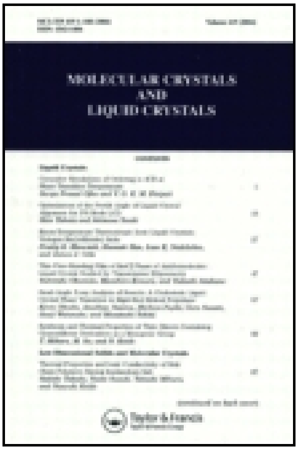

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Optical Activity in the Blue Phase of a Cholesteric Liquid Crystalt

Terrence K. Brog [a] [b] & Peter J. Collings [a]

[a] Department of Physics, Kenyon College, Gambier, Ohio, 43022, U.S.A.

[b] Department of Nuclear Engineering, University of Michigan, Ann Arbor, Michigan, 48109

To cite this article: Terrence K. Brog & Peter J. Collings (1980): Optical Activity in the Blue Phase of a Cholesteric Liquid Crystalt, Molecular Crystals and Liquid Crystals, 60:1-2, 65-72

To link to this article: http://dx.doi.org/10.1080/00268948008072425

Mol. Cryst. Liq. Cryst., 1980, Vol. 60, pp. 65–72
0026-8941/80/6001-0065$04.50/0

Printed in the U.S.A.

Optical Activity in the Blue Phase of a Cholesteric Liquid Crystal†

TERRENCE K. BROG‡ and PETER J. COLLINGS
Department of Physics, Kenyon College, Gambier, Ohio 43022, U.S.A.

(*Received September 24, 1979; in final form November 2, 1979*)

Optical activity measurements in the blue phase of cholesteryl decanoate are presented for three different visible wavelengths. The optical activity of the blue phase is reduced from its value in the cholesteric phase, approaching zero nearly continuously at the blue phase to isotropic liquid transition. In agreement with previous work on the blue phase, the wavelength dependence of the optical activity indicates that the blue color of the phase is due to a region of anomalous optical activity and selective reflection at approximately 450 nm. The results also provide evidence for two distinct blue phases in this cholesteric liquid crystal.

INTRODUCTION

The transition from a cholesteric liquid crystal of short pitch to an isotropic liquid is more complex than the corresponding transition in nematic liquid crystals. For approximately a 0.5°C interval below the transition to an isotropic liquid, another liquid crystal phase, the blue phase, is thermodynamically stable. Little is known about the structure of the blue phase. Microscopically, a platelet structure is visible if the blue phase is viewed under reflected light.[1] Density measurements show an extremely weak transition from the cholesteric phase to the blue phase, followed by another transition from the blue phase to the isotropic liquid.[2–6] Nuclear magnetic resonance spectroscopy demonstrates that long range orientational order is present in the blue phase, but also suggests that the preferred direction must change drastically over distances on the order of a pitch.[7] Finally, Bergmann and

---

† Research supported in part by the National Science Foundation under Grant No. SPI/77-26309 and the Research Corporation under Grant No. C-903.

‡ Present address: Department of Nuclear Engineering, University of Michigan, Ann Arbor, Michigan 48109.

Stegemeyer report that a region of selective reflection and anomalous optical activity occurs in the blue phase, but at a longer wavelength than these same effects occur in the cholesteric phase.[8] The authors contend that it is this change in the wavelength for selective reflection which causes the white cholesteric phase to appear blue when the transition to the blue phase takes place. In addition, more recent measurements in this same laboratory point to the existence of two thermodynamically stable blue phases in this narrow 0.5°C interval.[9] The region of anomalous optical activity and selective reflection occurs at slightly different wavelengths in each phase.

Saupe has suggested a model for the blue phase in which a cubic lattice of disclinations with a spacing of half a pitch occurs in a cholesteric liquid crystal.[10] Exactly how this structure forms is not clear. More recently, a phenomenological theory of the cholesteric-isotropic phase transition has been proposed.[11,12] The relationship between the pitch and the correlation length for short-range nematic-like ordering is the crucial factor in this theory; in fact, the authors suggest that an intermediate phase with non-spiral symmetry and small order parameter can exist if the two lengths are comparable. The optical properties of such a phase have not yet been calculated, so additional work of this type is certainly needed.

In hopes of gaining more insight into the structure of the blue phase, we decided to perform an experiment which measured the temperature dependence of the optical activity in the blue phase. The results presented in this article should therefore augment the data reported by Bergmann and Stegemeyer, since their optical activity measurements were taken at one temperature in the supercooled blue phase.

EXPERIMENTAL PROCEDURE

The liquid crystal used in this experiment was cholesteryl decanoate, obtained from the Eastman Kodak Company and recrystallized from an acetone-water mixture. The smectic A-cholesteric transition occurred at 78°C, the cholesteric-blue phase transition occurred at 91.5°C, and the blue phase-isotropic liquid transition occurred at 92°C.

The experimental apparatus is shown in Figure 1. The sample was contained in a 1 cm spectrophotometer cell, located at the center of a long double oven arrangement. The temperature of both ovens was proportionally controlled using sensor thermocouples. Based on previous experiments with this oven arrangement, the temperature gradient over the part of the sample illuminated by the laser was no more than 0.03°C.

Three different visible wavelengths were used, 632.8 nm from a He-Ne laser, and 514.5 nm and 488.0 nm from an Argon-Ion laser. The results

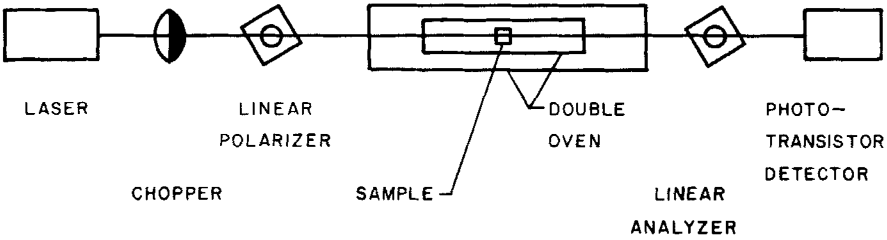

FIGURE 1 Experimental apparatus. Both ovens were proportionally controlled using sensor thermocouples. The output of the phototransistor detector went to a lock-in amplifier using the chopper signal as a reference. Rotation angles were determined by a scale attached to the analyzer.

obtained with increasing temperature are shown in Figure 2. The transition temperatures, T_c, differ slightly for each wavelength since each experiment was performed at a different time; in addition, the 632.8 nm measurement used a different sample of cholesteryl decanoate.

EXPERIMENTAL RESULTS

Two important features are evident in Figure 2. The first is the rapid increase in the optical activity with decreasing wavelength. The second is the continuous decrease in optical activity with increasing temperature, with no apparent discontinuity at the blue-isotropic phase transition, but with a slight discontinuity midway through the blue phase.

The increase in optical activity with decreasing wavelength is not surprising in light of Bergmann and Stegemeyer's measurement.[8] In their cholesteryl nonanoate sample, the optical activity increased as the wavelength approached the anomalous region around 480 nm. Likewise, extrapolation of our data seems to indicate that the anomalous region for cholesteryl decanoate lies around 450 nm. To arrive at this estimate, we graphed the square of the wavelength versus one over the optical activity times the wavelength squared for points at a given temperature below the isotropic transition. For optical activity measurements in the cholesteric phase, these graphs would be straight lines.[13] For our data, however, the lines were slightly curved but all had a wavelength squared intercept around $(450\text{ nm})^2$. This result, indicating an anomalous region at shorter wavelength, is further strengthened by the observation that even when the blue phase of cholesteryl decanoate is supercooled, it does not appear green at all, while Bergmann and Stegemeyer report that at lower temperatures cholesteryl nonanoate does appear green.[8] It is also interesting to note that the pitch of cholesteryl nonanoate just below the blue phase is about 360 nm,[8] while the pitch in cholesteryl decanoate just below

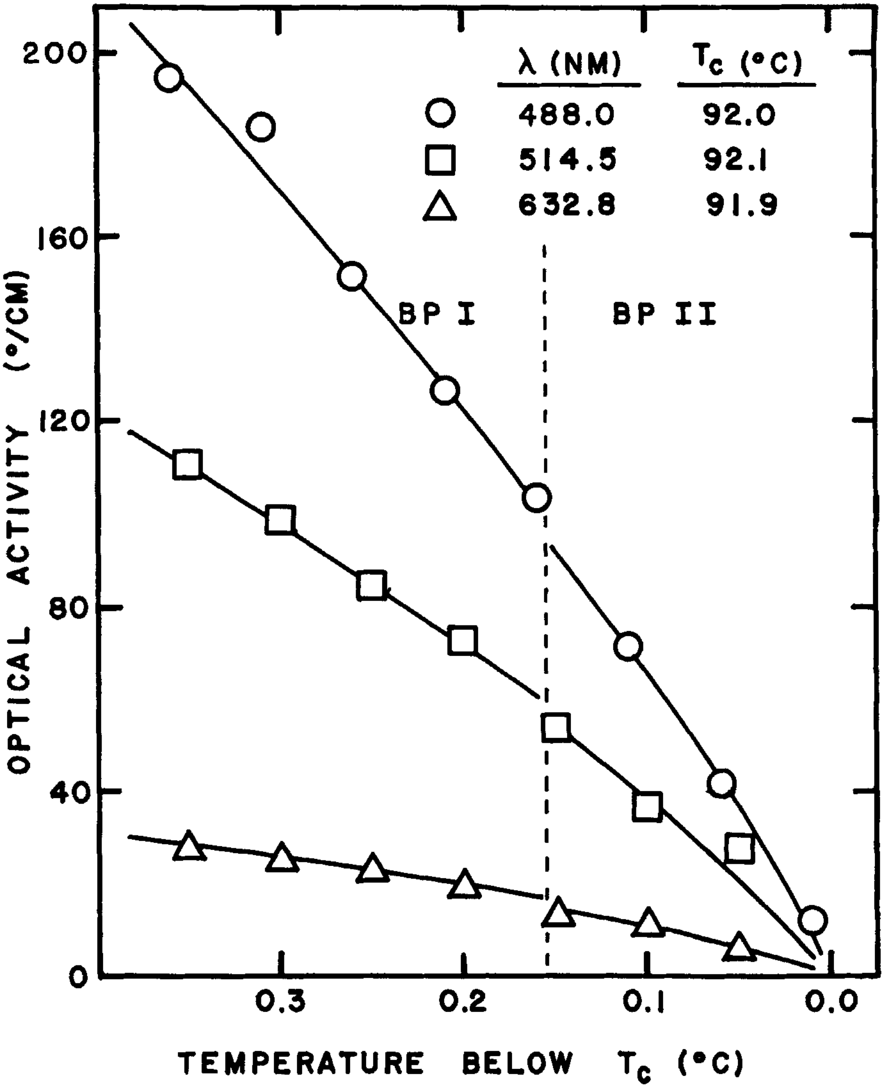

FIGURE 2 Optical activity in the blue phase of cholesteryl decanoate. The rotation was clockwise to an observer looking back along the beam. Data points were reproducible to within ±3%. The transition temperatures differ slightly because each wavelength experiment was performed at a different time. The solid lines have been added to accent the slight discontinuity in the data at approximately 0.16°C below the isotropic transition.

the blue phase is 330 nm.[14] Thus the wavelength for maximum selective reflection and anomalous optical activity increases by roughly one-third in both liquid crystals. The same effect seems to take place in quite a different liquid crystal, cholesteryl myristate. The anomalous region shifts from 310 nm in the cholesteric phase to 420 nm in the blue phase, again an increase of about one-third.[8] If this shift is representative of the blue phase in general, it certainly is an important fact which any theory for the blue phase must explain.

The absence of a large discontinuity in the optical activity at the blue-isotropic phase transition is an interesting finding. Afterall, Armitage and Price have shown that it is the cholesteric-blue phase transition which is the weak one, and not the blue-isotropic phase transition.[4,5] We repeated the 632.8 nm measurement many times, sometimes taking data at smaller temperature intervals. No significant indication of a discontinuity ever appeared. If one is present, it is safe to place an upper bound of 5°/cm on the discontinuity at 632.8 nm. Physical properties at other liquid crystal to isotropic phase transitions behave quite differently. Typically, the variation throughout the liquid crystal phase is never more than two times the discontinuity at the transition. Here the variation is eight times the discontinuity! The slight discontinuity occuring about 0.16°C below the isotropic transition is readily explained by the existence of two different blue phases.[9] Since the region of anomalous optical activity is at slightly shorter wavelengths in the higher temperature blue phase (BP II),[9] the optical activity decreases upon entering that phase from the lower temperature blue phase (BP I).

DISCUSSION

The fact that a region of anomalous optical activity exists in the blue phase indicates that either the helical structure of cholesteric liquid crystals is still present in some form in the blue phase, or that another structure lacking inversion symmetry forms in place of the usual cholesteric structure. Bergmann and Stegemeyer[8] argue that the Saupe model[10] for the blue phase is not consistent with their narrow selective reflection band. They contend that a structure composed of cholesteric domains with a random distribution of helical axes would have an extremely broad selective reflection band due to the strong dependence of selective reflection on the angle between the helical axis and the direction of light propagation. This would be true if the cholesteric domains were typically many pitches in size, but the Saupe model suggests that the size of the unit cell is on the order of half a pitch. As Chandrasekhar and Prasad[15] have shown theoretically, selective reflection is a weak effect even when the size of the cholesteric sample is on the order of five pitches. Therefore, the question of how light propagates through the structure suggested by Saupe is a difficult one. The spiral structure of the cholesteric phase is still present, so some optical activity and selective reflection should occur. Perhaps, the light is affected by the structure in some average sense, producing a sharp selective reflection band at a longer wavelength than the tightest spiral present. It is interesting to note that as shown in the two dimensional structure of Figure 4(b) of Ref. 10, the pitch along a diagonal is greater than along a side. In a three dimensional structure, the possibility exists of an even greater pitch than that present in the two dimensional structure. Based on the optical measurements to date, therefore, the Saupe model should not necessarily be abandoned.

Two possible explanations (or a combination of both) come to mind in considering the lack of a discontinuity in the optical activity at the blue phase to isotropic liquid transition. The wavelength of maximum selective reflection in the blue phase decreases as the temperature is increased.[8,9] Since this would move the anomalous region for optical activity farther away from the wavelengths of light used in this experiment, one would expect the optical activity to decrease. The change in the wavelength of maximum selective reflection, however, is less than 100 nm, which might reduce the optical activity in half for 632.8 nm light, but definitely not to one-eighth of its value at the cholesteric to blue phase transition. At 632.8 nm, the optical activity is just not that sensitive to the exact position of the maximum in the selective reflection 200 nm away. The other possible explanation is that the order parameter is decreasing rapidly in the blue phase. Measurements of the orientational order parameter in the cholesteric phase demonstrate that the order parameter in another cholesteric liquid crystal is about 0.32 and decreasing quickly just before the cholesteric to blue phase transition.[16] If this temperature dependence continues in the blue phase, it would cause a rapid decrease in whatever birefringence might be present and therefore a similar decrease in the optical activity. These two effects occurring simultaneously might be the reason the optical activity gets so small toward the high temperature end of the blue phase.

CONCLUSION

It is clear that recent interest in the blue phase has begun to bring forth a wealth of information concerning this little-understood liquid crystal phase. Yet only one theoretical attempt to explain the complexity of the cholesteric-isotropic transition region has been reported.[11,12] Certainly more theoretical work is called for. It must be pointed out, however, that this first theoretical attempt contains many exciting possibilities. The blue phase might be a phase with an order parameter less than 0.32, the limit of stability for nematic-like order.[17] The transition from blue phase to isotropic liquid might therefore be more of a structural phase change than an orientational phase change. Unlike other liquid crystal to isotropic phase transitions, any latent heat or volume change at the transition would not come mainly from the vanishing of all orientational order, but from the complete melting of a long range structure within the liquid crystal. Whatever the result of future work on the blue phase turns out to be, it certainly has an excellent chance of being quite interesting.

Acknowledgement

The authors wish to express their gratitude to the Department of Chemistry, College of Wooster, for the use of their Argon-Ion laser.

References

1. D. Coates and G. W. Gray, *Phys. Lett.*, **45A**, 115 (1973); **51A**, 335 (1975).
2. F. P. Price and J. H. Wendorff, *J. Phys. Chem.*, **75**, 2839 (1971); **75**, 2849 (1971).
3. S. A. Jabarin and R. S. Stein, *J. Phys. Chem.*, **77**, 399 (1973).
4. D. Armitage and F. P. Price, *J. App. Phys.*, **47**, 2735 (1976).
5. D. Armitage and F. P. Price, *J. Chem. Phys.*, **66**, 3414 (1977).
6. D. Demus, H. G. Hahn, and F. Kuschel, *Mol. Cryst. Liquid Cryst.*, **44**, 61 (1978).
7. P. J. Collings and J. R. McColl, *J. Chem. Phys.*, **69**, 3371 (1978).
8. K. Bergmann and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **82**, 1309 (1978).
9. K. Bergmann and H. Stegemeyer, *Z. Naturforsch.*, **34a**, 251 (1979); K. Bergmann, *et al.*, *Z. Naturforsch*, **34a**, 253 (1979); P. Pollman and G. Scherer, *Z. Naturforsch.*, **34a**, 255 (1979).
10. A. Saupe, *Mol. Cryst. Liquid Cryst.*, **7**, 59 (1969).
11. S. A. Brazovskii and S. G. Dmitriev, *Sov. Phys. JETP*, **42**, 497 (1976).
12. S. A. Brazovskii and V. M. Filev, *Sov. Phys. JETP*, **48**, 573 (1978).
13. P. E. Sokol and J. T. Ho, *App. Phys. Lett.*, **31**, 487 (1977).
14. R. Pindak and J. T. Ho, *Phys. Lett.*, **59A**, 277 (1976).
15. S. Chandrasekhar and J. S. Prasad, *Mol. Cryst. Liquid Cryst.*, **14**, 115 (1971).
16. P. J. Collings, T. J. McKee, and J. R. McColl, *J. Chem. Phys.*, **65**, 3520 (1976).
17. R. Alben, *Mol. Cryst. Liquid Cryst.*, **13**, 193 (1971).