

Solute and Temperature Induced Pitch Changes and Pretransitional Effects in Cholesteric Liquid Crystals

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The effect of non-chiralic solute molecules on the pitch of cholesteric mixtures of cholesteryl chloride and cholesteryl nonanoate has been studied as a function of the composition and the temperature. The occurrence of a pretransition to the smectic state at low CC content is established. In the pretransitional state the pitch decreases exponentially with increasing temperature and is extremely sensitive against the addition of most organic molecules. In the normal cholesteric state the pitch increases with increasing temperature. In this state only a very limited number of non-chiralic molecules exert an appreciable influence on the pitch.

It is well established that the pitch of cholesteric phases is very sensitive against the addition of chiralic (optically active) molecules. Pitch (and correspondingly color-) changes may however also be induced by non-chiralic molecules such as organic vapors (CHCl_3 ; CCl_4)¹ or aromatic molecules (azobenzene, stilbene)². These effects are of considerable importance since they may be exploited (1) for the detection of small amounts of organic vapors¹, (2) for quantitative analytical applications² and (3) for the (reversible) generation of colored pictures on cholesteric layers^{2, 3}.

The pitch changes induced by solute molecules in mixtures of cholesteryl chloride (CC) with cholesteryl esters depend critically on the composition and the temperature. Depending on these parameters a given molecule may produce a positive (red) or a negative (blue) shift of P ^{1, 4}. Moreover the sensitivity of the pitch (color) response depends critically on the composition and on the temperature. In order to study the influence of the molecular arrangement of the cholesteric phase on the color response we studied pitch changes in mixtures of cholesteryl chloride (CC) and cholesteryl nonanoate (CN) induced by the addition of azobenzene, stilbene and trinitrobenzene as a function of the composition and the temperature. This paper summarizes some important results obtained with *cis*- and *trans*-azobenzene.

Experiments and Results

The pitch was determined by measuring the transmission of the cholesteric solutions with a Cary 17 spectrometer. In order to prepare cholesteric solu-

tions in the planar, texture, the samples were sandwiched between flat quartz plates separated by about 50 μm . Thus the wavelength of maximum reflectivity, λ_m , was related to the pitch $\lambda_m = nP$. The mean refractive index of cholesteryl derivatives is $n \sim 1.5$ ⁵. The temperature was monitored to an accuracy of 0.2 °C.

Dependence of pitch on composition: In Fig. 1 the wavelength of maximum reflectivity, λ_m , of a pure CC:CN mixture is plotted as a function of the molar percentage of CC for two different temperatures (22 °C and 30 °C). For 22 °C the λ_m versus composition plot exhibits the same behavior as re-

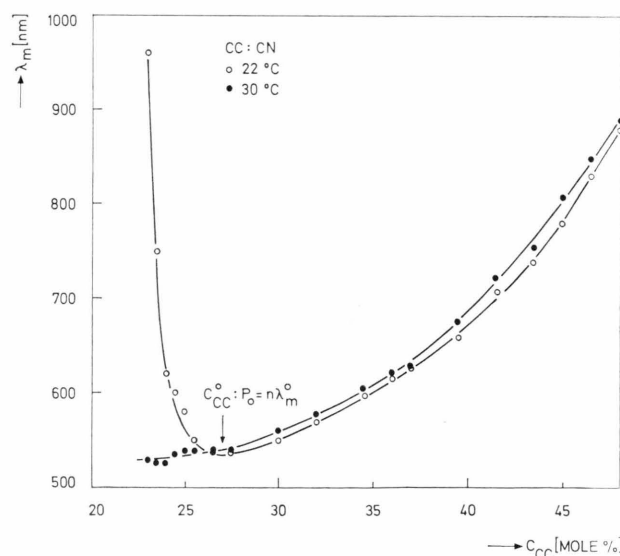


Fig. 1. Dependence of the wavelength of maximum reflectivity, λ_m , of a cholesteric mixture of cholesteryl chloride (CC) and cholesteryl nonanoate (CN) on the molar percentage of CC. For $T=22^\circ\text{C}$ the pitch has a minimum $P_0 = n \lambda_m^0$ at $C_{\text{CC}}=28$ mole %. However, for temperatures above $T=30^\circ\text{C}$ the pitch decreases monotonously with decreasing CC content.

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ported by Adams et al.⁴: the pitch has a minimum pitch, P_0 , at a molar percentage of cholesteryl chloride of $C_{CC}^0 = 28$ mole-%. The pitch increases sharply with decreasing CC content at $C_{CC} < C_{CC}^0$. At $C_{CC} > C_{CC}^0$ the pitch increases less dramatically with increasing CC content. At $C_{CC} = 70$ mole-% and 22 °C the pitch becomes infinite, i. e. the mixture is nematic⁶. Figure 1 shows that at temperatures above 30 °C no anomalous increase of the pitch with decreasing CC content is observed.

Temperature induced pitch change: According to Adams et al.⁴ two states of the cholesteric mixtures are distinguished by a different sign in the temperature dependence of the pitch: for $C_{CC} < C_{CC}^0$ the pitch decreases with increasing temperature ($\Delta P/\Delta T < 0$) and for $C_{CC} > C_{CC}^0$ it is $\Delta P/\Delta T > 0$ (cf. Figure 1). Figure 2 shows that the pitch decreases exponentially with increasing temperature for mixtures characterized by $C_{CC} < C_{CC}^0$.

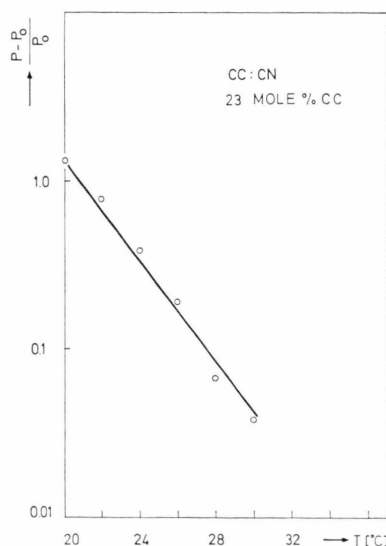


Fig. 2. Temperature dependence of the relative pitch change $(P - P_0)/P_0$ of a pure CC:CN mixture containing 23 mole % CC ($C_{CC} < C_{CC}^0$). At about 30 °C the pitch P has reached the minimum value $P_0 \approx 750$ nm (cf. Figure 1).

A most important result is that the anomalous temperature behavior of the cholesteric mixtures (at $C_{CC} < C_{CC}^0$) is no longer observed at high temperatures ($T > 30$ °C). This has first been observed by Stegemeyer and Mainusch⁸ who studied the phase diagram of the CC:CN mixture in more detail. These authors showed that the minimum value of the pitch (P_0) shifts to lower values of the molar percentage of CC with increasing temperature. Obviously the anomalous state of the cholesteric mixture is destroyed by increasing the temperature.

Solute induced pitch changes: Addition of *cis*- and *trans*-azobenzene leads to characteristic pitch changes. Depending on the CC content and the temperature two states of the cholesteric phase are clearly distinguishable (cf. Fig. 3 and Figure 4).

(1) At $C_{CC} < C_{CC}^0$ both isomers produce a very strong blue shift (cf. Figure 4). A blue shift of

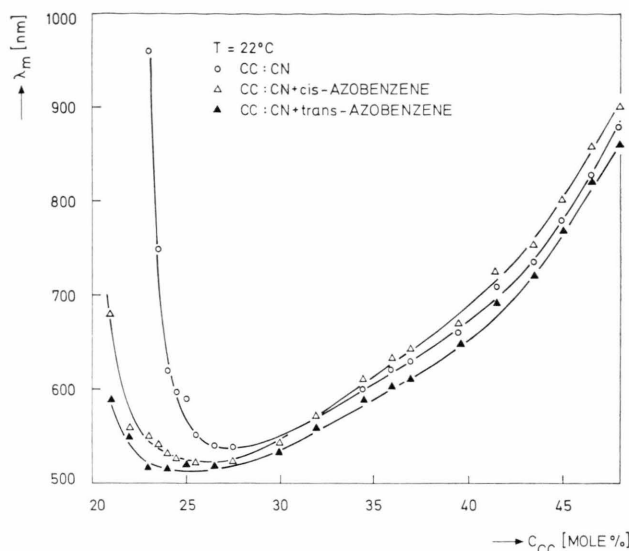


Fig. 3. The effect of *cis*- and *trans*-azobenzene on the pitch (or λ_m) of cholesteric mixtures with cholesteryl chloride (CC) and cholesteryl nonanoate (CN) of variable CC content.

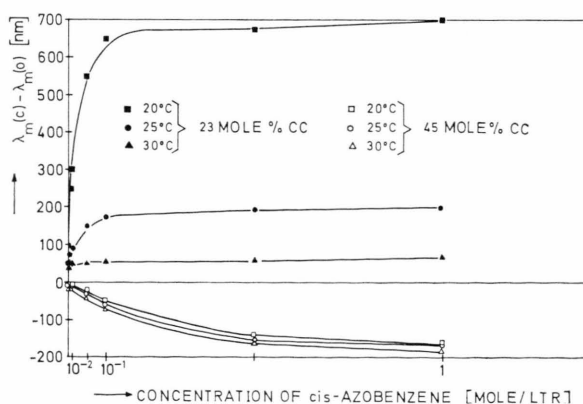


Fig. 4. Concentration dependence of the effect of *cis*-azobenzene on the pitch of two different cholesteric mixtures ($C_{CC} = 23$ mole% and $C_{CC} = 45$ mole%). The shift $\Delta \lambda_m = \lambda_m(c) - \lambda_m(0)$ is plotted as a function of the azobenzene concentration c . $\lambda_m(0)$ is the value of the wavelength of maximum reflectivity, λ_m , of the pure solvent. The mixture with 23 mole% CC is in the pretransitional state ($C_{CC} < C_{CC}^0$) at temperatures smaller than 30 °C. The mixture with 45 mole% CC is in the normal cholesteric state ($C_{CC} > C_{CC}^0$) above 20 °C.

about 500 nm is caused by the addition of only 5×10^{-2} mole azobenzene per liter of liquid crystal. However, the pitch changes only slightly with the solute concentration at azobenzene concentrations larger than 10^{-1} M (cf. Fig. 4) upper part. Figure 5 shows that the anomalous increase of the pitch ($\lambda_m(c) - \lambda_m^0$) at cholesteryl chloride contents $C_{CC} < C_{CC}^0$ is strongly suppressed by the addition of azobenzene. The anomalous red shift of the pitch, $P - P_0$, decreases exponentially with increasing azobenzene concentration.

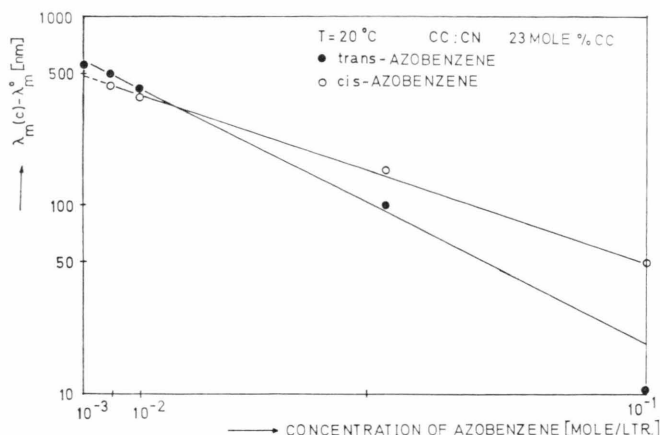


Fig. 5. Concentration dependence of the effect of *cis*- and *trans*-azobenzene on the wavelength of maximum reflectivity of a cholesteric mixture containing 23 mole% CC. λ_m^0 is the value of λ_m of the pure solvent at $C_{CC} = C_{CC}^0$ ($\lambda_m^0 \approx 750$ nm). At 20 °C the mixture is in the anomalous (pretransitional) state.

It is characteristic for the state $C_{CC} < C_{CC}^0$ that most non-chiral solute molecules (stilbene, trinitrobenzene, naphthalene) induce a strong blue shift of the pitch. At temperatures above 30 °C the extremely sensitive cholesteric state has vanished (cf. Fig. 4 curve for 23 mole-% CC at 30 °C).

(2) At $C_{CC} > C_{CC}^0$ the two azobenzene isomers induce only relative small changes in the pitch. However, the *cis*- and *trans*-isomers induce shifts in opposite directions (cf. Figure 3). For small azobenzene concentrations ($c \leq 10^{-1}$ M) the pitch changes linearly with the solute concentration (cf. lower part of Figure 4).

Discussion

The above results strongly suggest that the cholesteric mixtures undergo a pretransition to the smectic phase at cholesteryl chloride concentrations smaller than the concentration C_{CC}^0 and at temperatures below about 30 °C. This is supported by the fact that

the mixtures characterized by $C_{CC} < C_{CC}^0$ slowly transform to the smectic phase after several hours.

It thus appears that the anomalous increase of the pitch with decreasing CC content at $C_{CC} < C_{CC}^0$ is due to the formation of small smectic clusters. It is easily conceivable that smectic clusters embedded in the cholesteric phase would lead to an increase in the pitch:

The cholesteric phase is usually considered as being built up of two dimensional nematic layers where the molecules in adjacent layers are twisted by a small angle $\langle \theta \rangle$. The average twist angle $\langle \theta \rangle$ has been related by Keating⁹ to the anharmonicity of the forces opposing the relative twisting motion of adjacent molecules. According to this dynamical model $\langle \theta \rangle$ is proportional to the temperature and inversely proportional to the moment of inertia I_0 with respect to a rotation about an axis perpendicular to the long axis of the molecules:

$$\langle \theta \rangle = AT/I_0.$$

Consider a smectic group of m molecules (length L and diameter d_0) which are parallel to each other and which are stuck together end-to-end. If this group has an assumed quadratic cross section (side length: $\sqrt{m}d_0$), its moment of inertia with respect to a rotation about an axis perpendicular to the long axis of the molecules is given by $I = mI_0(1 + m d_0^2/L^2)$. For small m ($m \ll L^2/d_0^2$) $I \approx mI_0$.

For simplicity it will be assumed for the following considerations that the pretransitional state contains smectic clusters of equal size containing m molecules. The average twist angle $\langle \theta_D \rangle$ between two nematic layers separated by a distance D is then given by

$$\langle \theta_D \rangle = n_f \langle \theta_0 \rangle + N_m \langle \theta_m \rangle. \quad (1)$$

n_f is the average number of free molecules and N_m the average number of clusters contained within the distance D . Therefore $D = n_f d_0 + N_m \sqrt{m} d_0$. If the number of free molecules is large compared to the number N_m of clusters one obtains from the above equation for the relative pitch change:

$$(P - P_0)/P_0 = N_m \sqrt{m}/n_f. \quad (2)$$

This relation predicts an increase of the pitch with increasing number of smectic clusters and with the size of these clusters. Concerning the temperature and the solute dependence of the pitch this simple model leads to the following conclusions:

Temperature induced pitch changes: In his theory on heterophase fluctuations Frenkel¹⁰ derived simple relations for the number of clusters (containing m molecules) in metastable undercooled states. Neglecting the surface energy of the clusters relative to the latent heat of transition the number of smectic clusters N_m containing m molecules is approximately given by¹⁰

$$N_m \approx n_f \exp \{ \lambda m (T - T_0) / k T_0^2 \}. \quad (3)$$

This equation is valid for temperatures which are close to the smectic-cholesteric transition temperature T_0 . In the supercooled state ($T < T_0$) it is $\lambda < 0$ and the number of clusters (of size m) increases exponentially with decreasing temperature. Equation (3) thus predicts that the pitch increases exponentially with decreasing temperature in complete accordance with the experimental finding presented in Figure 2. The slope of the $\log [(P - P_0)/P_0]$ versus T plot of Fig. 2 yields an estimate of the number of clusters. For $\lambda \sim 0.5$ kcal/mol one obtains with the help of Eq. (3) $m \sim 100$. It can easily be verified that an exponential decrease of the pitch with increasing

temperature is also obtained if a distribution of smectic clusters of different size is considered.

Solute induced pitch changes: The extremely large effect of small amounts of solute on the pitch in the region $C_{CC} < C_{CC}^0$ is also easily explained by the existence of a pretransition. According to Raoult's law the smectic-cholesteric transition temperature T_0 is lowered by the addition of solute: the change in T_0 (ΔT_0) is proportional to the solute concentration. Equation (3) predicts therefore that the anomalous red shift of the pitch ($P - P_0$) decreases exponentially with the solute concentration. This prediction is in accordance with the experimental findings of Figure 5.

In the normal cholesteric state ($C_{CC} > C_{CC}^0$) the molecular statistical theory of Goossens¹¹ predicts that the pitch change induced by the solute is proportional to the solute concentration ($P - P_0 \propto c$). This is in accordance with the results obtained for the cholesteric mixture containing 45 mole-% CC at temperatures above 20 °C and at solute concentrations smaller than 10^{-1} M (cf. Figure 4).

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