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

Electro—Optic and Dielectric Studies in Cholesteric Liquid Crystal Mixtures

C. K. Shashidharan Nalr [a] & Kolluri V. Ramanaiah [a]
[a] Department of Physics, PSG College of Technology, Coimbatore, 641 004, India

Version of record first published: 13 Dec 2006.

To cite this article: C. K. Shashidharan Nalr & Kolluri V. Ramanaiah (1983): Electro—Optic and Dielectric Studies in Cholesteric Liquid Crystal Mixtures, Molecular Crystals and Liquid Crystals, 103:1-4, 271-285

To link to this article: http://dx.doi.org/10.1080/00268948308071059

Mol. Cryst. Liq. Cryst., 1983, Vol. 103, pp. 271–285
0026-8941/83/1034-0271/$18.50/0

Printed in the United States of America

Electro–Optic and Dielectric Studies in Cholesteric Liquid Crystal Mixtures

C. K. SHASHIDHARAN NAIR and KOLLURI V. RAMANAIAH
Department of Physics, PSG College of Technology, Coimbatore 641 004, India

(Received May 1, 1983; in final form July 18, 1983)

In binary mixtures of cholesteryl chloride and cholesteryl alkanoates, the threshold field for the cholesteric to nematic transformation depends on the length of the alkanoate ester chain. The threshold field also depends on the pitch, the dielectric anisotropy and the twist elastic constant of the mixtures. This paper describes the experiments performed to establish the role of these three parameters in the observed variation of threshold field with alkanoate ester chain length in such binary mixtures.

The temperature dependence of threshold field, dielectric anisotropy and pitch has been studied. From these experiments the relative response of the various mixtures to applied electric fields has been established. In most of the mixtures, temperature ranges over which pretransitional effects do not predominate, have been identified. Twist elastic constants of the mixtures in these temperature ranges have been calculated. It has been shown that both the intrinsic response of the mixtures to applied electric fields, and the twist elastic constants do not show a regular variation with chain length of the alkanoate ester tail. Some observations suggest that mixtures containing non-smectogenic alkanoates show different temperature dependence of threshold field as compared to those containing smectogenic alkanoates.

INTRODUCTION

The electric field induced cholesteric to nematic (CN) transformation has been studied by a number of workers. In one of the earliest studies made by Wysocki *et al.*,[1] using equimolar binary mixtures of cholesteryl chloride with various cholesteryl alkanoates, it was shown that at 21 °C, the threshold field for the CN transformation increased linearly with increasing chain length of the alkanoate ester tails.

The threshold field for the CN transformation depends on the pitch, the dielectric anisotropy and twist elastic constant of the mixtures.

Therefore in order to provide a better understanding of the effect of alkanoate ester chain length on threshold field, it would be necessary to study the role of all the three parameters–the pitch, the dielectric anisotropy and twist elastic constant, in the phenomenon. To this end, the authors took up a detailed investigation of the CN transformation in binary mixtures of cholesteryl chloride with various cholesteryl alkanoates. The temperature dependence of threshold field was established. The dielectric anisotropy of the mixtures was determined using a capacitance-voltage technique. The variation of pitch of the mixtures with temperature was studied using a light scattering technique.

EXPERIMENTAL

The threshold voltage for the CN transformation in cholesteric film samples viewed under a polarising microscope, was defined[2] as that voltage at which first noticeable signs of transformation appeared. Employing that definition, the temperature dependence of threshold voltage for a 65.2 : 34.8 mole % mixture of cholesteryl chloride and cholesteryl nonanoate was studied. Complete pitch compensation was reported in that mixture at 42 °C. In the present study, the first mixture taken up was also of the same constituents and composition. Experiments to study the temperature variation of threshold voltage with temperature were performed to confirm the definition of threshold voltage. In subsequent mixtures, the same molar ratio of constituents was maintained. The threshold voltages were measured both by microscopic examination and by a Depolarised Light Intensity (DLI) technique reported by Cornelia Motoc *et al.*.[3] The experimental arrangement for the study of threshold voltage was a polarising microscope fitted with a hot stage and an on-partial off mode of temperature control, giving a control of 0.1 °C. The microscope was fitted with an RCA 931A photomultiplier tube (PMT) to record the intensity of transmitted light. Standard sandwich cells of tin oxide coated glass and mylar spacers were used. Cell surfaces were prepared for parallel alignment by rubbing. (These cells were used for the measurement of dielectric anisotropy and pitch measurements also). The cell under study was placed on the hot stage of the microscope. A d.c. voltage was applied to the cell. The applied voltage was increased in steps and the field of view was observed. As the voltage was increased from zero, a series of textural changes were observed, leading to the formation of the fingerprint texture. At the threshold for the CN transformation, the fingerprint texture began to break up. This was accompanied by a sharp decrease in the intensity of transmitted light. Increase in applied voltage beyond threshold was accompanied by a progressive darkening of the field of view and decrease in transmitted light intensity. The transmitted light intensity measurements thus helped to establish the threshold voltage with better precision. The DLI technique was also used to confirm the measurements and to determine pitch compensation temperatures.

For the determination of dielectric anisotropy, a d.c. orienting field was used, together with an alternating measuring field. The cell under study was placed on the hot stage of the polarising microscope and connected to a commercial capacitance bridge. The bridge had the facility for applying the d.c. orienting field together with a 1KHz measuring field, through the measurement terminals. Both orienting and measuring fields were therefore applied to the same set of electrodes, i.e., the tin oxide surfaces. Microscopic examination was also along this direction. The orienting field was increased in steps. A few minutes after the application of each step, the capacitance was measured. Thus capacitance-voltage data were acquired. This was supplemented with microscopic observation and transmitted light intensity measurements, for the determination of dielectric anisotropy, as explained under the section dealing with the results of these experiments.

Light scattering from the fingerprint texture has been the subject of extensive study.[4-8] For the purpose of the present investigation, pitch measurements were made by studying light scattering from the electric field induced fingerprint texture. In this texture, the cholesteric acts as a grating. When light from a He-Ne laser was passed through the sample, normal to the plane of the film, it gave rise to a diffraction pattern on the opposite side, consisting of concentric rings when viewed on a screen. The diffraction pattern was scanned by a photomultiplier tube and the output of the PMT recorded on a strip chart recorder. The complete experimental setup is described in our earlier paper.[9]

RESULTS AND DISCUSSIONS

The following alkanoates were studied in binary mixtures with cholesteryl chloride.

i. Cholesteryl nonanoate
ii. Cholesteryl myristate
iii. Cholesteryl laurate
iv. Cholesteryl butyrate

a. Threshold field measurements

The first mixture to be studied was a 65.2 : 34.8 mole % mixture of cholesteryl chloride and cholesteryl nonanoate respectively. As mentioned earlier, this was studied with the intention of establishing the definition of threshold voltage. The results are shown in Figure 1 by the lines marked ‘1’. The crosses represent data obtained by microscopic examination and the open triangles represent data obtained by the DLI technique. Data for this mixture are presented mainly for

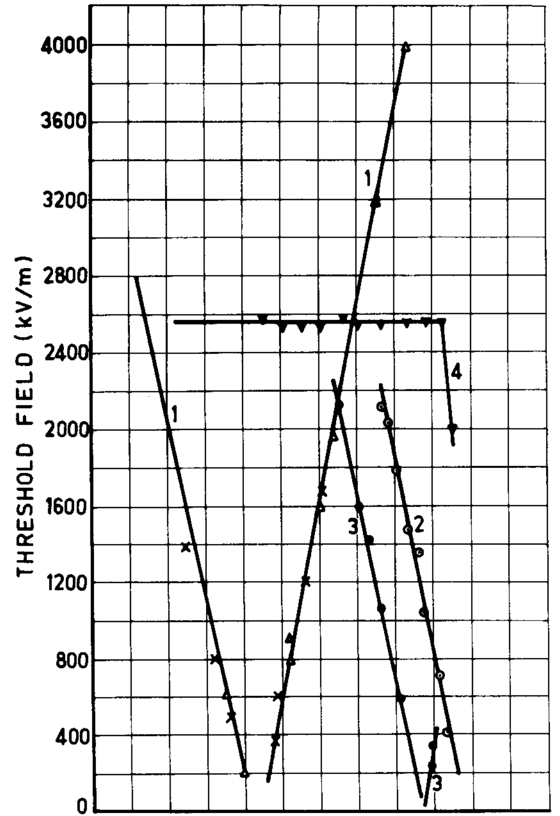

FIGURE 1 Variation of threshold field with temperature for binary mixtures of cholesteryl chloride with various cholesteryl alkanoates. 1. Cholesteryl nonanoate 34.8 mole %, 2-cholesteryl myristate 34.8 mole %, 3-Cholesteryl laurate—34.8 mole %, 4-Cholesteryl butyrate—45 mole %.

comparison with other mixtures. The sample thickness was 25 μm, the pitch compensation temperature was 42 °C and cholesteric to isotropic transition temperature was 68 °C. All other mixtures studied were of the same molar ratio as this mixture, unless otherwise indicated.

The cholesteryl chloride and cholesteryl myristate mixture had a cholesteric to isotropic transition temperature of 68 °C. The threshold field data for this mixture (sample thickness 36 μm) are shown in Figure 1 by the line marked '2'. Complete pitch compensation could not be seen as the material passed into the isotropic phase before complete compensation could be observed. This is consistent with the observations of Sackmann and Mohwald.[10]

The data for cholesteryl laurate are shown by lines marked '3' in Figure 1. The cell spacing in this case was 55.9 μm. Complete pitch compensation was observed in this case. DLI studies gave a pitch compensation temperature of 62.5 °C. The cholesteric to isotropic transition temperature was 65.5 °C.

In the case of cholesteryl butyrate, the 65.2 : 34.8 mole % mixture did not transform, even for voltages high enough to cause dielectric breakdown of the samples. To study this phenomenon, two other compositions of the same constituents were tried out—a 50 : 50 mole % mixture (mixture 1) and a 55 : 45 mole % mixture (mixture 2) of cholesteryl chloride and cholesteryl butyrate respectively. Of these, the equimolar mixture could not be transformed (dielectric breakdown), while the behaviour of the other is interesting. Data for this mixture are marked '4' in Figure 1. (Sample thickness 35.2 μm). The threshold field remains fairly constant at all temperatures, but just below the cholesteric to isotropic temperature of 68 °C, the threshold field falls sharply. A similar zero slope of threshold field with temperature was observed by Wysocki *et al.*,[1] in an equimolar mixture of cholesteryl proprionate and cholesteryl chloride. This phenomenon is discussed further under a subsequent section.

b. Dielectric anisotropy measurements

It has been shown by Kashnow *et al.*,[11] that for a cholesteric film subjected to an electric field, the effective dielectric constant in the fingerprint texture is $\epsilon_{av} = \frac{1}{2}(\epsilon_1 + \epsilon_2)$, while in the nematic state it is ϵ_1. Here ϵ_1 and ϵ_2 are the dielectric constants measured parallel and perpendicular to the long molecular axes respectively. In the electric field induced fingerprint texture, the helical axes are perpendicular to the direction of the electric field. In the present study, since the capacitance was also measured in the direction of the orienting field, the measured dielectric constant in the fingerprint texture is ϵ_{av}. In the field induced nematic state, the molecules are all aligned in the direction of the electric field, i.e., normal to the electrodes. A measurement of capacitance in this direction therefore gives ϵ_1. The dielectric anisotropy $\Delta\epsilon = (\epsilon_1 - \epsilon_2)$ may be calculated from the relation, $\Delta\epsilon = 2(\epsilon_1 - \epsilon_{av})$.

The formation of the fingerprint texture and the CN transformation were confirmed by transmitted light intensity measurements and by microscopic observation. The fingerprint texture was completely formed at voltages typically 6% short of the threshold voltage, and was stable till the threshold. Over this range of voltages, the measured capacitance also did not show any appreciable change. The dielectric anisotropies of the various mixtures were thus determined at various temperatures. These values are shown in Figure 2. In all the cases (except in the case of cholesteryl butyrate), there is a range of temperatures over which the dielectric anisotropy does not vary much. With the approach of the cholesteric to isotropic transition temperature, it decreases. In the case of cholesteryl butyrate (mixture 2), only

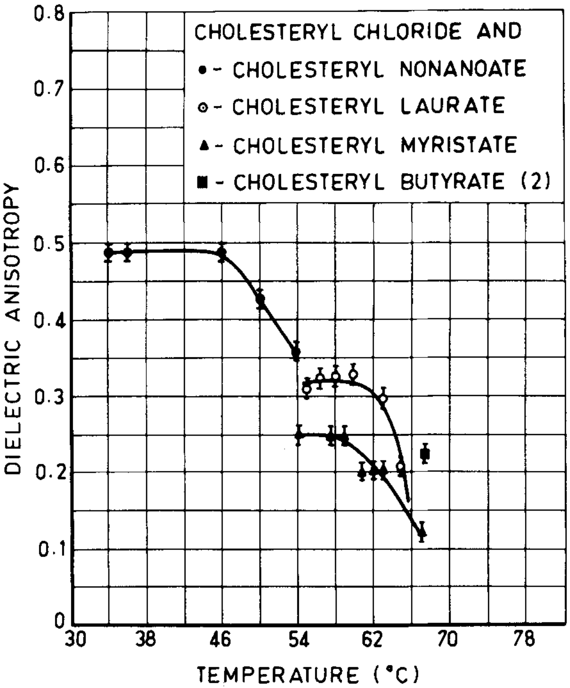

FIGURE 2 Variation of dielectric anisotropy of the mixtures with temperature.

one measurement could be made close to the cholesteric isotropic transition temperature. At lower temperatures, the measurement was complicated by fluid flow effects. The other mixtures containing cholesteryl butyrate could not be transformed into the nematic state. Hence ϵ_1 for these mixtures could not be measured.

A comparison of the dielectric anisotropies of the various mixtures (except cholesteryl butyrate) in the temperature-independent regions, shows that the dielectric anisotropy decreases with increasing alkanoate ester chain length.

c. Measurement of Pitch

Freshly prepared samples of the cholesterics usually did not give any diffraction pattern when He–Ne laser light was passed through it. On applying an electric field strong enough to transform the material into the nematic state, and subsequently switching off the field, a diffraction pattern consisting of a circular ring surrounding a bright central spot could be observed on a screen placed on the far side of the film. The ring was formed by a cone of diffracted light having its apex at the sample and the undiffracted central beam as axis. The semivertical angle of this cone gives the diffraction angle. A photomultiplier tube (PMT) scanning the diffraction ring diametrically, perpendicular to the axis of the diffraction cone (at a fixed distance from the sample), registers a large central maximum M_0 corresponding to the undiffracted direct beam and two symmetrically placed maxima M_1 and M_1' on either side of M_0 corresponding to the diffraction ring. Microscopic examination of the sample revealed a combination of the planar texture and a hazy fingerprint texture. The diffraction pattern observed was presumably due to Bragg reflections from randomly oriented scattering centres as was observed by T. Harada *et al.*[4]

When a low voltage was applied to the cell, another set of maxima M_2 and M_2' were nucleated at angles typically 25% less than that for M_1 and M_1' respectively. Microscopic examination showed large scale fingerprint texture formation. As the applied voltage was increased, and M_2 and M_2' grew stronger while M_1 and M_1' weakened. M_2 and M_2' were strongest just below the threshold for the CN transformation. Under this condition, microscopic examination showed complete formation of the fingerprint texture. M_2 and M_2' were thus associated with the fingerprint texture. During the process of formation of the fingerprint texture, only the intensity of M_2 and M_2' increased while their angle did not change for voltages less than threshold. Thus, pitch calculations were made using the diffraction angle for M_2, at applied voltages typically 10% less than the corresponding threshold voltage at that temperature.

Masao Kawachi *et al.*[5] proposed a model for light scattering from nematic-cholesteric mixtures with perpendicular boundary conditions. According to this model, the initial maximum M_1 is due to Bragg reflections from randomly oriented scattering centres, while the application of electric field causes the cholesteric to align itself with the helical axes parallel to the plane of the film. It is now fairly well known,[12] that for a cholesteric in the fingerprint texture, the helical axis is parallel to the plane of the film. Therefore in the case of the cholesterics reported herein, the model proposed by Masao Kawachi *et al.* was adopted. If θ is diffraction angle corresponding to M_2, then the following relation holds good.

$$\sin\theta = \frac{N\lambda}{D} \tag{1}$$

where D is the optical lattice spacing, N is the diffraction order and λ is the wavelength of light used.

Masao Kawachi *et al.* had used perpendicular oriented cells and had concluded that the optical lattice spacing D was equal to the pitch of the cholesteric. This was based on the observation that when an electric field was applied to the nematic-cholesteric mixture, *two* new maxima had nucleated between M_0 and M_1, while in the case of the parallel oriented samples described herein, only one maximum (M_2) was formed. Further M_2 was formed at an angle about 25% less than that for M_1, but not midway between M_0 and M_1 as observed by Kramarenko *et al.*[6] Based on these observations, it was concluded that the optical lattice spacing D is equal to half the pitch in the case of the parallel oriented samples. A similar relation was used by Sackmann *et al.*[7] Thus Eq. (1) was used for pitch calculations. The temperature-dependence of pitch was thus studied. The variation of pitch with temperature is shown for the mixtures containing cholesteryl nonanoate, cholesteryl laurate and cholesteryl myristate in Figures 3, 4 and 5 respectively. In all these cases, pitch increases with temperatures approaching pitch compensation. In the case of cholesteryl laurate, data corresponding to temperatures greater than the pitch compensation temperature could not be obtained, as the diffraction orders were buried in background radiation. In the case of cholesteryl myristate, complete pitch compensation could not be observed, but the trend of the threshold field data (Figure 1) and the pitch data (Figure 5) in the cholesteric range indicate a tendency towards compensation.

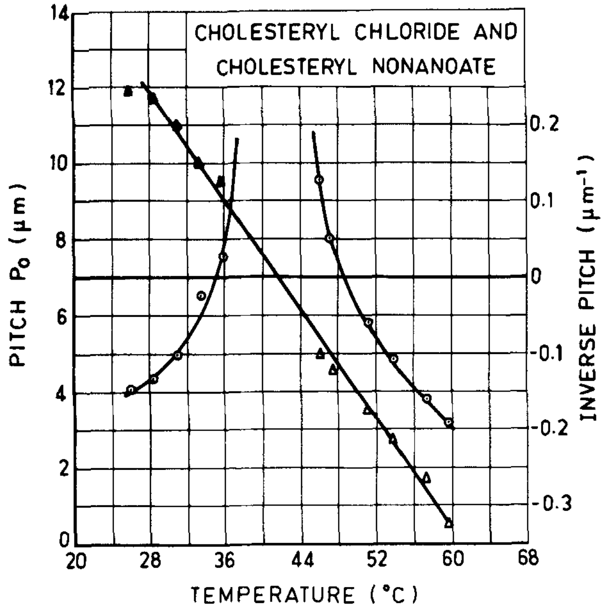

FIGURE 3 ○—Variation of pitch with temperature in the cholesteryl nonanoate-cholesteryl chloride mixture. △—Variation of inverse pitch with temperature.

The 65.2 : 34.8 mole % mixtures of cholesteryl chloride and cholesteryl butyrate did not give a diffraction pattern. The two other mixtures–the equimolar mixture (mixture-1) and the one containing 55 mole % of cholesteryl chloride (mixture-2), did give diffraction patterns and pitches of both these mixtures were determined. Data for these are presented in Figure 6. Both the mixtures display remarkable temperature independence of pitch. This explains the low slope of threshold voltage variation with temperature in mixture-2 (Figure 1). Also, the observation that the transformation could not be induced in mixture 1 may be attributed to the fact that the pitch was too low.

The relative response of the various mixtures to applied electric fields are presented in Figure 7. This figure shows the variation of threshold field of the various mixtures with pitch. The cholesteryl laurate and cholesteryl myristate mixtures show a large increase in threshold field at the lower end of the pitch scale. To understand this phenomenon, the inverse pitch is plotted as a function of temperature for the respective mixtures in Figures 3, 4 & 5. The curves include the pitch compensation temperature as one of the data points (inverse pitch is zero). In the case of cholesteryl myristate, the pitch compensation temperature was determined by extrapolation of threshold field

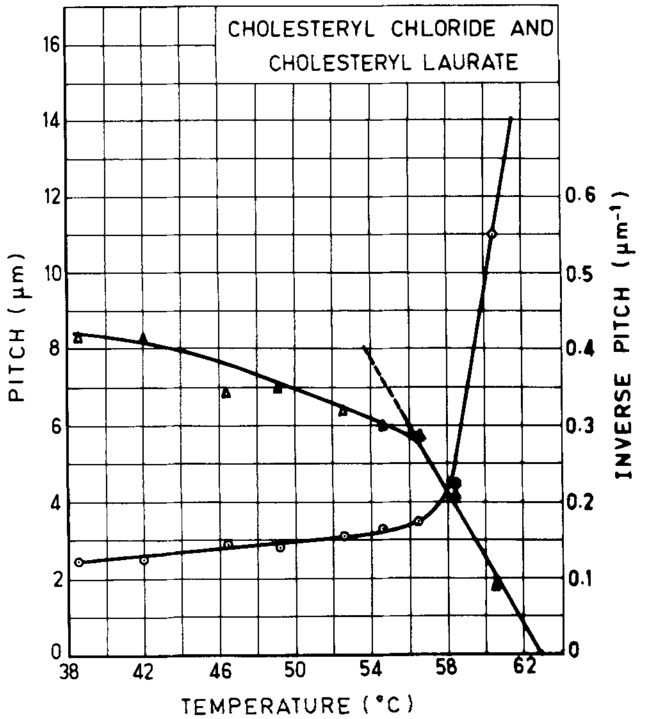

FIGURE 4 ○—Variation of pitch with temperature in the cholesteryl laurate-cholesteryl chloride mixture. △—Variation of inverse pitch with temperature.

data to zero threshold field. This gives a pitch compensation temperature of 69 °C. In the case of cholesteryl nonanoate, negative values of inverse pitch represent the data obtained at temperatures higher than the pitch compensation temperature, where the handedness of the cholesteric helix is reversed. Normally, the mixtures could be expected to show a linear variation of inverse pitch with temperature, with the pitch compensation temperature lying on this line.[13] Now, since the threshold field also varies linearly with temperature upto the pitch compensation temperature, it may readily be seen that under such conditions, the threshold field (E_T) varies inversely with pitch (P_0) upto the pitch compensation temperature. In the case of cholesteryl nonanoate, fairly linear behaviour of inverse pitch is seen (Figure 3), but in the case of cholesteryl laurate (Figure 4) and cholesteryl myristate (Figure 5), marked deviation from linearity is observed at low temperatures. Such deviation may be attributed to the tendency of the mixture to form a smectic phase at low temperatures.[14-16] This

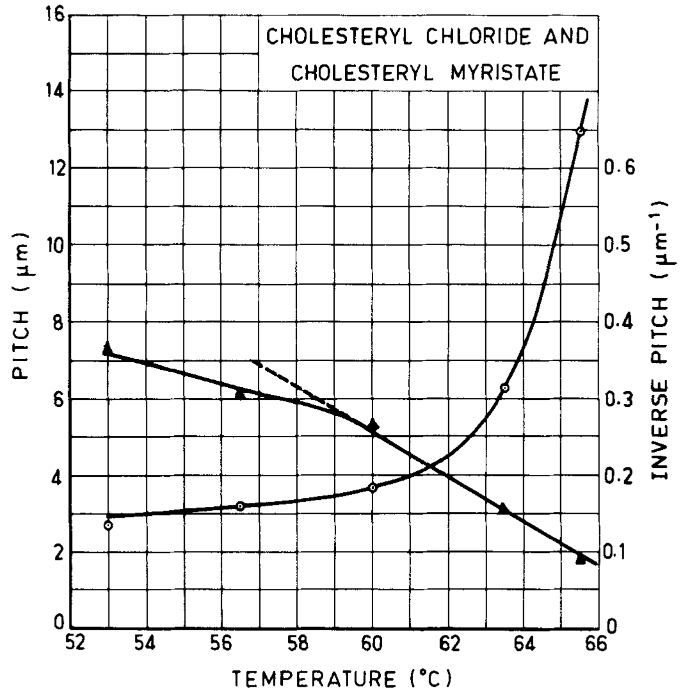

FIGURE 5 o—Variation of pitch with temperature in the cholesteryl myristate—cholesteryl chloride mixture. ▲—Variation of inverse pitch with temperature.

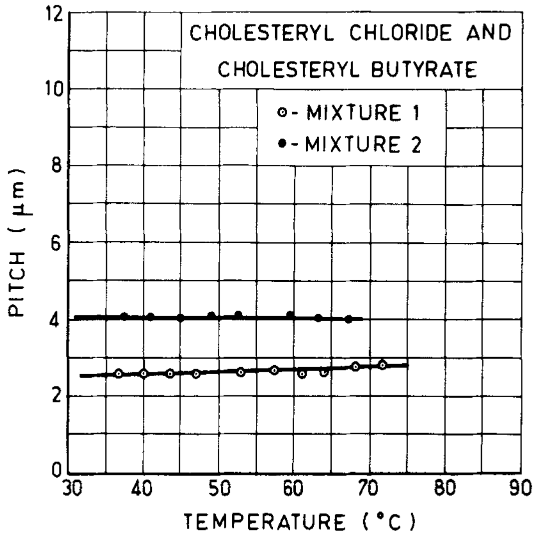

FIGURE 6 Variation of pitch with temperature. Mixture 1-50 : 50 mole % cholesteryl chloride and cholesteryl butyrate. Mixture 2-55 : 45 mole % cholesteryl chloride and cholesteryl butyrate.

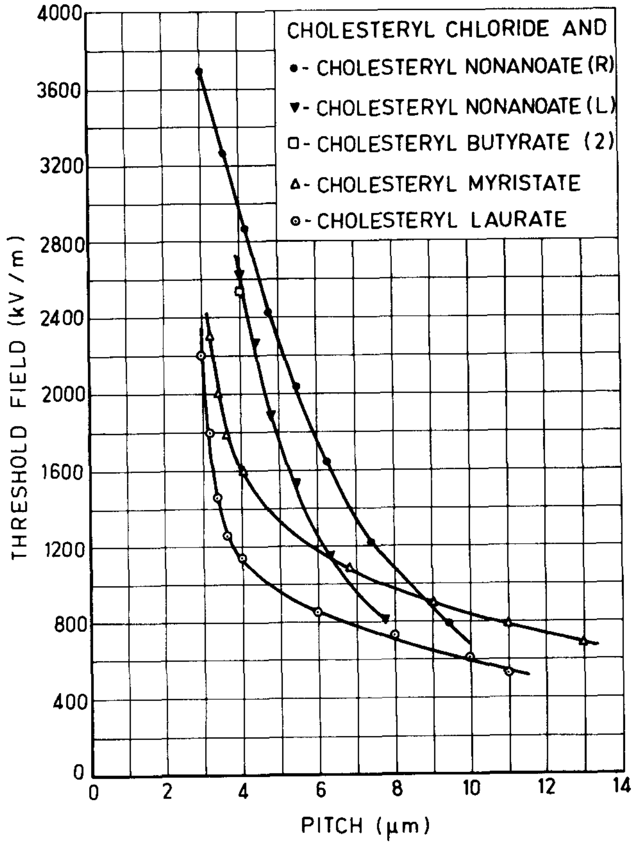

FIGURE 7 Relative response of the various mixtures to applied electric fields. Figure shows variation of threshold field with pitch: L : $T < 42\,^{\circ}\mathrm{C}$; R : $T > 42\,^{\circ}\mathrm{C}$.

accounts for the large increase in threshold field with pitch at the lower end of the pitch scale in Figure 7 in the cholesteryl laurate and the cholesteryl myristate mixtures. However, in the temperature range in which the inverse pitch shows linear behaviour, the threshold field E_T varies linearly with inverse pitch. Therefore $P_0 E_T$ is independent of temperature in this region.

The expression for the threshold field for the CN transformation is

$$E_T = \frac{\pi^2}{P_0}\left(\frac{K_{22}}{\epsilon_0 \Delta\epsilon}\right)^{1/2} \tag{2}$$

where E_T is the threshold field, P_0 is the pitch of the cholesteric, K_{22} is the twist elastic constant and $\Delta\epsilon$ is the dielectric anisotropy. The dielectric anisotropy data (Figure 2), show that in all the mixtures except cholesteryl butyrate, there is a range of temperatures over which $\Delta\epsilon$ is fairly independent of temperature. Therefore, considering that temperature region in each mixture over which both P_0E_T and $\Delta\epsilon$ are independent of temperature, it may be seen from equation (ii), that K_{22} is also independent of temperature. Such temperature regions for the three mixtures are indicated below,

Cholesteryl nonanoate—28 °C—46 °C
Cholesteryl laurate—56 °C—60 °C
Cholesteryl myristate $\simeq$ 59 °C

In these temperature ranges pretransitional effects from the low temperature smectic phase and from the high temperature isotropic phase are not predominant. It is therefore possible to compare the relative intrinsic response of the three mixtures to electric fields in this region. The quantity P_0E_T for each mixture, in these temperature regions, serves as an indication of the response of these mixtures to electric fields. The lower the value of this quantity, the better the response of the cholesteric to electric fields. The twist elastic constants for these mixtures in these regions may also be compared. The results are shown in table I. The values of P_0E_T and K_{22} show no regular trend in terms of length of the ester tails of the alkanoates present in the mixtures. A study of the complete homologous series of alkanoates would show whether the twist elastic constants also exhibit odd even effects.

In the case of cholesteryl butyrate (mixture 2), the sharp decrease in the threshold field at 67.5 °C may be attributed to a decrease in twist

TABLE I

Twist elastic constants of the mixtures

Sl. No.	Alkanoate mixed with cholesteryl chloride	Mole % cholesteryl chloride	P_0E_T (V)	Temperature[a] (°C)	$\Delta\epsilon$	K_{22} ($\times 10^{-11}N$)
1	Cholesteryl Nonanoate	65.2	7.6	46	0.49	0.26
2	Cholesteryl laurate	65.2	4.3	58	0.33	0.05
3	Cholesteryl myristate	65.2	7.0	59	0.25	0.11

[a] Some convenient temperature in the range where both P_0E_T and $\Delta\epsilon$ are independent of temperature for each mixture.

elastic constant (Eq. 2) close to the cholesteryl-isotropic transition temperature, as $\Delta\epsilon$ may reasonably be expected to show the same temperature dependence close to the transition temperature as for the other mixtures. Moreover, the pitch remains constant throughout the cholesteric range.

The temperature-independence of threshold field observed in the case of the cholesteryl butyrate mixture and in earlier work in a cholesteryl propionate mixture,[1] suggests two distinct types of temperature-dependence of threshold field between the lower and higher homologues. The cholesteryl butyrate and lower homologues are not smectogenic, while the cholesteryl nonanoate and higher homologues are smectogenic. At this stage, it would be difficult to draw any correlation between the smectogenic tendency of a pure mesogen to its behaviour in a binary mixture with cholesteryl chloride, however, such differences in behaviour are significant. A more detailed study involving all the homologues in the series would be necessary to conclusively prove the effects suggested herein.

CONCLUSIONS

The variation of threshold field with pitch for the different binary mixtures of cholesteryl alkanoates with cholesteryl chloride has been established. The value of $P_0 E_T$ has been shown to be an indication of the relative intrinsic response of these mixtures to electric fields. It has also been shown that neither $P_0 E_T$ nor the twist elastic constant of the mixtures varies regularly with alkanoate ester chain length. Two distinct types of temperature dependency of threshold field has been observed amongst the smectogenic and non-smectogenic homologues.

References

1. J. Wysocki, J. Adams and W. Haas, *Mol. Cryst. Liq. Cryst.*, **8**, 471 (1969).
2. J. J. Wysocki, J. E. Adams and D. J. Olechna, *Liquid Crystals and Ordered Fluids*, Edited by Julian F. Johnson and Roger S. Porter, (Plenum Press, New York, 1970), pp. 423–424.
3. Cornelia Motoc, Iuliana Cuculescu and Maria Honciuc, *Mol. Cryst. Liq. Cryst.*, **45**, 215 (1978).
4. T. Harada and P. Crooker, *Mol. Cryst. Liq. Cryst.*, **30**, 79 (1975).
5. Masao Kawachi, Osamu Kogure, Katsumi Kato, *Japan J. Appl. Phys.*, **17**, 1245 (1978).
6. N. L. Kramarenko, I. V. Kurnosov and Yu.V. Naboikin, *Mol. Cryst. Liq. Cryst.*, **47**, 7 (1978).

7. E. Sackmann, S. Meiboom, L. C. Snyder, A. E. Meixner and R. E. Dietz, *J. Am. Chem. Soc.*, **90**, 3567 (1968).
8. G. Durand, *Compt. Rend.*, **B264**, 1251 (1967).
9. C. K. Shashidharan Nair and Kolluri V. Ramanaiah, National Symposium on Instrumentation (NSI 7), Bangalore, India, 1982.
10. E. Sackman and H. Mohwald, *J. Chem. Phys.*, **58**, 5407 (1973).
11. R. A. Kashnow, J. E. Bigelow, H. S. Cole and C. R. Stein, *Liquid Crystals and Ordered Fluids* Edited by Julian F. Johnson and Roger S. Porter (Plenum Press, New York, 1974), Vol. 2, p. 483.
12. P. E. Cladis and M. Kleman, *Mol. Cryst. Liq. Cryst.*, **16**, 1 (1972).
13. S. Chandrasekhar, *Liquid Crystals* (Cambridge Univ. Press, London, 1977), Chap. 4, p. 227.
14. J. E. Adams and W. E. L. Haas, *Mol. Cryst. Liq. Cryst.*, **15**, 27 (1971).
15. J. E. Adams, W. Haas and J. J. Wysocki, *Liquid Crystals and Ordered Fluids*, Edited by Julian F. Johnson and Roger S. Porter, (Plenum Press, New York, 1970), p. 468.
16. Shu-Hsia Chen and J. J. Wu, *Mol. Cryst. Liq. Cryst.*, **87**, 197 (1982).