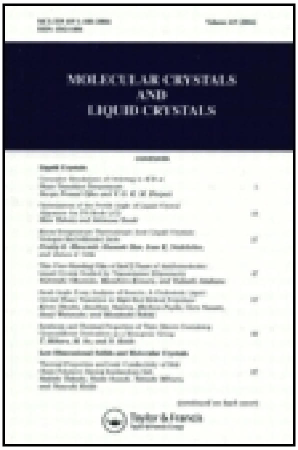

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Composition and Temperature Dependence of the Pitch in Cholesteric Binary Mixtures

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Composition and Temperature Dependence of the Pitch in Cholesteric Binary Mixtures

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In the cholesteric phase of mixtures of cholesteric cholesteryl chloride (CC) with nematic *p*-ethoxy benzylidene-*p*-*n* butylaniline (EBBA), as well as with nematic *p*-[(*p*-ethoxy-benzylidene)amino]benzonitrile (PEBAB), the pitch has been determined as a function of temperature and composition. For a CC weight fraction $x \lesssim 0.8$ we used the "variable wedge" method; for $x \gtrsim 0.8$ we determined the wavelength of maximum reflection λ_0 and the average refractive index $\bar{n}$ and employed the relation $\lambda_0 = \bar{n}p$. We show that $\bar{n}$ can vary appreciably as a function of composition in a cholesteric binary system. For each composition the reciprocal pitch can be fitted reasonably well to a linear function of the temperature, except in the vicinity of phase transitions. It appears that the slope of the linear function, i.e. $d(p^{-1})/dT$, is always positive. We discuss the results in relation to recently developed expressions for the pitch as a function of temperature and composition.

1 INTRODUCTION

It is well known that the pitch p of the cholesteric helix in binary liquid crystal mixtures depends on the constituent properties, the composition and the temperature.

Friedel[1] observed in 1922 that mixtures of a right- and lefthanded cholesteric exhibit inversion of the screw sense of the cholesteric helix as one passes through a critical composition. More surprising was the helix inversion in mixtures of nematix *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) and cholesteric cholesteryl chloride (CC), deduced from measurements of the wavelength for maximum reflection by Saeva and Wysocki[2] in 1970. In similar measurements Finkelmann and Stegemeyer[3] observed even a twofold inversion of the helical screw sense in mixtures of two cholesterics with the same helix screw sense in the pure state. During the past decade the wavelength for maximum reflection has been determined as a function of composition in a series of cholesteric binary liquid crystal mixtures, some of them exhibiting an inversion of the helical screw sense.

The first quantitative treatment of the pitch dependence on composition in binary mixtures was reported in 1968 by Adams, Haas and Wysocki.[4] Since then several approaches to the helical interaction in a cholesteric liquid crystal have been used to explain qualitatively the composition dependence of the pitch in binary systems (e.g. Adams and Haas;[5] Nagakiri, Kodama and Kobayashi;[6] Stegemeyer and Finkelmann;[7] Pochan and Hinman;[8] Kozawaguchi and Wada;[9] Wulf;[10] Bak and Labes;[11] and the present authors[12]).

However there is little information about the temperature dependence of the pitch in binary mixtures; this subject forms an essential part of the present paper.

The most striking conclusions from the pitch p versus temperature T results for one component cholesteric systems with a lefthanded as well as a righthanded helical screw sense are.[13,14]

1 $d(p^{-1})/dT$ is roughly constant in a temperature region sufficiently far away from transitions to smectic phases.

2 in this temperature range $d(p^{-1})/dT$ has the same sign as p (in this paper we take $p > 0$ for a righthanded helix and $p < 0$ for a lefthanded helix); i.e. the cholesteric helix winds itself up with increasing temperature (CEEC possibly shows an exception[15]).

The latter result can be explained by Keatings theory[16] in which the temperature dependence of p is ascribed to the thermal excitations of twiston modes in a system with anharmonic restoring forces.

For cholesteric binary systems like nematic-cholesteric mixtures scarce information is available about the temperature dependence of p for limited ranges of the composition x. A systematic study of $p(x, T)$ for binary mixtures covering the complete composition range has not been undertaken until now. In connection with conclusions 1) and 2) above for one component cholesterics, such measurements would be of particular interest for binary systems with or without an inversion of the helical screw sense as a function of composition. To fill this gap we have measured $p(x, T)$ for the cholesteric binary systems consisting of nematic *p*-ethoxybenzylidene-*p*-*n*-butylaniline (EBBA) and cholesteric cholesteryl chloride (CC) and for the system consisting of nematic *p*-[(*p*-ethoxybenzylidene)amino]-benzonitrile (PEBAB) and cholesteric CC for the whole composition range.

II EXPERIMENTAL RESULTS

In mixtures of nematic EBBA (resp. PEBAB) and cholesteric CC we determined the pitch of the cholesteric helix as a function of composition and of temperature. For mixtures with CC weight fraction $x \lesssim 0.8$ the "variable wedge" method of Grandjean-Cano[17] was used. The isotropic liquid mixtures were introduced between a flat microscope glass and a plano-convex lens and then cooled down to the cholesteric mesophase. Beforehand both the microscope glass and the lens were rubbed in one direction, enforcing the molecules along the walls to orient parallel to the rubbing direction. After a slight mechanical distortion the helical axis oriented itself perpendicular to the adjacent glass walls and under a polarizing microscope the well known Grandjean discontinuities could be seen. The pitch of the helix is determined by measuring the radii of the concentric circular discontinuities.

In the composition range $x \lesssim 0.8$ we used the following two methods to determine the sense of rotation of the cholesteric helix. First we observed the optical rotation of a linearly polarized light-wave with wavelength λ. In our case $\lambda < |p|$, so that the spiral formed by the plane of polarization, as the linearly polarized wave propagates through the medium, has a sense of rotation opposite to that of the cholesteric helix.[18] Secondly we rotated the lens relative to the microscope glass around the concentric axis.[19] The easy directions of the cholesteric at the adjacent walls then also rotate relative to each other. It is not difficult to convince oneself that the radii of the discontinuities will increase resp. decrease, depending on the direction of the relative rotation of the lens and the microscope glass and also depending on the sense of rotation of the cholesteric helix. This elegant method gives however some experimental difficulties. For example, during the rotation of the lens relative to the microscope glass the separation between them must remain constant. A change in the sample thickness comparable with the pitch causes a shift in the radii of the discontinuities. For this reason this experiment is hard to perform in short pitch cholesterics.

When the pitch becomes smaller than 0.5 μm in the CC-rich region, a determination of p with the variable wedge method is rather complicated. In this region, corresponding to $x \gtrsim 0.8$, it becomes preferable to determine p from the wavelength λ_0 of maximum reflection by employing the relation

$$\lambda_0 = \bar{n}p \tag{1}$$

where $\bar{n}$ is an average refractive index. The measurements of the wavelength of maximum reflection were carried out with a Beckman DK 2A far U.V. automatically recording spectrophotometer on cholesteric films of different thicknesses, while the helical axis of the cholesteric liquid crystal was oriented parallel to the incident light. In Figure 1 we present λ_0 as a function of temperature for the monotropic cholesteric liquid crystal phase of CC. The sense of rotation of the helix was obtained by observing the circular dichroism.

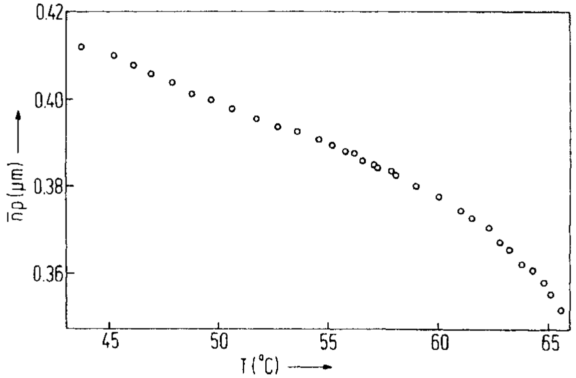

FIGURE 1 The wavelength of maximum reflection $\lambda_0 = \bar{n}p$ of cholesteryl chloride as a function of temperature.

The indices of refraction of the cholesteric mesophases were determined with an Abbe refractometer. A thin cholesteric film was sandwiched between the hypotenuse planes of two rectangular prisms. After a slight mechanical distortion the helical axis of the cholesteric liquid crystal oriented itself perpendicular to the adjacent boundaries. From the critical angle of total reflection of the liquid crystal–glass boundary we determined n_e and n_0 using lightwaves polarized parallel resp. perpendicular to the helical axis. Dreher[20] and Pelz[21] *et al.* showed that n_0 is in good approximation equal to the average index of refraction $\bar{n}$ in the relation $\lambda_0 = \bar{n}p$. Furthermore we have to take into account the dispersion of the refractive indices. To obtain $\bar{n}$ for the appropriate wavelengths we used the simplified dispersion formula of Böttcher and Graber.[22]

$$\bar{n}^2 = 1 + \frac{c\lambda_c^2\lambda^2}{\lambda^2 - \lambda_c^2} \tag{2}$$

c is a parameter that depends on temperature and composition, while the parameter λ_c mainly depends on composition; λ is the wavelength of light in vacuum. For CC we get $\lambda_c = 107$ nm independent of temperature; this is the same value as Demus and Wartenberg[13] reported for a series of cholesteryl esters. As an example we show in Figure 2 the refractive indices n_e and n_0 for $\lambda = 5893$ Å for a CC weightfraction $x = 0.40$ in the EBBA–CC system, as a function of temperature.

In Figure 3 we present the refractive index $\bar{n}$, for a wavelength $\lambda = 5893$ Å, as a function of composition in the cholesteric binary system EBBA–CC for a temperature $T = 50$°C as well as for a reduced temperature $T = T_c - 10$ for each composition; T_c is the clearing temperature of the mixture under

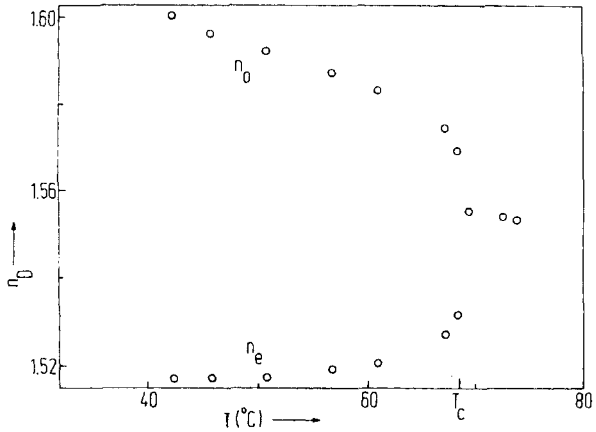

FIGURE 2 The refractive indices n_0 and n_e for $\lambda = 5893$ Å, as a function of temperature, of an EBBA–CC mixture with 40 percent weightfraction of CC.

consideration. It is interesting to note that $\bar{n}$ can vary appreciably in a binary system for which the constituents differ in refractive indices. This is the case for example in cholesteric binary systems consisting of a cholesteric cholesteryl derivative and a nematic, or in systems consisting of a cholesteric cholesteryl derivative and a chiral nematic. A chiral nematic liquid crystal has a cholesteric mesophase and consists of molecules that differ only from the ordinary nematic molecules in having at least one asymmetric center.

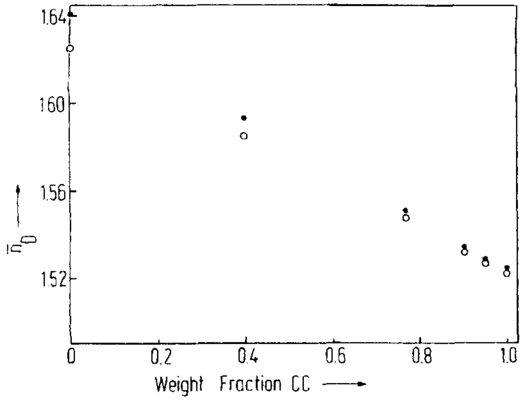

FIGURE 3 The refractive index $\bar{n}_D$ as a function of composition of the EBBA–CC system system for $\lambda = 5893$ Å. The open circles refer to temperatures 10 degrees below T_c, where T_c is the clearing temperature of the mixture under consideration; and the filled circles refer to a temperature $T = 50$°C.

Until now most of the work in this field is done on the determination of the wavelength λ_0 of maximum reflection as a function of composition in cholesteric binary systems. These experimental $\lambda_0(x)$ data were compared with derived expressions for the pitch as a function of composition, by assuming $\bar{n}$ = constant. In this way the dispersion, the temperature dependence and the composition dependence of the refractive indices is neglected. In binary systems consisting of molecules of comparable shape the assumption $\bar{n}$ = constant is reasonable, giving errors of only a few percent. However when the constituents of the cholesteric binary system differ appreciably in shape this assumption can give rise, as shown in Figure 3, to systematic deviations of the order of 7 percent.

With increasing temperature the experimental λ_0 versus temperature curve often shows a decrease as one approaches the cholesteric–isotropic transition (see Figure 1). However, in our opinion this information is not sufficient to conclude that p also decreases as one approaches the cholesteric–isotropic transition temperature; in particular because $\bar{n}$, as shown in Figure 2, also decreases towards the cholesteric–isotropic transition. Since $p = \lambda_0/\bar{n}$ it is possible that these two effects just cancel each other. Unfortunately we do not have sufficiently accurate experimental data to prove this point, but the direct pitch determinations with the variable wedge method do not show a significant decrease of the pitch in the vicinity of the cholesteric–isotropic transition.

With decreasing temperature the pitch of a cholesteric helix increases considerably on approaching a cholesteric–smectic phase transition.[13,14] This means that in this pretransitional region the helix starts to unwind. In an intermediate composition range around $x = 0.35$ (CC weight fraction) of the EBBA–CC system we also found a smectic phase at lower temperatures. In the cholesteric to smectic pretransitional region of the cholesteric phase the pitch also increases with decreasing temperature, but sufficiently far away from the transition the pitch increases with increasing temperature over a temperature range of about 30°C. So we conclude that the temperature dependence of the pitch, which we discuss in this paper, is an intrinsic property of the cholesteric mesophase and not due to the onset of a smectic phase.

We express our data in terms of the reciprocal pitch p^{-1}. The quantity p^{-1} is more convenient to deal with mathematically, since it passes through zero continuously at the point on a compositional diagram where the pitch has a singularity.[5] Furthermore $p^{-1} = q/2\pi$ is a measure for the helical twisting power of the cholesteric liquid crystal; q is the wave vector of the cholesteric helix. For a given composition the reciprocal pitch can be described reasonably well with a linear function of temperature, except in the vicinity of a phase transition. As an example we present in Figure 4 the experimental

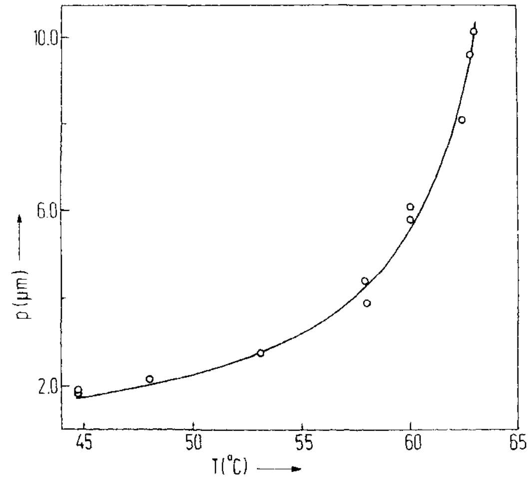

FIGURE 4 Experimental results for the pitch as a function of temperature of an EBBA–CC mixture with 64 percent weightfraction of CC. The curve represents a hyperbolic function fitted to the experimental points.

pitch versus temperature data for a mixture of the EBBA–CC system with $x = 0.64$ together with a curve representing the function $p = (a_1 + a_2 T)^{-1}$, fitted to the experimental points. Here $a_1 = -1.75$ and $a_2 \equiv d(p^{-1})/dT = 0.026$ are numbers that result from the least squares fitting procedure. So for a given composition $d(p^{-1})/dT$ is constant over the measured cholesteric existence region, except near a phase transition. For each composition we covered a temperature range of the cholesteric mesophase of some tens of degrees.

Figure 5 shows the reciprocal pitch p^{-1} as a function of temperature for various compositions over the whole composition range of the EBBA–CC system. We also plotted here the linear functions $p^{-1} = a_1 + a_2 T$ fitted to the experimental points. It turns out that $d(p^{-1})/dT$ is always positive independent of the sign of p, i.e. irrespective of the cholesteric helix has a righthanded or a lefthanded helical screw sense. Thus for a lefthanded helix the spiral unwinds itself with increasing temperature and for a righthanded helix the cholesteric spiral winds itself up with increasing temperature; whereas in one-component cholesteric systems the spiral always winds itself up with increasing temperature for a righthanded as well as for a lefthanded helical screw.

The temperature dependence of the reciprocal pitch $d(p^{-1})/dT$ is plotted in Figure 6 versus the weight fraction of CC in the EBBA–CC system. The

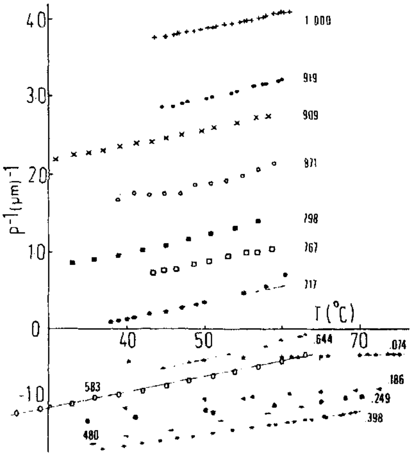

FIGURE 5 Experimental results for the reciprocal pitch as a function of temperature for various CC weightfractions x of the EBBA–CC system. The solid lines represent linear functions fitted to the experimental data.

cholesteric phase of CC is monotropic, i.e. it can only be obtained by supercooling below the crystalline–isotropic transition temperature. The CC-rich mixtures are also monotropic. This makes it hard to carry out the measurements and is a reason for the scatter of experimental points in the CC-rich region. In the composition region $0.8 < x < 1$ we also measured the pitch as a function of temperature for some compositions with the variable wedge method. Besides the effects associated with supercooling, the small value ($\lesssim 0.5$ μm) of the pitch makes these variable wedge measurements

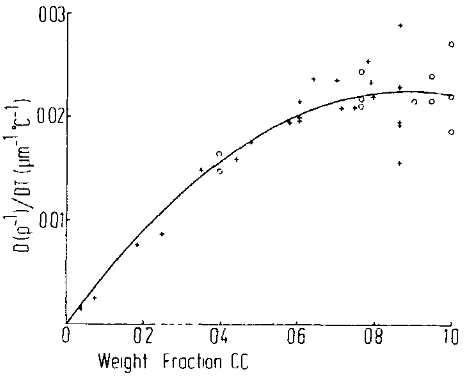

FIGURE 6 The temperature dependence of the reciprocal pitch $d(p^{-1})dT$ as a function of the CC weightfraction in the EBBA–CC system (0 reflection + variable wedge method). The drawn curve represents a quadratic function fitted to the experimental data.

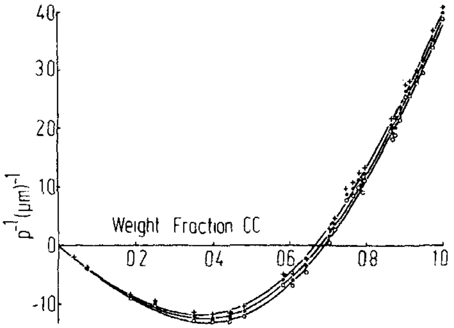

FIGURE 7 The reciprocal pitch in the EBBA–CC system as a function of composition, for three reduced temperatures + $T_c - 5$, · $T_c - 10$, ⊙ $T_c - 15$; where T_c is the clearing temperature for the mixture under consideration. The drawn curves represent polynomials of the 4th degree in the CC weight fraction fitted to the experimental data.

even more unattractive. This resulted in considerable scatter of the experimental points, amounting deviations of the order of 50 percent in a plot like Figure 6. However the scatter of the datapoints was practically random, because it changed the curves fitted to the data only slightly. For the sake of clarity these points were omitted in the figures.

Figure 7 shows the reciprocal pitch in the EBBA–CC system as a function of composition, for three reduced temperatures $t = T_c - T$; T_c is the cholesteric–isotropic transition temperature for a given composition. Thus each curve does not represent an isotherm, but refers to temperatures that are t°C below the cholesteric–isotropic transition temperature for each mixture. A mixture of EBBA with a small amount of CC gives a cholesteric liquid crystal with a lefthanded helical structure. With increasing concentration of CC, p^{-1} first decreases to a minimum and then increases to become zero at $x = 0.65$. This implies that for this particular composition the mixture is nematic for one specific temperature. Further increase of the CC fraction yields a cholesteric with a righthanded helical structure. Consequently the EBBA–CC system exhibits an inversion of the helical screw sense, as reported recently by Kozawaguchi and Wada.[9]

As mentioned before we also examined the cholesteric binary system consisting of nematic PEBAB and cholesteric CC. The experimental results for this system are comparable to that of the EBBA–CC system, described above; i.e. the PEBAB–CC system exhibits inversion of the helical screw sense, $d(p^{-1})dT$ is independent of temperature for each composition and $d(p^{-1})/dT$ is positive over the whole composition range. Later on, we will discuss in some detail the slight differences that occur between the results of these two systems. As an example we plotted in Figure 8 the experimental

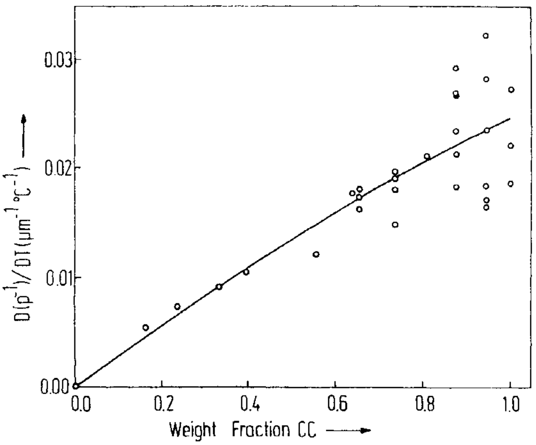

FIGURE 8 The temperature dependence of the reciprocal pitch $d(p^{-1})/dT$ as a function of the CC weightfraction in the PEBAB-CC system. The drawn curve represents a quadratic function fitted to the experimental data.

values for the PEBAB-CC system of $d(p^{-1})/dT$ versus the CC weightfraction x, together with a curve representing a quadratic function of x, fitted to the experimental points.

III DISCUSSION

A Composition dependence of the pitch

It has been known for some time that a requirement for the formation of a cholesteric phase is that at least a fraction of the constituent molecules be chiral, i.e. lack a center or plane of symmetry. Even highly dilute solutions of chiral molecules in nematics form a helical structure while on the other hand the intermolecular interactions are of short-range character and are essentially restricted to nearest neighbors. This implies that in a molecular picture one must associate a certain twisting power with a pair of neighboring chiral molecules as well as with a nearest neighbor pair consisting of a chiral and a nematogenic molecule.

With a pairwise molecular orientational interaction in a simple molecular field, without further specifying the specific interactions, one easily arrives at an expression for the reciprocal pitch that is quadratic in the concentration of one of the components

$$p^{-1}(x, T) = x^2 p_{11}^{-1} + 2x(1 - x)p_{12}^{-1} + (1 - x)^2 p_{22}^{-1} \qquad (3)$$

Here $p_{11}^{-1}(p_{22}^{-1})$ is the reciprocal pitch of component 1 (resp. 2) and is a measure for the twisting power of a pair of molecules of component 1 (resp. 2); p_{21}^{-1} describes the orientational interaction between a molecule of component 1 and a molecule of component 2 and x is the weightfraction of component 1. For a cholesteric binary system consisting of a nematic and a cholesteric liquid crystal we obtain

$$p^{-1}(x, T) = x^2 p_{CC}^{-1} + x(1 - x)p_{CN}^{-1} \tag{4}$$

where the index C stands for the cholesteric and N for the nematic component. The numbers that resulted from a least squares computer fit of Eq. (4) to the experimental data are listed in Table I.

TABLE I

Values of p^{-1} (μm^{-1}), as a measure for the helical twisting power obtained from a least squares fit of expression (4) to the experimental data at various reduced temperatures.

	EBBA–CC system		PEBAB–CC system	
	p_{CN}^{-1}	p_{CC}^{-1}	p_{CN}^{-1}	p_{CC}^{-1}
T_c − 5 (°C)	−7.70	4.02	−5.41	3.77
T_c − 10 (°C)	−7.93	3.89	−5.56	3.65
T_c − 15 (°C)	−8.19	3.78	−5.71	3.53
T_c − 20 (°C)			−5.73	3.78

During the past decade the wavelength of maximum reflection λ_0 has been determined as a function of composition in several cholesteric binary systems. For the analyses most authors arrive at a relation in which the reciprocal pitch is a quadratic function of the concentration of one of the components of the binary system, although the starting assumptions and the interpretation of the parameters may be different. These quadratic functions fit the exhaustive data on this subject reasonably well. However in systems in which the reciprocal pitch deviates strongly from linearity the computed quadratic curves show systematic deviations from the experimental data. Moreover, particularly in those systems the constituents usually differ appreciably in structure and the refractive index $\bar{n}$ can vary considerably as a function of composition. Therefore the assumption $\bar{n}$ = constant in the whole composition range and for all temperatures, may introduce another systematic error, if one determines the pitch from the relation $\lambda_0 = \bar{n}p$. At first sight one is therefore inclined to ascribe these systematic deviations between the experimental pitch data and the fitted curve, that is quadratic in the concentration of one of the components, to the use of a constant $\bar{n}$.

However these systematic deviations also occurred in systems we corrected for the concentration, temperature and wavelength dependence of $\bar{n}$. We obtained these systematic deviations using weight concentrations as well as molecular concentrations and irrespective of the data referred to a constant temperature or to a reduced temperature. The best fits were obtained with weight concentrations when the data were at constant temperature. Unfortunately it is not always possible to obtain the experimental pitch values at a constant temperature over the whole composition range in a binary cholesteric system. For example in the PEBAB–CC system the mesomorphic temperature ranges of the two constituent liquid crystals do not overlap, so it is impossible to find a temperature at which the cholesteric mesophase exists over the whole composition range. It is of course possible to use polynomials for the description of the reciprocal pitch of a binary system as a function of composition. But only polynomials of the 4th degree (or higher) in the concentration of one of the components can describe the reciprocal pitch as a function of composition in cholesteric binary systems without systematic deviations of the fitted polynomial from the experimental values. The solid lines in Figure 7 are polynomials of the 4th degree in the weight fraction of CC, fitted to the experimental data.

Recently we showed that the molecular theory of Goossens[23] for cholesteric liquid crystals, extended to a composition dependent theory for binary systems by Stegemeyer and Finkelmann[7] and by the present authors,[12] provides a mathematically satisfactory description of the observed dependence of the pitch on composition in cholesteric binary systems. This is not surprising, because the reciprocal pitch in this case is a ratio of two quadratic functions, having five adjustable (intermolecular interaction) parameters. The above mentioned quadratic functions only have three parameters, and a polynomial of the 4th degree also has 5 adjustable parameters. However if one requires a consistent physical interpretation of these intermolecular interaction parameters from Goossens' theory, there should exist certain relations between them which reduce the actual number of parameters to three. As we showed,[12] it appeared that only simple systems for which the reciprocal pitch versus composition relation does not deviate strongly from linearity, allow such a consistent physical interpretation of the parameters.

All the experimental results, published in the literature, of reciprocal pitch versus composition in cholesteric binary systems show, that the helical sense of a nematic with a small amount of a cholesteric cholesteryl derivative is lefthanded, regardless of the helical screw sense of the cholesteric compound. This means that in the quadratic expressions (3) and (4) for the reciprocal pitch the parameters p_{12}^{-1} and p_{CN}^{-1} become negative, independent of the sign of the other parameters. As one can see in Table I, for the systems we examined indeed $p_{\mathrm{CN}}^{-1} < 0$ for all the measured temperatures. From these data one sometimes concludes that nematogenic molecules in these mixtures act as if they had an intrinsic lefthanded helical twisting power, although nematic molecules do have a plane or center of symmetry and are optically inactive. Furthermore in cholesteric binary systems, consisting of a cholesteric cholesteryl derivative and a chiral nematic both with a righthanded helical screw sense, the reciprocal pitch versus composition curves always deviate from linearity towards a lefthanded helix; sometimes the helical screw sense even becomes lefthanded in an intermediate composition region.[3] However upon adding small amounts of optically active materials to nematics, several authors obtained righthanded cholesteric phases. Moreover cholesteric binary systems consisting of a nematic and a chiral nematic with a righthanded helix show a righthanded cholesteric phase in the whole composition range. So we agree with Kozawaguchi and Wada[9] in concluding that the induced lefthanded helical twisting power ascribed to nematics is probably due to orientational interactions between the nematic and cholesteric molecules, rather than to latent properties of molecules that exhibit a nematic mesophase.

The molecules of a cholesteryl derivative have several asymmetric centers and the influence of all centers is not necessarily the same. So possibly a nematic molecule (or an aliphatic chain, like the 3β side chain of some cholesteryl derivatives) interacts with other asymmetric centers of a molecule derived from cholesteryl than the cholesteryl steroid ring system does. The first interaction tends to form a lefthanded helix (resulting in $p_{\mathrm{CN}}^{-1} < 0$) while the second strives to a righthanded helical structure. In this way one can qualitatively understand, that a nematic with a small amount of a cholesteryl derivative forms a lefthanded helix regardless of the helical screw sense of the cholesteric phase of that particular cholesteryl derivative. Furthermore it would be consistent with the results of Leder,[24] who found an experimental relation between the helical twisting power $(\bar{n}p)^{-1} = \lambda_0^{-1}$ (in $\mu\mathrm{m}^{-1}$) determined at room temperature and the length d (in Å) of the 3β chain of the cholesteryl skeleton:

$$(\bar{n}p)^{-1} = -7.5d + 15.6$$

So the steroid ring system plus the 17 carbon side chain is effectively righthanded and an increase of the chain length at the 3β carbon reduces the righthandedness by a factor proportional to the 3β side chain length. One may also ascribe the above mentioned orientational interactions partly (or totally) to repulsive forces, resulting in a cholesteric phase that can be attributed to a specific packing tendency, as is done by Baessler *et al.*[25]

Examining the results in Table I, one sees that the values of $p_{\mathrm{CC'}}^{-1}$ differ somewhat for the two systems. This may show the shortcomings of the use of quadratic functions, which leave systematic deviations of the fitted curve from the experimental points. Furthermore the values of p_{CN}^{-1} are higher in the EBBA–CC system. The structural difference between the EBBA molecules and the PEBAB molecules is the butyl endgroup of EBBA versus the cyano endgroup of PEBAB. The EBBA endgroup is longer and should therefore, in the picture described above, enhance the tendency to form a lefthanded helix through orientational interaction with the cholesteryl derivative. Thus the EBBA–CC system should have a more negative value of p_{CN}^{-1}.

B Temperature dependence of the pitch

Among the theoretical expressions describing the reciprocal pitch behavior as a function of composition in cholesteric binary systems, there is no one that can explain explicitly the temperature dependence of the pitch in these mixtures. The temperature dependence is only implicitly given in the parameters. To find an expression that describes the temperature dependence of the pitch in cholesteric binary systems as a function of composition, we can simply differentiate the formulae (3) and (4). Differentiating (4) gives for our binary systems consisting of a nematic and a cholesteric compound,

$$d(p^{-1})/dT = x^2\, d(p_{CC}^{-1})/dT + x(1-x)d(p_{CN}^{-1})/dT \tag{5}$$

$d(p_{CC}^{-1})/dT$ is the temperature dependence of the cholesteric compound, $d(p_{CN}^{-1})/dT$ results from the interaction between the cholesteric and the nematic molecules; x is the weight fraction of the cholesteric compound. This quadratic function fits the data of the EBBA–CC and the PEBAB–CC system quite well, as shown in the Figures 6 and 8, The parameters that result from the least squares fits are for the EBBA–CC system: $d(p_{CC}^{-1})/dT = 0.022$; $d(p_{CN}^{-1})/dT = 0.050$, and for the PEBAB–CC system $d(p_{CC}^{-1})/dT = 0.025$ and $d(p_{CN}^{-1})/dT = 0.029$. The errors in the parameters are such that the values of $d(p_{CC}^{-1})/dT$ for both systems overlap each other.

One component systems From the information in the literature concerning the variation of the pitch of the cholesteric helix with temperature in one component cholesteric systems one can draw the following conclusions when considering a temperature region sufficiently far away from transitions to a smectic phase:

1) $d(p^{-1})/dT$ has the same sign as p itself, i.e. the cholesteric spiral winds itself up with increasing temperature. Possibly CEEC has the reversed temperature behavior, but the information in the literature on this compound is contradictory.[15]

2) $d(p^{-1})/dT$ is constant in such a temperature range.

Two component systems There is only scarce information available about the temperature dependence of p in binary cholesteric systems as a function of composition. For example Pindak[26] *et al.* and Stegemeyer[27] measured the wavelength λ_0 of maximum reflection in the binary cholesteric system consisting of CC (righthanded helix) and CN (cholesterylnonanoate, lefthanded helix) as a function of temperature in the composition region $0 < x < 0.6$ (x is the weight fraction of CC); Nagakiri[6] *et al.* carried out λ_0 measurements in the cholesteric binary system consisting of nematic MBA (p-methoxy benzylidene p-aminophenyl acetate) and cholesteric CP (cholesteryl propionate, lefthanded helix) as a function of composition, and published for some compositions the data as a function of temperature. These results together with our data concerning the EBBA–CC and PEBAB–CC systems show that in these binary mixtures:

1) $d(p^{-1})dT$ has not always the same sign as p itself, as is the case in one component cholesteric liquid crystals.

2) $d(p^{-1})dT$ seems to be constant in a temperature range sufficiently far away from phase transitions.

In the EBBA–CC and PEBAB–CC systems $d(p^{-1})/dT$ is positive in the whole composition range, as shown in the Figures 6 and 8, while the helical screw sense changes, with increasing weight fraction of CC, from a lefthanded to a righthanded one at an intermediate composition. In other words in these systems the cholesteric helix tends to be more righthanded with increasing temperature irrespective of the helical sense is righthanded or lefthanded. The two other systems mentioned (CC–CN and MBA–CP) show a reversal of sign of $d(p^{-1})/dT$ at an intermediate concentration and also here $d(p^{-1})/dT$ has not always the same sign as p itself. So the temperature dependence of the cholesteric helix cannot be a simple winding up of the helical screw with increasing temperature as the result for the one component systems suggest, but depends on the specific properties and the interactions between the constituent molecules.

If we describe the temperature dependence of the pitch in the MBA–CP system (only published for three compositions[6]) as a function of composition with expression (5), this should yield a positive value for $d(p_{\mathrm{CN}}^{-1})/dT$, whereas $d(p_{\mathrm{CC}}^{-1})/dT$ is negative. We can explain these results for cholesteric binary systems qualitatively in a way consistent with the hypothesis of Section IIIA, that nematic chains have orientational interactions with other parts (or other asymmetric centers) of the cholesteryl skeleton than the cholesteryl skeleton itself. In fact the parameter $d(p_{\mathrm{CN}}^{-1})/dT$, resulting from the orientational interaction between a nematic and a cholesteric molecule, is positive in these cases, where the cholesteric compound is a cholesteryl derivative, independent of the sign of $d(p_{\mathrm{CC}}^{-1})/dT$. Whereas $d(p_{\mathrm{CC}}^{-1})/dT$ depends strongly on the 3β carbon endchain of the cholesteric molecule it changes sign, like p, with changing 3β chain length. Thus we can describe the temperature dependence of the pitch $d(p^{-1})/dT$ as a function of composition in a cholesteric binary system with an expression, that is quadratic in the weight fraction of one of the components; without giving an explicit physical interpretation of the parameters.

The temperature dependence of the helical pitch in a cholesteric liquid crystal is described explicitly by the dynamic theory of Keating[16] and is in 1972 modified by Böttcher.[28] Keating showed that thermally excited molecular rotations around a short molecular axis parallel to the helix axis can lead to a nonvanishing time average of the rotation angle and hence to a twist between neighboring cholesteric layers, provided that the forces opposing the rotation are anharmonic. Böttcher also introduced the viscous damping of the molecular rotations. The theory predicts that the reciprocal pitch is a linear function of the temperature in a temperature range sufficiently apart from a transition temperature. Indeed in the appropriate temperature ranges, one can fit almost all the reciprocal pitch versus temperature data reasonably well to a linear function $p^{-1} = b_1 + b_2 T$, where b_1 and $b_2 \equiv d(p^{-1})/dT$ are the fitting parameters. The theory of Keating gives an interpretation to the parameter b_2, but cannot explain the existence of a nonzero b_1. Furthermore an extension of Keatings theory to a two component system is rather ambiguous. So although Keatings theory gives a physical explanation for the temperature dependence of the pitch, it cannot explain the behavior of the pitch in binary cholesteric systems. Stegemeyer and Finkelmann[29] calculated the pitch in dilute solutions, using the Goossens potential together with a rotational distribution function with respect to hindered rotations around the molecular long axis. The temperature dependence of the reciprocal pitch is then hidden in the rotational order parameter, and seems to be in rough agreement with experimental results.

Furthermore two recently developed theories of the temperature-dependent pitch in cholesteric liquid crystals are worth mentioning.

Van der Meer *et al.*[30] published a molecular statistical theory for a one component cholesteric liquid crystal. The interaction between the chiral molecules is derived in terms of the orientations of the long molecular axes. The derivation is based on the electric multipole expansion in analogy with Goossens'[23] theory. Furthermore the molecules are assumed to behave as if they were cylindrically symmetric. The authors show that, if only the induced dipole–dipole and the dipole–quadrupole dispersion energies are taken into account, a temperature independent cholesteric pitch is obtained. In analogy with Keating[16] they then propose an extra term in the expansion, that produces an asymmetric potential. It is found that the reciprocal pitch is approximately a linear function of temperature in agreement with experiments.

Lin-Liu[31] *et al.* used a general form for the intermolecular potential between chiral molecules that behave statistically as cylinders. They examine a planar model for the cholesteric and then their interaction potential is essentially the same as that used by Van der Meer[30] *et al.* Thus although Lin-Liu *et al.* used a different approach the results for the temperature-dependent pitch are essentially the same. These two theories can describe the behavior of the temperature dependent pitch, but a physical interpretation of the parameters remains difficult.

IV SUMMARY

We described the composition dependence of the reciprocal pitch and of the temperature dependence of the reciprocal pitch, $d(p^{-1})/dT$ with functions, that are quadratic in the concentration of one of the components. For the composition dependence of the pitch there are several theories that give an explicit physical explanation for the parameters in these quadratic functions. However there remain systematic deviations between the quadratic curve and the experimental reciprocal pitch data. The quadratic expressions fit quite well the temperature dependence of the reciprocal pitch $d(p^{-1})/dT$ as a function of composition, but there is no theory that delivers an explicit explanation for the parameters involved. Physical reasons for the temperature variation of the pitch are given for example by Keating[16] and Stegemeyer.[29]

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