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

Temperature and Composition Dependence of the Pitch of Cholesteryl Chloride-Cholesteryl Nonanoate Mixtures

Sadao Masubuchi [a] , Tadashi Akahane [a] , Kazuhira Nakao [a] & Toshiharu Tako [a]

[a] Research Laboratory of Precision Machinery and Electronics, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama, 227, Japan

Version of record first published: 28 Mar 2007.

To cite this article: Sadao Masubuchi , Tadashi Akahane , Kazuhira Nakao & Toshiharu Tako (1977): Temperature and Composition Dependence of the Pitch of Cholesteryl Chloride-Cholesteryl Nonanoate Mixtures, Molecular Crystals and Liquid Crystals, 38:1, 265-274

To link to this article: http://dx.doi.org/10.1080/15421407708084392

Mol. Cryst. Liq. Cryst., 1977, Vol. 38, pp. 265–274

Printed in Holland

Temperature and Composition Dependence of the Pitch of Cholesteryl Chloride–Cholesteryl Nonanoate Mixtures

SADAO MASUBUCHI, TADASHI AKAHANE, KAZUHIRA NAKAO, and TOSHIHARU TAKO

Research Laboratory of Precision Machinery and Electronics, Tokyo Institute of Technology, Nagatsuta-cho, Midori-ku, Yokohama 227, Japan

(*Received August 31, 1976; in final form October 26, 1976*)

Temperature and composition dependence of the pitch in cholesteryl chloride and cholesteryl nonanoate mixtures have been obtained by means of the selective reflection–total reflection method, the Bragg-like reflection method and the optical rotatory power method. The results are analyzed using the generalized long range distortion theory. The temperature variations of the molar twisting power between component molecules of the mixture have been determined.

INTRODUCTION

It is known that when cholesteric liquid crystals are mixed, the resultant pitch depends not only on composition but also on temperature. The composition dependence of the pitch for a binary or a ternary liquid crystal mixture has been studied by many authors.[1–13] Kozawaguchi and Wada[14,15] extended the continuum theory for binary mixtures. They explained experimental results by considering the difference of elastic constants in component molecules. Bak and Labes[16,17] generalized the long range distortion theory by including the probability that the introduced chiral molecules occupy the point of observation. The composition dependence of helical twisting power of binary and ternary liquid crystal mixtures was analyzed by this theory. Stegemeyer and Finkelmann[18] formulated the twisting power—concentration relationship in binary mixtures applying Goossens theory and discussed the shape of twisting power—concentration curves. Adams and Haas[19] extended the linear additive law for pitch dependence in binary mixtures of cholesterics by including first order interactive effects. An apparently widely diverse collection of experimental data was effectively treated by the resulting expression.

In this paper, we report the composition and temperature dependence of the pitch in cholesteryl chloride (CC)—cholesteryl nonanoate (CN) mixtures. These experimental results are analyzed using the generalized long range distortion theory. Based on this theory, the dependence of molar twisting power between molecules of the components are discussed.

EXPERIMENTAL METHODS

Cholesteryl nonanoate (CN) and cholesteryl chloride (CC) used in our experiments are commercially obtained and used without further purification. Purity is determined with a differential scanning calorimeter[20,21] and purities of the CC and that of the CN are 99.6% and 99.4% respectively. These two components are heated up to the isotropic phase, stirred well and used as a sample. The sample is introduced in the isotropic phase between the two heated 20 mm × 25 mm semi-cylindrical prisms spaced about 12 μm apart. The system is allowed to cool into the cholesteric range. Sliding the prisms towards each other gives Grandjean plane textures. A temperature-controlled oven within the accuracy of 0.1°C is placed around the sample cell to keep the temperature of the cholesteric film constant. The light beam from the monochromator passes through a pin hole 1 mmϕ and a slit and then falls on the sample centrally. The light spot is a 2 mm × 0.2 mm rectangular area perpendicular to the incident plane. The temperature of the sample is measured by a thermocouple placed in a 1 mm × 10 mm hole drilled in one of the prisms. The large heat capacity of the prism keeps the temperature fluctuation lower than 0.02°C. Temperature distribution of the film is checked by measuring the colour distribution of CN film sandwiched between the prisms and is less than 0.1°C.

For determination of the structural pitch P, there are three cases:

a) 0.4 μm $< \lambda_0 <$ 1.1 μm (the spectral range of a silicon photo detector S780-5BU, Hamamatsu T.V. Co.). For normal incidence, a cholesteric liquid crystal reflects the circular polarized light in the same sense as the sample, that is, a right handed mixture reflects right handed circular polarized light. At the center wavelength of the selective reflection λ_0 (inversion wavelength), the transmitted light has a minimum value.[22] Above the critical angle for total reflection, the transmitted light disappears.[23] The average refractive index n of the sample is obtained by measuring the critical angle of total reflection for perpendicular polarized light, n is given by

$$n = \left(\frac{n_p^2 + n_n^2}{2}\right)^{1/2}, \tag{1}$$

where n_p and n_n are the refractive index parallel and perpendicular to the long axis of a molecule respectively. Then the pitch is determined by[24]

$$P = \frac{\lambda_0}{n}. \tag{2}$$

b) 1 μm $< \lambda_0 <$ 2 μm. At an angle θ_B for perpendicular polarized light of wavelength λ, transmission decreases due to Bragg-like reflection. The pitch is then[25]

$$P = \lambda \times (n^2(\lambda) - n_g^2(\lambda)\sin^2\theta_B)^{-1/2}. \tag{3}$$

Where n_g is the refractive index of the prism.

c) 2 μm $< \lambda_0$. In this case a sodium light (589 nm) falls normally on the sample. The plane of polarization of the transmitted light rotates due to the optical activity in cholesterics.

The pitch can be calculated from the optical rotatory power r by the relation[22,26]

$$P = \frac{r\lambda^2}{45(\Delta n)^2}. \tag{4}$$

Where Δn is the birefringence and represents the difference between the maximum and the minimum indices of refraction in a cholesteric layer, and λ is the wavelength of the sodium light. For detailed experimental procedure, refer to Ref. (27).

EXPERIMENTAL RESULTS

Figure 1 shows the transmission spectra in a mixture of CN 80 mole percent. The optical pitch (wavelength at transmittance minimum) varies with temperature. The depth of the dip decreases near the clearing temperature. The incident angle dependence of the transmission at the wavelength of 1 μm is shown in Figure 2. At an angle of 42 degree, Bragg-like reflection occurs and transmission has a dip. Figure 3 shows the temperature dependence of the rotatory power in a mixture of 35 mole percent of CN. At 56°C the sample becomes nematic and the sign of rotatory power changes.

Figure 4 shows the temperature dependence of helical twisting power P^{-1} for the CC–CN mixtures. When the helical sense of the mixture is right

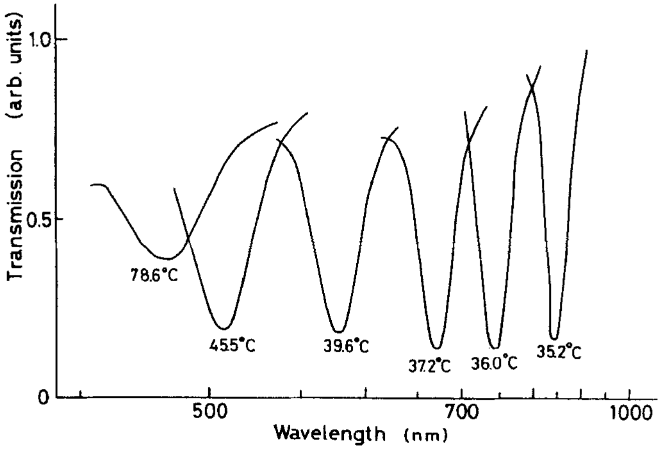

FIGURE 1 Transmission spectra in a mixture of CN 80 mole percent. Incident light is left circularly polarized. It has a dip at the wavelength of selective reflection for normal incidence (optical pitch). The optical pitch decreases with increasing temperature.

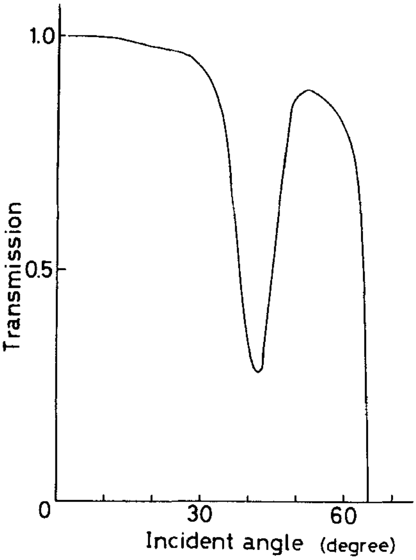

FIGURE 2 Incident angle dependence of light transmission through a cholesteric film of CN 20 mole percent mixture. Incident light is perpendicular polarization with $\lambda = 1.0\ \mu m$. At an angle of 42 degree, Bragg-like reflection occurs and transmission has a sharp dip. Transmitted light disappear above an angle of 65 degree due to total reflection. From the value of the critical angle of total reflection, the mean refractive index n can be obtained.

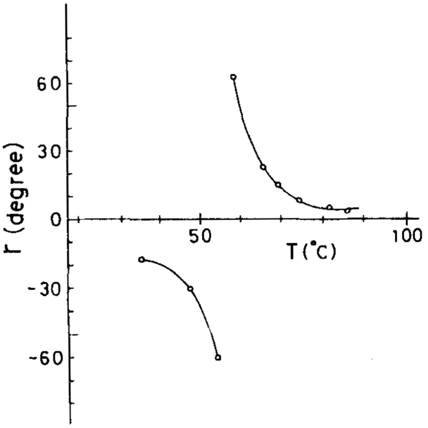

FIGURE 3 Temperature variation of the optical rotatory power in a mixture of 35 molar percent of CN. At 56°C the inversion of helical sense occurs and the sign of the optical rotatory power changes.

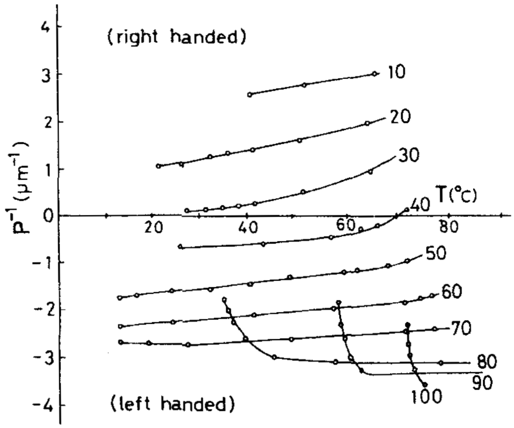

FIGURE 4 Temperature dependence of helical twisting power P^{-1} in CC–CN mixtures. The figures attached to the curves indicate molar percentage of CN.

handed, the pitch is taken as positive. The sample of 40 mole percent of CN has nematic structure at 70°C and the inversion of the helical sense around that temperature occurs. The large change in P^{-1} of the sample of 100, 90 and 80 mole percent of CN is attributable to the onset of the smectic phase. As the mole fraction of CN decreases, the helical twisting power at a certain temperature increases monotonously except in the smectic region. P^{-1} increases with increasing temperature in all the samples.

ANALYSIS OF EXPERIMENTAL DATA

Figure 5 is a plot of P^{-1} vs mole fraction for samples at 10°C, 20°C, 30°C and 40°C below the clearing temperature. When the sample consists of only CN, the helical twisting power is negative. As the mole ratio of CC increases, the negative twisting power is suppressed by the positive twisting power of CC and the helical twisting power of the mixture increases. The composition dependence of P^{-1} at the four temperatures have the same character.

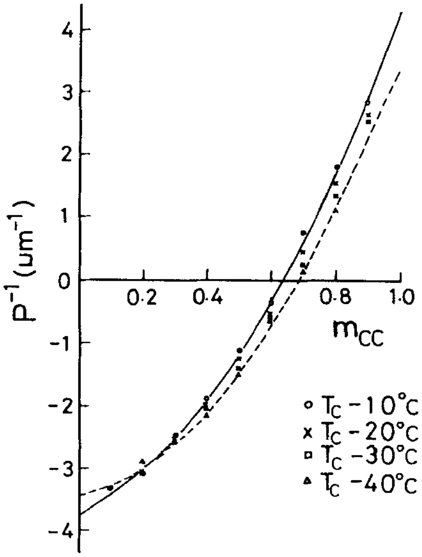

FIGURE 5 Composition dependence of helical twisting power P^{-1} at some temperatures. Solid line (○) and broken one (△) are plots of Eq. 4 with parameters given by Figure 7.

Let us now analyze the experimental results based on the generalized long range distortion theory derived by Bak and Labes. For a binary cholesteric mixture the equation for relating pitch and composition is given by[16]

$$\frac{1}{2P}\frac{1}{M} = (N\beta_{CC,CC} - N\beta_{CN,CN})m_{CC} + N\beta_{CN,CN} + N\delta\beta_{CC,CN}m_{CC}(1 - m_{CC}). \tag{5}$$

Where

$$M = \left\{\left(\frac{M_{CC}}{d_{CC}} - \frac{M_{CN}}{d_{CN}}\right)m_{CC} + \frac{M_{CN}}{d_{CN}}\right\}^{-1} = \text{molar density of the mixture,}$$

M_{CC} (M_{CN}) = molecular weight of CC(CN),
d_{CC} (d_{CN}) = density (g/cm^3) of CC(CN),
m_{CC} = molar ratio of CC,
N = Avogadro's number,
$\delta\beta_{CC,CN} = 2\beta_{CC,CN} - \beta_{CC,CC} - \beta_{CN,CN}$.

In Figure 6, $(2PM)^{-1} - N\delta\beta_{CC,CN}m_{CC}(1 - m_{CC})$ is plotted vs mole fraction of CC to obtain the molar twisting powers. An approximate value of $d = 0.95$ g/cm^3 is taken for all the samples. The value of $N\delta\beta_{CC,CN}$ is adjusted using the least square method so that the data fall on a straight line. By extrapolating the straight line in Figure 6 to $m_{CC} = 0$ and 1, the molar twisting powers $N\beta_{CN,CN}$ and $N\beta_{CC,CC}$ are obtained. Figure 7 shows the variation of molar twisting power with temperature obtained in this manner.

DISCUSSION

Bak and Labes showed that $(2PM)^{-1} - N\delta\beta_{AB}m_A(1 - m_A)$ vs m_A becomes linear after the value $N\delta\beta_{AB}$ was adjusted for three sets of binary mixtures. Those are made with all the possible pairs of three cholesteric liquid crystals: cholesteryl chloride, cholesteryl-2-(2-ethoxyethoxy) ethyl carbonate and *p*-(4-cyanobenzalamino)-cinnamic acid active amyl ester. Both of the helical senses of the two components in these mixtures are right handed.[17,18] In our case, however, CN is left handed and therefore the helical sense of the components is opposite. We see that the corrected pitch—mole fraction relation for CC and CN mixture is also linear in Figure 6. It shows that the pitch—concentration relationship formulated in Eq. 5 by Bak and Labes is satisfactory in explaining the variation of binary cholesteric mixtures with opposite helical sense.

The $N\beta_{CC,CC}$ and the $N\beta_{CN,CN}$ shown in Figure 7 compare favorably with the values obtained by Bak and Labes. They obtained 8.4, 9.1 and 9.4 × 10^6 cm^2 as the molar twisting powers of CC and mentioned that the small discrepancy for these data is attributable to the different degree of purity in the sample materials.[16,17] From Figure 7, however, we observe that the small discrepancy is also due to the temperature dependence of molar twisting powers of CC. It is, therefore, necessary to take the temperature variation into consideration in order to discuss the value of molar twisting powers.

Molar twisting powers between the same molecules ($|N\beta_{CC,CC}|$ and $|N\beta_{CN,CN}|$) increase with temperature. But that of the different molecules ($|N\beta_{CC,CN}|$) decreases as the temperature approaches the clearing point. It is interesting to note that temperature coefficient of $N\beta_{CC,CN}$ near clearing point is larger than those at the lower temperature.

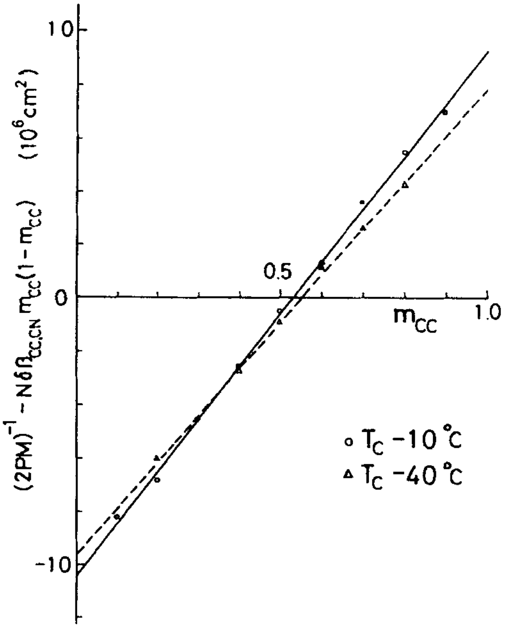

FIGURE 6 Plot of $(2PM)^{-1} - N\delta\beta_{CC,CN}m_{CC}(1 - m_{CC})$ vs mole fraction of CC at $T_c - 10°C$ (○) and $T_c - 40°C$ (△). The notation is given in Eq. 5.

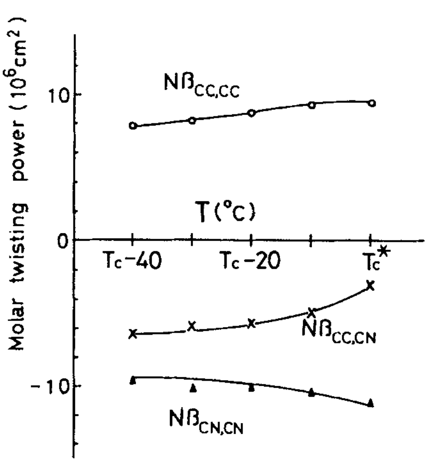

FIGURE 7. Temperature dependence of molar twisting power between molecules of CN and CC. T_c^* is temperature just below the clearing point. The notation is given in Eq. 5.

Adams and Haas introduced a specific rotation θ, which is defined as $(2nP)^{-1}$, where n is the mean refractive index and P is the pitch corresponding 180° rotation. They expressed the relation between specific rotation θ and weight fraction of component A, α in a binary cholesteric mixture as[19]

$$(2nP)^{-1} = \theta = \alpha\theta_A + (1 - \alpha)\theta_B + \alpha(1 - \alpha)k. \tag{6}$$

Where $\theta_A(\theta_B)$ is specific rotation of A(B) molecule and k represents a measure of interaction between A and B molecules. They obtained θ_A, θ_B and k for CP–MBA mixture, CC–MBBA mixture and COC–CB mixture. On the other hand, Eq. 5 is represented using weight fraction of A molecule w_A as[16]

$$\frac{1}{nP} = \frac{2dN}{M_A + (M_B - M_A)w_A} \times \left\{\frac{M_B}{M_A}\beta_A w_A + \frac{M_A}{M_B}\beta_B(1 - w_A) + \Delta\beta_{AB} w_A(1 - w_A)\right\}. \tag{7}$$

Where P = pitch (360° rotation),

w_A = weight fraction of A,

n = mean refractive index,

$$\Delta\beta_{AB} = 2\beta_{AB} - \left\{\left(\frac{M_B}{M_A}\right)\beta_A + \left(\frac{M_A}{M_B}\right)\beta_B\right\},$$

$$d = \frac{d_B}{1 + \left(\frac{d_B}{d_A} - 1\right)w_A} = \text{density of the mixture,}$$

M_A, M_B, d_A and d_B are defined in Eq. 5.

Comparing terms of Eq. 6 and Eq. 7, one can see that β_A, β_B and $\Delta\beta_{AB}$ can be obtained from θ_A, θ_B and k without analyzing the original data in the case of $M_A = M_B$ as

$$\beta_A = \frac{1}{2dN}\frac{M_A^2}{M_B}n\theta_A,$$

$$\beta_B = \frac{1}{2dN}M_B n\theta_B,$$

$$\Delta\beta_{AB} = \frac{1}{2dN}M_A nk. \tag{8}$$

In the mixture of CF and CN in Ref. 19, the molecular weight difference between them is about 29%, so $\beta_{CN,CN}$ can not be obtained using Eq. 8. In the CC–MBBA mixture the difference is about 50%. To obtain $\beta_{CN,CN}$ in the CF–CN system and $\beta_{CC,CC}$ in CC–MBBA mixture, it should be calculated after the procedure mentioned above using the original data.

CONCLUSION

The structural pitch of CC and CN mixtures has been obtained as a function of temperature. The experimental results are analyzed using the generalized long range distortion theory. Based on this theory, the temperature dependence of molar twisting power between molecules of the components are determined. Molar twisting power between CC molecules and that between CN molecules increase with increasing temperature. On the other hand, molar twisting power between CC and CN molecules decreases as the temperature increases.

References

1. J. L. Fergason, N. N. Goldberg, and R. J. Nadalin, *Mol. Cryst.*, **1**, 309 (1966).
2. J. Adams, W. Haas, and J. Wysocki, *Phys. Rev. Lett.*, **22**, 92 (1969).
3. H. Baessler and M. M. Labes, *J. Chem. Phys.*, **52**, 631 (1970).
4. J. E. Adams and W. E. L. Haas, *Mol. Cryst.*, *Liquid Cryst.*, **15**, 27 (1971).
5. F. J. Kahn, *Appl. Phys. Lett.*, **18**, 231 (1971).
6. W. Haas and J. Adams, *J. Electro Chem. Soc.*, **118**, 1372 (1971)
7. L. B. Leder, *J. Chem. Phys.*, **55**, 2649 (1971).
8. T. Nakagiri, H. Kodama, and K. K. Kobayashi, *Phys. Rev. Lett.*, **27**, 564 (1971).
9. F. D. Saeva and J. J. Wysocki, *J. Am. Chem. Soc.*, **93**, 5928 (1971).
10. H. Stegemeyer and K. J. Mainusch, *Chem. Phys. Lett.*, **16**, 38 (1972).
11. L. B. Leder, *J. Chem. Phys.*, **58**, 1118 (1973).
12. J. Voss and E. Sackmann, *Z. Naturfor.*, **28a**, 1469 (1973).
13. J. W. Park and M. M. Labes, *Mol. Cryst.*, *Liquid Cryst.*, **31**, 355 (1975).
14. H. Kozawaguchi and M. Wada, *Japan. J. Appl. Phys.*, **14**, 651 (1975).
15. H. Kozawaguchi and M. Wada, *Japan. J. Appl. Phys.*, **14**, 657 (1975).
16. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **62**, 3066 (1975).
17. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **63**, 805 (1975).
18. H. Stegemeyer and H. Finkelmann, *Chem. Phys. Lett.*, **23**, 227 (1973).
19. J. Adams and W. Haas, *Mol. Cryst.*, *Liquid Cryst.*, **30**, 1 (1975).
20. Thermal Analysis Newsletter No. 5 (Perkin–Elmer Co.).
21. Thermal Analysis Newsletter No. 6 (Perkin–Elmer Co.).
22. H. de Vries, *Acta Cryst.*, **4**, 219 (1951).
23. R. Dreher and G. Meier, *Phys. Rev.*, **8**, 1616 (1973).
24. T. Tako, T. Akahane, and S. Masubuchi, *Japan. J. Appl. Phys.*, **14**, suppl. 14-1, 425 (1975).
25. J. L. Fergason, *Mol. Cryst.*, **1**, 293 (1966).
26. I. Teucher, K. Ko, and M. M. Labes, *J. Chem. Phys.*, **56**, 3308 (1972).
27. S. Masubuchi, T. Akahane, K. Nakao, and T. Tako, *Mol. Cryst.*, *Liquid Cryst.*, **35**, 135 (1976).