi$ has the temperature dependence

$$\xi = \xi_0 \left( \frac{T}{T^*} - 1 \right)^{-0.5}, \tag{1}$$

where $T^*$ is an apparent critical temperature. The pretransitional increase $\delta K_{22}$ of the twist elastic constant is then predicted in the various theories to have the following possible forms:

$$\delta K_{22} = A \left( \frac{T}{T^*} - 1 \right)^{-0.75} \quad \text{(de Gennes}^1\text{)}, \tag{2}$$

$$\delta K_{22} = A \left( \frac{T}{T^*} - 1 \right)^{-1} \quad \text{(Chen and Lubensky}^7\text{)},$$

$$\delta K_{22} = A \left( \frac{T}{T^*} - 1 \right)^{-0.5} \quad \text{(Chu and McMillan}^8\text{)}. \tag{4}$$

Since the pretransitional increase $\delta\lambda_p$ of the pitch is expected to be proportional to $\delta K_{22}$,[1,9] the different theories predict

$$\lambda_p = \lambda_0 + B \left( \frac{T}{T^*} - 1 \right)^{-\xi} \tag{5}$$

where $\lambda_0$ is the intrinsic optical pitch in the absence of the smectic-C transition, and the exponent $\zeta = 0.75$, 1, and 0.5 according to de Gennes,[1] Chen and Lubensky,[7] and Chu and McMillan,[8] respectively.

Because of the weakness of the actual divergence in $\delta\lambda_p$ before the first-order transition occurs, we have found it necessary to determine $\lambda_0$ independently. This was done by measuring $\lambda_p$ in mixtures of CE3 doped with known quantities of cholesteryl chloride (CC).[18] Four mixtures with weight concentration $x$ of CC of 0.070, 0.104, 0.139 and 0.163 were studied. One expects the presence of CC to lower the transition temperature and hence suppress the pretransitional contribution to $\lambda_p$. The value of $\lambda_p$ was found to increase with increasing $x$, showing that CE3 and CC have opposite chirality. Without the influence of a smectic transition, the reciprocal pitch of a binary system has been shown to be the result of a simple weighted linear combination of the reciprocal pitch of the constituents.[19] At a given temperature away from the transition and with sufficiently high doping, the data should follow the relation

$$\lambda_p^{-1} = (1 - x)\lambda_0^{-1} - x\lambda_{CC}^{-1}, \tag{6}$$

where $\lambda_{CC}$ is the optical pitch of pure CC. Equation (6) implies that a plot of $\lambda_p^{-1}$ versus $x$ at a fixed temperature should be a straight line which extrapolates to give $\lambda_0^{-1}$ at $x = 0$. For example, Figure 2 shows such a plot at 125°C, from which we obtain $\lambda_0(125°\text{C}) = 370\,\text{nm}$. For the temperature dependence of $\lambda_0$, we have used the temperature coefficient $\lambda_0^{-1}(d\lambda_0/dT) = -2.8 \times 10^{-3}\,\text{K}^{-1}$, which has been found to be a fairly universal value among many sterol and non-sterol cholesterics that do not have smectic phases.[11, 18, 20, 21]

With this independent knowledge of $\lambda_0$, a non-linear least-squares fit of the data to Eq. (5) has been made. The results are $\zeta = 0.82 \pm 0.15$ and $T^* = (342 \pm 2)\,\text{K}$. The rather large uncertainty in the fitting parameters is a direct result of the first-order nature of the transition and the concomitant small extent of the pitch divergence compared to its intrinsic value. Within this uncertainty, the optimum value of the exponent $\zeta$ appears to favor de Gennes' theory of the nematic or cholesteric to smectic-C transition. It would be desirable to find another compound with a smaller latent heat in which this result can be verified.

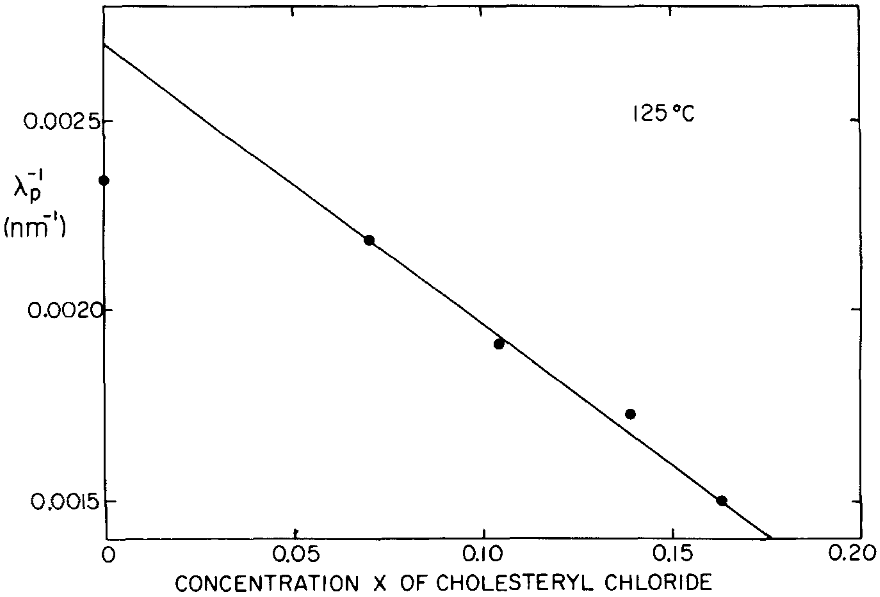


FIGURE 2 Reciprocal of $\lambda_p$ as a function of the weight concentration $x$ of cholesteryl chloride in CE3. The line is a linear extrapolation.

## Acknowledgements

We would like to thank Professor G. W. Gray and Dr. D. G. McDonnell for our samples of CE3, and M. A. Smith for technical assistance. This work was supported by the National Science Foundation under Grant No. DMR 78–07206.

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