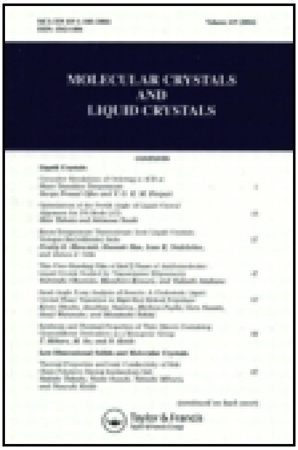

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Molecular Twisting Power of Cholesteryl Propionate, Nonanoate and Myristate

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Molecular Twisting Power of Cholesteryl Propionate, Nonanoate and Myristate†

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We have measured the pitch of cholesteryl propionate-nonanoate mixture at different weight ratio for various temperature. The pitch of ternary mixture, cholesteryl propionate, nonanoate and myristate, was also measured as a function of temperature and concentration of cholesteryl myristate when the weight ratio of propionate and nonanoate is kept equal. The molar twisting power (β) was calculated by employing Bak and Labes' equation and the relation between twisting power and temperatures is found to be linear for cholesteryl propionate, nonanoate and myristate in the temperature range away from transitions.

For the mixture with smectic mesophase the temperature coefficient of the pitch is anomalous. The ν (critical exponent describing the divergence of the smectic correlation length) for cholesteryl nonanoate is found to be 0.611 which is in excellent agreement with de Gennes' prediction.

INTRODUCTION

It is well known that the pitch of cholesterics can be changed by pressure, temperature and concentration. In the binary mixture of the cholesteric liquid crystal, the relation between pitch, temperature and concentration has been investigated by many authors.[1–7] Chen and Chou[8] also had calculated the molar twisting power of cholesteryl propionate and acetate by using the equation derived by Bak and Labes. They found that the molar twisting power is linear in temperature for the temperature range which is away from the transitions. The dependence of pitch on concentration had been studied theoretically by many people.[9–13] Bak and Labes, by extending the concept

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of the long range distortion induced by chiral molecules in a nematic matrix, have obtained an equation governing the pitch–concentration relation for multicomponent liquid crystal mixtures. It is a phenomenological equation and seems that it can explain the experimental data quite successfully.

In this paper, we report the data on composition and temperature dependence of the pitch in the cholesteryl propionate–nonanoate mixture and cholesteryl propionate (CP), nonanoate (CN) and myristate (CMy) mixture. Bak and Labes' equation was used to compute the molecular twisting power for those samples. The relation between the molecular twisting power and temperature is discussed. Because of the presence of cholesteryl nonanoate and cholesteryl myristate, in which they have a smectic-A phase at lower temperature, the mixture shows smectic-A mesophase when the weight ratio of CN and CMy is large. The influence of smectic phase on the pitch is also discussed.

EXPERIMENTAL

A Schimadzu double beam spectrophotometer was employed to measure the reflected peak of the sample when it was arranged perpendicular to the light beam.[14] The sample was sandwiched between slide glass and cover glass and heated by a block heater. The temperature was controlled within 0.1°C and the reflected wavelength was measured with an accuracy of ±5 Å.[8] The cholesteric compounds were purchased from Merck and used without further purification. Their transition temperatures were determined by Reichert Thermovar. Cholesteryl propionate (CP) shows a melting point at $T = 96$°C and a clear point at $T = 114$°C. Cholesteryl nonanoate (CN) melts at $T = 80$°C to cholesteric mesophase and becomes normal liquid at $T = 91$°C when heating. Upon cooling, CN changes to cholesteric phase at $T = 91$°C and transfers to smectic phase at $T = 74$°C, then solidifies by supercooling. By heating, cholesteryl myristate (CMy) melts to smectic phase at $T = 70$°C, becomes cholesteric phase at $T = 80$°C and shows a clearing point at $T = 85$°C. During the cooling from normal liquid, the sample shows no cholesteric phase and changes to smectic phase directly at $T = 80$°C. The solidified temperature can not be determined due to the supercooling. In the cholesteric phase of CMy, the reflected peak can not be detected in the visible and ultraviolet range. The mixture was obtained by mixing the cholesteric compounds in chloroform solution. In order to obtain a uniform color display, the glasses were cleaned by cleaning solution and rubbed. The sample was touched to make sure that the planar texture was formed before the data were taken. Masubuchi *et al.*[15] reported that there is a linear dependence of index of refraction or density on temperature for cholesteric mixture and the influence on the pitch due to the temperature dependence of refractive index and density is quite small when compared with the twisting angle change caused by temperature itself. The value of $\bar{n} = 1.5$ and $d = 1$ g/cm^3, which was used in calculating the twisting power, seems to be a reasonable one. The accuracy for the twisting power of cholesteric component should be within 10%.

RESULTS AND DISCUSSION

A Binary mixture of cholesteric liquid crystal

Figure 1 shows the temperature dependence of the pitch for the binary mixture at different weight ratios. The pitch was obtained by $p = \lambda/\bar{n}$, where

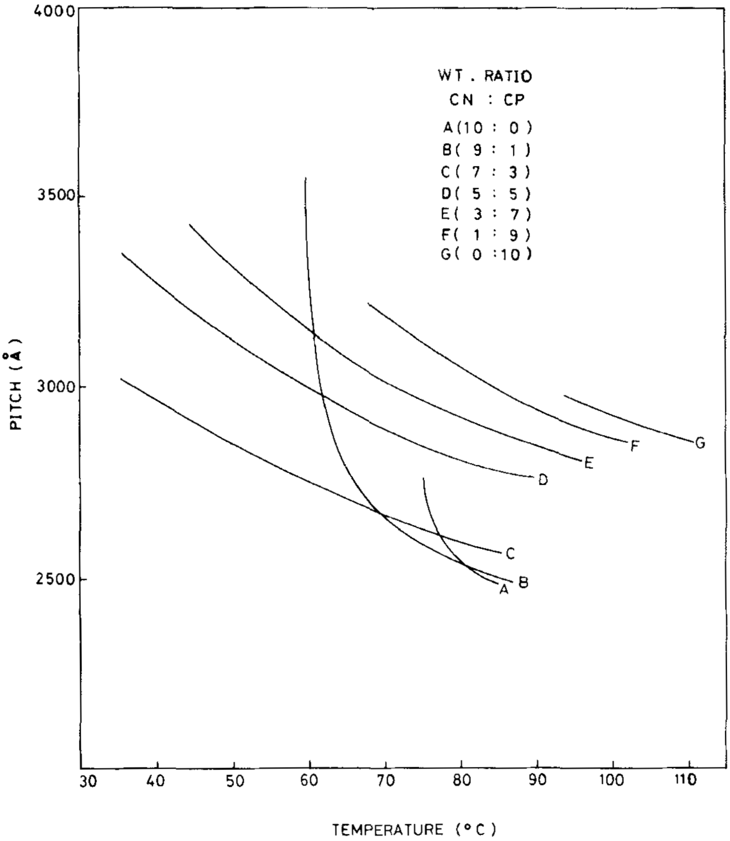

FIGURE 1 Temperature dependence of pitch in cholesteryl nonanoate—propionate mixture at different weight ratios.

λ is the wavelength of the reflected peak and $\bar{n}$ is the average index of refraction of cholesteric mixture. The value of $\bar{n}$ is chosen to be 1.5 and it scarcely varies with temperature.[16–18] It is obvious that curves A and B have extremely high temperature coefficient and the mixture for those two curves with a large proportion of CN shows a smectic phase at lower temperature. This indicates clearly that the anomalous temperature dependence of pitch is linked with the pretransitional effect at the cholesteric–smectic phase transition.

The molar twisting power was computed by using the precise pitch–concentration relation which was derived by Bak and Labes. The equation for binary mixture can be written as:

$$\frac{M_{\mathrm{CP}} + (M_{\mathrm{CN}} - M_{\mathrm{CP}})W_{\mathrm{CP}}}{2pd} - \mathrm{N}\Delta\beta_{\mathrm{CN,CP}}(1 - W_{\mathrm{CP}}) = \mathrm{N}\beta_{\mathrm{CN}}\left(\frac{M_{\mathrm{CP}}}{M_{\mathrm{CN}}}\right) + \mathrm{N}\left(\frac{M_{\mathrm{CN}}}{M_{\mathrm{CP}}}\beta_{\mathrm{CP}} - \frac{M_{\mathrm{CP}}}{M_{\mathrm{CN}}}\beta_{\mathrm{CN}}\right)W_{\mathrm{CP}} \quad (1)$$

where $W_{\mathrm{CP(CN)}}$ = weight fraction of the cholesteryl propionate (nonanoate) and N is Avogadro's number

$$d = \frac{d_{\mathrm{CN}}}{1 + (d_{\mathrm{CN}}/d_{\mathrm{CP}} - 1)W_{\mathrm{CP}}}$$

is the density (g/cm^3) of the mixture and $d_{\mathrm{CP(CN)}}$ is the density of the cholesteryl propionate (nonanoate). The parameter $\Delta\beta_{\mathrm{CP,CN}}$ is defined as:

$$\Delta\beta_{\mathrm{CP,CN}} = 2\beta_{\mathrm{CP,CN}} - \left[\left(\frac{M_{\mathrm{CN}}}{M_{\mathrm{CP}}}\right)\beta_{\mathrm{CP}} + \left(\frac{M_{\mathrm{CP}}}{M_{\mathrm{CN}}}\right)\beta_{\mathrm{CN}}\right]$$

where $\beta_{\mathrm{CP(CN)}}$ is the effective (or mean) molecular twisting power between CP(CN) molecules only. When β is positive (negative), the helical structure is right (left) handed. In equation (1), the left-hand side is linear in W_{CP} and the plot is shown in Figure 2. Figure 2 is obtained by the least square fitting of three typical different temperatures at various weight fraction of CP. $M_{\mathrm{CP}} = 443$ g and $M_{\mathrm{CN}} = 527$ g were used. By letting $W_{\mathrm{CP}} = 0$, the values of the line intersecting at the vertical coordinate is equal to $M_{\mathrm{CP}}/2pd$, which is just $\mathrm{N}\beta_{\mathrm{CN}}(M_{\mathrm{CP}}/M_{\mathrm{CN}})$ by Eq. (1). In this way, we calculated the values for $\mathrm{N}\beta_{\mathrm{CN}}$ at different temperature and Figure 3 gives the results. From the slope of straight line and using the value of $\mathrm{N}\beta_{\mathrm{CN}}$, we can compute $\mathrm{N}\beta_{\mathrm{CP}}$ as a function of temperature and Figure 4 shows the value of $\mathrm{N}\beta_{\mathrm{CP}}$. Figure 3 and 4 imply that the data for the twisting power of CP and CN can be fitted in a linear relation with temperature for the temperature range away from the transition. The result is consistent with what Chen and Chou reported before. In other words, the relation between pitch of CP or CN and temperature is hyperbolic that was predicted by Keating.[19]

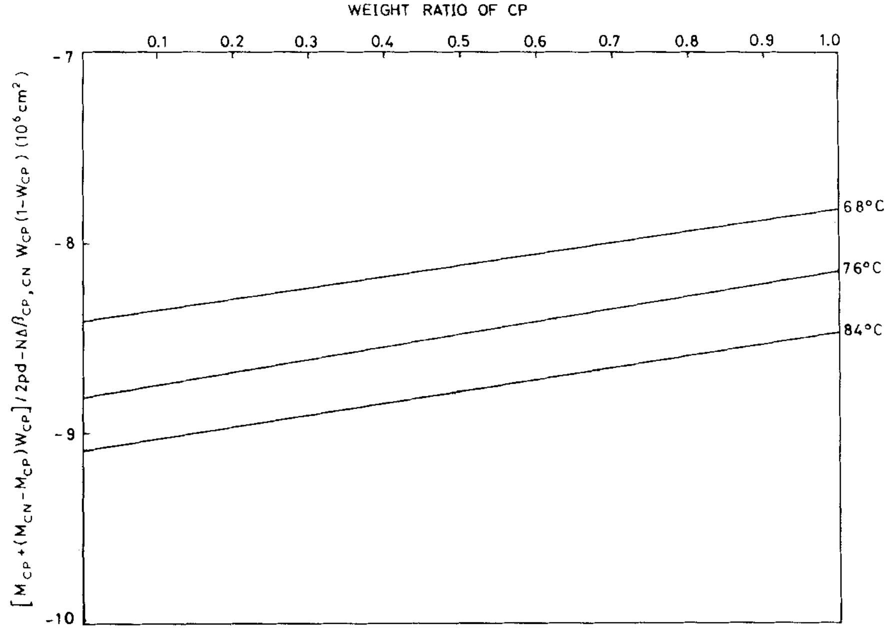

FIGURE 2 Plot of $[M_{CP} + (M_{CN} - M_{CP})W_{CP}]/2pd - n\Delta\beta_{CP,CN}W_{CP}(1 - W_{CP})$ vs weight ratio (W_{CP}) of cholesteryl propionate at different temperatures.

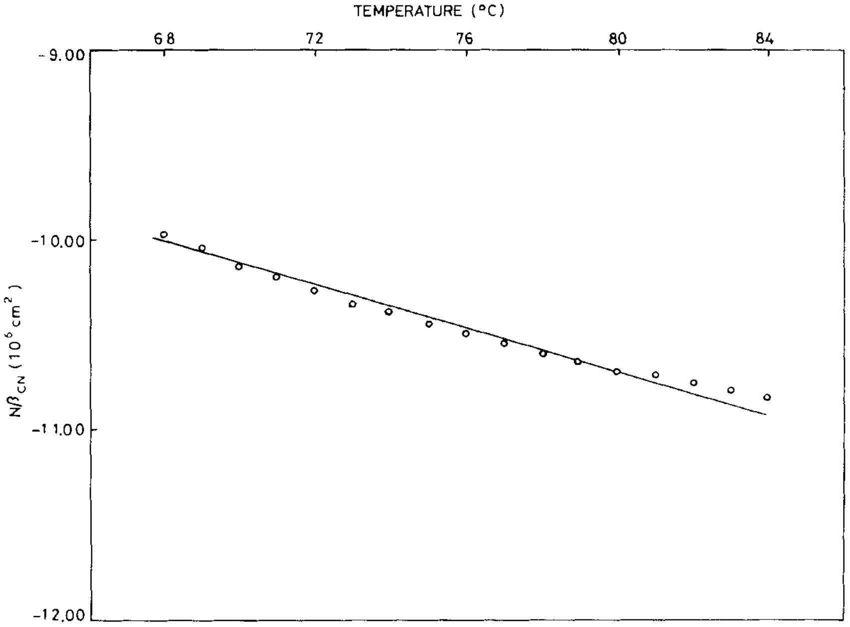

FIGURE 3 Dependence of molar twisting power of cholesteryl nonanoate on temperature.

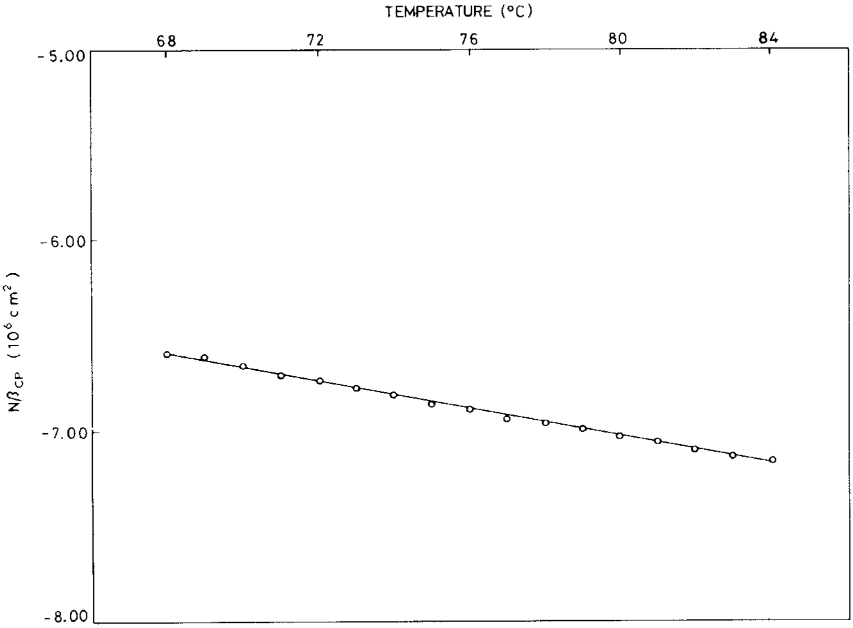

FIGURE 4 Dependence of molar twisting power of cholesteryl propionate on temperature.

We have used Eq. (1) to compute the values of $N\Delta\beta_{CP,CN}$ and it is found that their values are in the order of 10^5 cm^2 which is quite small (~10%) when it is compared with $N\beta_{CP(CN)}$.

It means that the deviation of molar twisting power ($N\beta_{CP,CN}$) between CP and CN from the average value of $N\beta_{CP}$ and $N\beta_{CN}$ is small. This can be accounted for the reason of the success of linear additive law. The dependence of $N\Delta\beta_{CP,CN}$ on temperature is shown in Figure 5.

When the cholesteric sample with a smectic phase at lower temperature, an equation similar to the elastic constant was proposed by de Gennes[20] as follows,

$$P = P_n + D(T - T_C)^{-\nu}$$

where ν = critical exponent describing the divergence of the smectic correlation length; P = the pitch of CN; and P_n = the intrinsic pitch of CN or the pitch for temperature away from the cholesteric–smectic transition temperature (T_C), namely, the pitch containing no smectic phase influence. We use the value of curve A in Figure 1 for P and $P_n = M_{CN}/2N\beta_{CN}d$, in which the value of $N\beta_{CN}$ in Figure 3 was employed. The plot of $\log(P - P_n)$ vs $\log(T - T_C)$ is shown by Figure 6. It is a straight line and its slope gives the value of $-\nu$ and $T_C = 74$°C is used. The value of ν is found to be 0.611

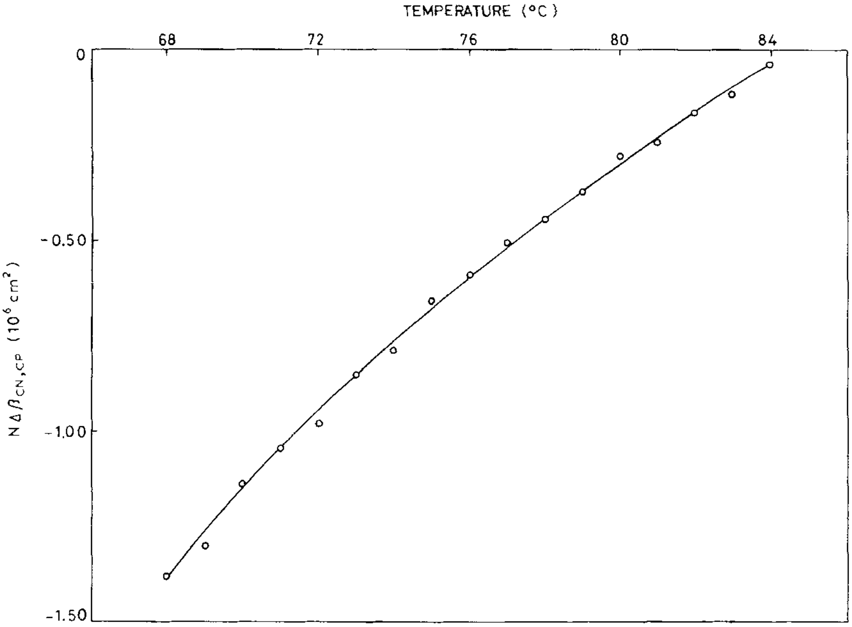

FIGURE 5 Temperature dependence of the molar twisting power deviation ($N\Delta\beta_{CN,CP}$) for cholesteryl nonanoate and propionate.

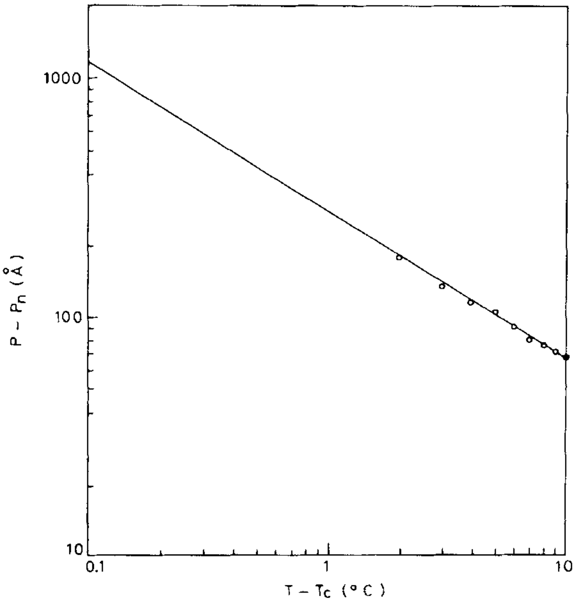

FIGURE 6 Plot of log ($p - P_n$) vs ($T = Tc$) for cholesteryl nonanoate when $Tc = 74°C$.

which is in good agreement with the values obtained by elastic constant measurements[21–23] and de Gennes' predication. Pindak *et al.*[24, 25] also reported the similar value of ν for CN. It is worthy to notice that the value of ν is quite sensitive to the choice of T_C which is hard to measure accurately.

B Ternary mixture of cholesteric liquid crystal

The equation governing the relation between pitch and weight fraction of the components can be written as:

$$\begin{aligned} \frac{1}{2pdMW_{CMy}} &- NM^{-1}\left[\frac{\beta_{CP}}{M_{CP}}\alpha + \frac{\beta_{CN}}{M_{CN}}(1-\alpha)\right]\frac{(1-W_{CMy})}{W_{CMy}} \\ &- N\frac{\delta\beta_{CP,CN}}{M_{CP}M_{CN}}\frac{\alpha(1-\alpha)(1-W_{CMy})^2}{W_{CMy}} \\ &= NM^{-1}\frac{\beta_{CMy}}{M_{CMy}} + N\left[\frac{\delta\beta_{CP,CMy}}{M_{CP}M_{CMy}}\alpha(1-W_{CMy})\right. \\ &\left.+ \frac{\delta\beta_{CN,CMy}}{M_{CN}M_{CMy}}(1-\alpha)(1-W_{CMy})\right]. \end{aligned} \tag{2}$$

Where $\delta\beta_{CP,CN} = 2\beta_{CP,CN} - (\beta_{CP} + \beta_{CN})$; $\delta\beta_{CP,CMy} = 2\beta_{CP,CMy} - (\beta_{CP} + \beta_{CMy})$; $\delta\beta_{CN,CMy} = 2\beta_{CN,CMy} - (\beta_{CN} + \beta_{CMy})$ and

$$M^{-1} = \left[\frac{\alpha(1-W_{CMy})}{M_{CP}} + \frac{(1-\alpha)(1-W_{CMy})}{M_{CN}} + \frac{W_{CMy}}{M_{CMy}}\right]$$

α = the weight fraction of CP component in the mixture of CP and CN only.
W_{CMy} = the weight fraction of CMy component in the total mixture of CP, CN and CMy compounds.

The right-hand side of Eq. (2) is linear in W_{CMy}. Thus a plot of the left-hand side of Eq. (2) vs W_{CMy} for a fixed α value should yield linear behavior over the composition range of W_{CMy}.

For the ternary mixture of CP, CN and CMy, Figure 7 shows the temperature dependence of pitch at different weight fraction of CMy when $\alpha = 0.5$. The figure also indicates the pretransitional smectic effect in curve G, H and I. The left-hand side of Eq. (2) is plotted for $\alpha = 0.5$ vs weight fraction of CMy (W_{CMy}) at different temperature and the least square method is used. Because that the molar twisting power is related to the intrinsic pitch of the cholesteric component by $N\beta = M/2pd$, we have avoided the data of curve G, H and I of Figure 7 in the least square fitting process. By extrapolating the straight line in Figure 8 to $W_{CMy} = 1$, the value of $N\beta_{CMy}$ at different temperature is

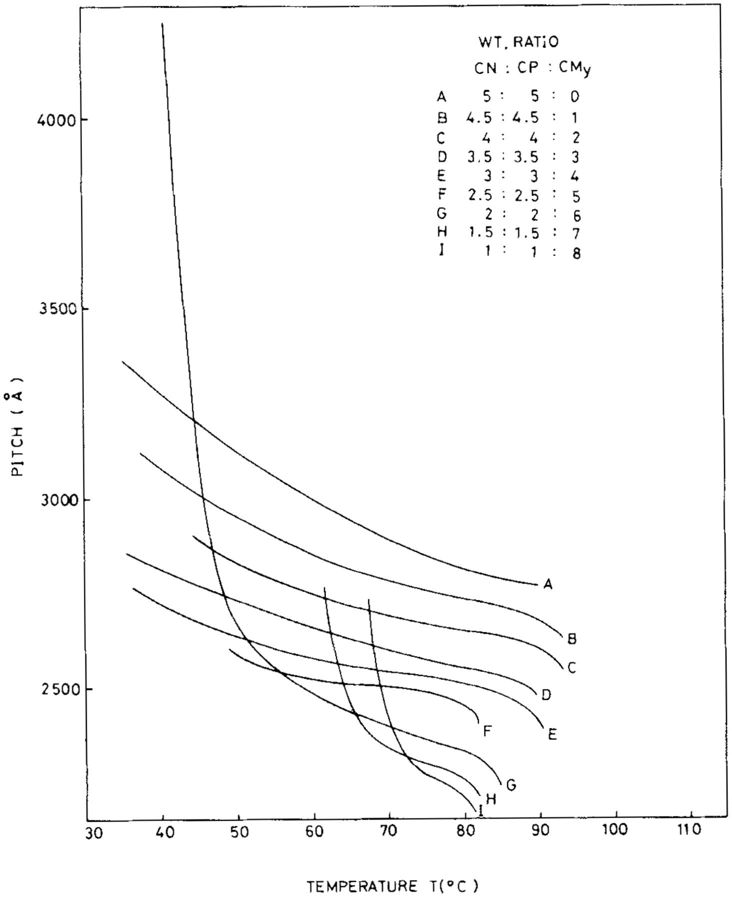

FIGURE 7 Temperature dependence of pitch in the cholesteryl nonanoate, propionate and myristate ternary mixture at different weight ratios of cholesteryl myristate when the weight ratio of cholesteryl nonanoate and propionate is equal.

obtained. Figure 9 shows the variation of molar twisting power for CMy with temperature obtained in this manner.

CONCLUSION

We have used the Bak and Labes' equation to calculate the molar twisting power for CP, CN and CMy and found that the twisting power is linear in temperature for the temperature range away from the transition. In other words, the pitch of cholesteric component is hyperbolically dependent on

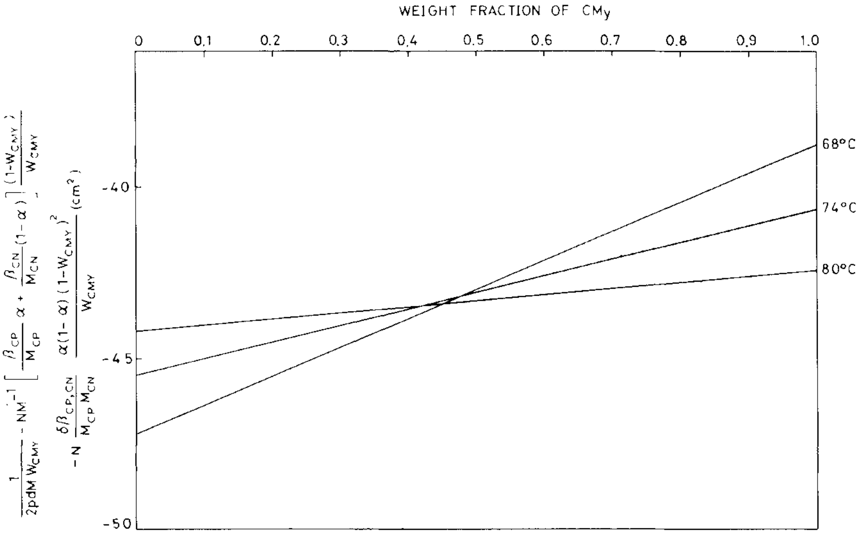

FIGURE 8 Plot of $1/2pdMW_{CMy} - NM^{-1}[(\beta_{CP}/M_{CP}) + (\beta_{CN}/M_{CN})(1-\alpha)](1-W_{CMy})/W_{CMy} - N(\delta\beta_{CP,CN}/M_{CP}M_{CN})\alpha(1-\alpha)(1-W_{CMy})^2/W_{CMy}$ vs weight fraction (W_{CMy}) of cholesteryl myristate at different temperatures.

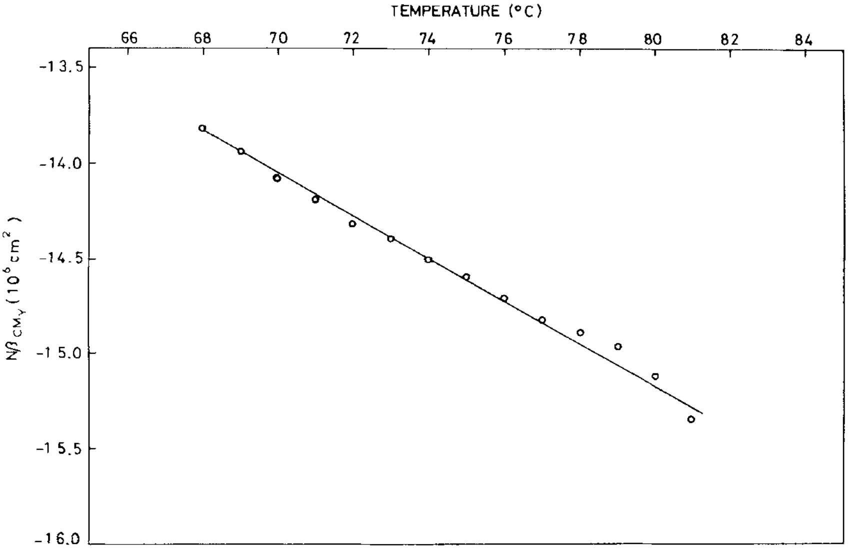

FIGURE 9 Dependence of molar twisting power of cholesteryl myristate on temperature.

temperature. For the component (mixture) with smectic phase at lower temperature, the pitch is greatly influenced by the pretransitional smectic effect. This phenomenon is clear indicated in Figure 1 and 7. The critical exponent for the smectic correlation length (ν) was computed and is equal to 0.611 that is agreed with the values obtained by the elastic constant measurements and de Gennes' prediction.

References

1. J. Adams and W. Haas, *Mol. Cryst. Liq. Cryst.*, **30**, 1 (1975).
2. F. Kahn, *Appl. Phys. Lett.*, **18**, 231 (1971).
3. J. Adams and W. Hass, *Mol. Cryst. Liq. Cryst.*, **15**, 27 (1971).
4. J. M. Schnur and D. E. Martire, *Mol. Cryst. Liq. Cryst.*, **26**, 213 (1973).
5. R. S. Pindak, C. C. Huang, and J. T. Ho, *S.S. Commun.*, **14**, 821 (1974).
6. H. Kozawaguchi and M. Wada, *Japan. J. Appl. Phys.*, **14**, 651 (1975).
7. S. Masubuchi, T. Akahane, K. Nakao, and T. Tako, *Mol. Cryst. Liq. Cryst.*, **38**, 265 (1977).
8. S. H. Chen and L. S. Chou, *Mol. Cryst. Liq. Cryst.*, **40**, 223 (1977).
9. W. J. A. Goossens, *Mol. Cryst. Liq. Cryst.*, **12**, 237 (1971).
10. P. G. de Gennes, *The Physics of Liquid Crystal* (Clarendon, Oxford, 1974), Chapt. 3 and 6.
11. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **63**, 805 (1975).
12. C. S. Bak and M. M. Labes, *J. Chem. Phys.*, **62**, 3006 (1975).
13. H. Kozawaguchi and M. Wada, *Japan. J. Appl. Phys.*, **14**, 657 (1975).
14. L. S. Chou, IEE Conf. Publication No. 177, 181 (1979).
15. S. Masubuchi, T. Akahane, K. Nakao, and T. Tako, *Mol. Cryst. Liq. Cryst.*, **35**, 135 (1976).
16. P. Gaubert, *Bull. Soc. Fr. Mineral.*, **36**, 174 (1913).
17. W. U. Muller and H. Stegemeyer, *Ber. Bunsenges. Phys. Chem.*, **77**, 20 (1973).
18. V. G. Rumyantsev, P. D. Berezin, L. M. Blinov, and I. N. Kompanets, *Sov. Phys. Crystallogr.*, **18**, 697 (1974).
19. P. Keating, *Mol. Cryst. Liq. Cryst.*, **8**, 315 (1969).
20. P. G. de Gennes, *S.S. Commun.*, **10**, 753 (1972).
21. L. Cheung, R. B. Meyer and H. Gruler, *Phys. Rev. Lett.*, **31**, 349 (1973).
22. M. Delaye, R. Ribotta and G. Durand, *Phys. Rev. Lett.*, **31**, 443 (1973).
23. L. Leger, *Phys.* Lett., **44A**, 535 (1973).
24. R. S. Pindak, C. C. Huang, and J. T. Ho, *Phys. Rev. Lett.*, **32**, 43 (1974).
25. R. S. Pindak, C. C. Huang, and J. T. Ho, *S.S. Commun.*, **14**, 821 (1974).