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On the Relationship between Cholesteric and Nematic Mesophases†

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Abstract—The close relationship between nematic and cholesteric mesophases was realized in 1922 by Friedel and the conversion of nematics into cholesteric systems has been the subject of considerable research since that date. In the present work the relationship between the chirality of the induced cholesteric mesophases produced from the addition of simple chiral molecules, of known absolute configuration, to *p*-methoxybenzylidene-*p'*-*n*-butylaniline (MBBA) and butyl-*p*-*p*-(ethoxyphenoxy carbonyl)phenyl carbonate (BPC) and the chirality of the solute has been investigated.

It was found that cholesteric mesophase chirality cannot be predicted from the chirality of the active solute alone even though the cholesteric mesophases produced by adding enantiomeric additives appear to be always enantiomeric. Predictions of the helical sense of the induced cholesteric mesophases require detailed energy calculations for the nematic-solute "complex" similar to those employed by Scheraga on helical macromolecules.

The sign of the Cotton effect of the cholesteric liquid crystal induced circular dichroism (LCICD) band in MBBA and BPC was found to be the same as the sign of the reflective circular dichroism of the cholesteric pitch band. This result indicates that deviations in the optical activity versus wavelength plots for certain cholesteric mesophases from the theoretical predictions of deVries can be attributed to a strong contribution from LCICD. The overlapping of Cotton effects of the same sign may be used to explain the phenomenon that in mixtures of chiral compounds with nematics the optical rotation, at a wavelength smaller than the λ_0 of the cholesteric pitch band, decreases as the quantity of the active component increases.

The close relationship between nematic and cholesteric mesophases was realized many years ago by Friedel⁽¹⁾ and the conversion of nematics into cholesterics has been the subject of considerable research⁽²⁻¹⁰⁾ since 1922.

It has been generally concluded that cholesteric mesophases can

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be produced simply by the addition of chiral molecules to nematic liquid crystals,⁽⁴⁻¹⁰⁾ and methods for identification of the cholesteric mesophases have ranged from light scattering⁽⁴⁾ to optical activity^(5,6,8) studies. Also, it has been recently shown^(8,10) that enantiomeric cholesteric mesophases could be produced by the addition of enantiomers of a helicene type molecule to *p*-methoxybenzylidene-*p'*-*n*-butylaniline (MBBA). However, optical rotation data measured as a function of temperature at a single wavelength clearly is not what one would expect for a cholesteric composition whose optical rotation versus wavelength data is consistent with the deVries equation⁽¹¹⁾; a rational for this disagreement has not yet been proposed.

In this communication we present some new experimental results obtained from the addition of simple chiral molecules of *known* absolute configuration to nematics. The relationship between the chirality of the induced cholesteric helix and the chirality of the single molecule is examined and a rational for the deviation of certain cholesteric systems from the deVries equation⁽¹¹⁾ is provided.

Nematic mesophases are normally viewed as a layered arrangement of associated molecules which do not have a helical (chiral) structural contribution.⁽¹²⁾ It is suggested that the nematic mesophase can be more accurately visualized as a dynamic situation where there exists both helical and non-helical structures and where the non-helical form possesses a lower free energy than the helical molecular array. The helical structure that exists in nematic mesophases must then have equivalent amounts of lefts and rights since the free energy difference between them is zero. Figure 1 describes the suggested dynamic situation that may take place in nematics.

Upon the addition of a chiral additive or introduction of any other dissymmetric perturbation, the delicate balance between helical and non-helical structures may be altered, from the situation described below, to one where one of the helical structures become energetically more favorable, i.e. the equilibrium is displaced. The distinction between helical enantiomers rests solely on the basis of a difference in diastereomeric interactions in the nematic-solute complex which results in an energy difference between helical structures,⁽¹³⁾ leading to a preference of one helix sense over the other. This is manifested by the existence of a cholesteric mesophase.

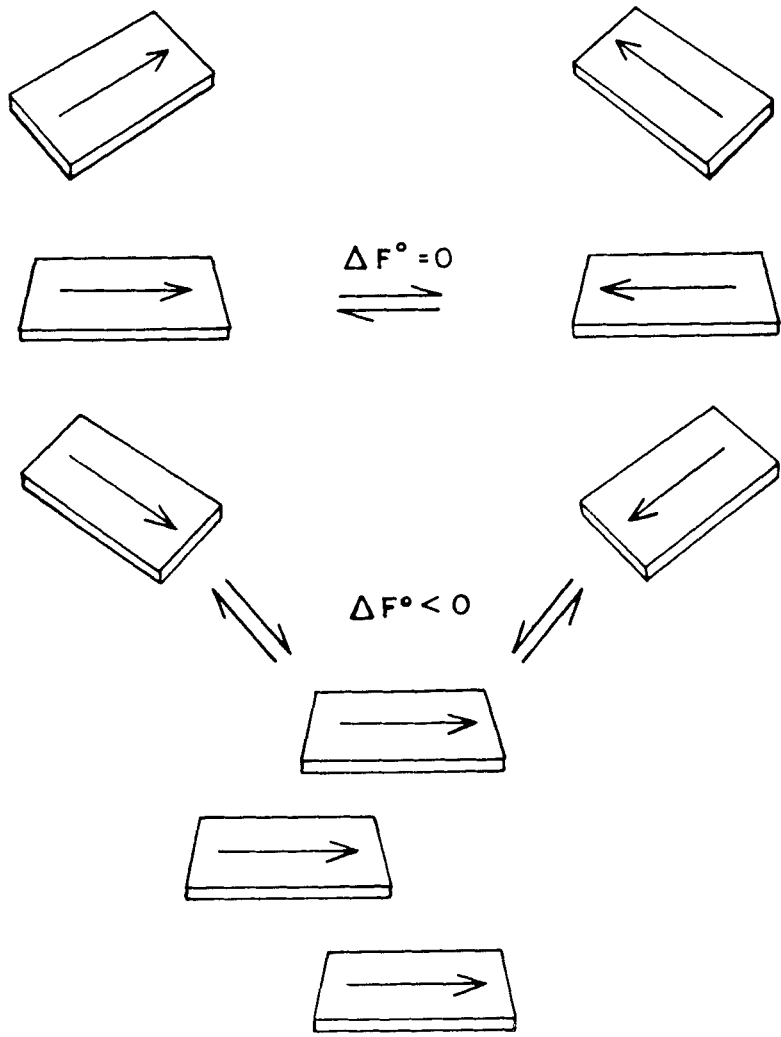


Figure 1. Proposed structural arrangement in nematic mesophases.

With the above mechanism in mind a variety of chiral molecules with a single chiral center of known absolute configuration were added to the nematic mesophases MBBA and butyl *p-p*-(ethoxyphenoxy-carbonyl) phenyl carbonate (BPC). The existence and chirality of the resulting cholesteric mesophases were determined by the liquid crystal induced circular dichroism (LCICD) method,^(14,15,16) which monitors the circular dichroism of the electronic transitions of the inactive nematic component. Table 1 summarizes the results.

The data in Table 1 reveal that cholesteric mesophases are indeed formed by the addition of chiral additives to nematic liquid crystals and the LCICD method provides a simple and unambiguous method for determining the existence and chirality of these cholesteric mesophases. Some general conclusions can also be made concerning the relationship between the chirality of the additive and the handedness of the resulting cholesteric helix. The sec.amyl group, which possesses the (*S*)-configuration in both the cinnamate (I) and

TABLE 1. Chirality of Cholesteric Mesophases Produced from Nematic Mesophases and Chiral Solutes

Chiral Solute ^c	MBBA ^a or BPC ^b Induced Cholesteric Mesophase Chirality ^d
I (<i>S</i>)-sec.amyl- <i>p</i> -aminocinnamate	R
II (<i>R</i>)-2-octyl- <i>p</i> -aminobenzoate	R
III (<i>S</i>)-2-octyl- <i>p</i> -aminocinnamate	L
IV (<i>S</i>)-sec.amyl- <i>p</i> -aminobenzoate	R
V (<i>R</i>)-2-octyl-ethylcarbonate	R
VI (<i>S</i>)-2-octyl-ethylcarbonate	L
VII <i>l</i> -menthol	R ^e

^a *p*-methoxybenzylidene-*p'*-*n*-butylaniline.

^b Butyl *p-p*-(ethoxyphenoxy-carbonyl) phenyl carbonate.

^c Concentration of solute was 5 wt %.

^d Obtained from the sign of the LCICD of the inactive nematic through a correlation between the sign of the LCICD band and the reflective circular dichroism of the pitch band.^(14,15,16) A cholesteric mesophase which reflects left-handed circularly polarized light in the region of its pitch band is by our definition a right-handed helix (i.e. the chirality of the cholesteric mesophase is the same as the sense of circularly polarized light that is transmitted in the region of λ_0). Circular dichroism measurements were performed on a Cary 61 Circular Dichroism Spectropolarimeter.

^e In agreement with the experimental results of H. Stegemeyer and K. J. Mainusch.^(6,8,10,17)

benzoate (IV) series produced right-handed helicoidal cholesteric mesophases in both MBBA and BPC. However, as one changes the cinnamate ester group from (*S*)-sec.amyl (I) to (*S*)-2-octyl (III) (same absolute configuration), opposite handed cholesteric mesophases are produced in the nematics used in this study. The (*S*)-2-octyl systems (III) and (VI) were found to induce left-handed helical structures while (*R*)-2-octyl additives (II) and (V) produced right-handed cholesteric helicoidal structures as does *l*-menthol. It is felt that it is strictly fortuitous that both nematics behave identically in the experiments summarized in Table 1. Addition of (*R*)- and (*S*)-2-octyl-ethylcarbonates (V and VI) respectively to the nematics, however, provides left- and right-handed helicoidal cholesteric structures. The handedness of cholesteric mesophases produced by the addition of simple chiral molecules to nematic mesophases can only be predicted by detailed energy calculations like those employed by Scheraga⁽¹⁸⁾ for macromolecules and not *a priori* from the chirality of the optically active additive alone. However, the cholesteric mesophases produced by adding enantiomeric additives appear to be always enantiomeric.

In correlating the sign of the LCICD within the electronic transitions of the inactive nematic material with the sign of the reflective circular dichroism of the cholesteric pitch band, it was observed that for both the nematic systems used in this study the two CD bands (LCICD and pitch band) were of the same sign. This would result in optical activity versus wavelength plots for these cholesteric mesophases which would deviate from the deVries equation.⁽¹¹⁾ This deviation is attributed to a strong contribution from LCICD. The overlapping of Cotton effects of the same sign would normally result in a reinforcing effect in the circular dichroism (CD) as CD bands interact strongly with one another and no significant effect if CD bands are non-interacting (neglecting a pitch dependence on LCICD intensities). The quantitation details of the pitch dependence on LCICD will be reported in a forthcoming publication.⁽¹⁹⁾

The optical rotatory dispersion (ORD) of interacting Cotton effects of the same sign on the other hand normally tend to cancel one another due to the dispersive nature of the curves. As a consequence, if one were observing the optical rotation of a cholesteric liquid crystal composition between ~ 350 and ~ 400 nm, described in

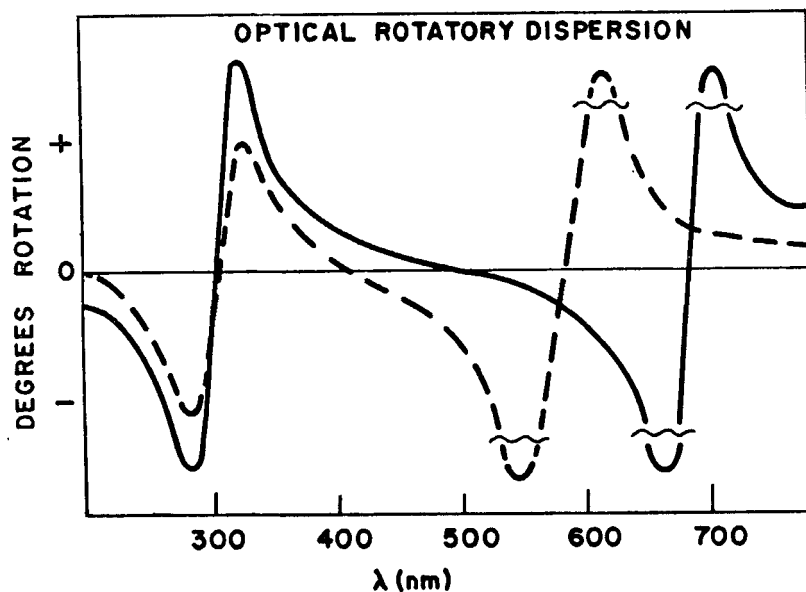


Figure 2. Optical rotatory dispersion (ORD) of a hypothetical cholesteric liquid crystal with a pitch band (λ_0) at ~ 700 nm (—) and ~ 600 nm (---) along with a single cholesteric liquid crystal induced CD band at ~ 300 nm.

Fig. 2, movement of the pitch band from ~ 700 nm to ~ 600 nm would result in a decrease in optical rotation. Thus, overlapping of CD bands (pitch and LCICD) of the same sign can be used to explain the phenomena that in mixtures of chiral compounds with nematics the optical rotation, at a wavelength smaller than the λ_0 of the cholesteric pitch band, decreases as the quantity of the active component increases.⁽²⁰⁾ However, the reverse effect could also be observed if one were monitoring the optical rotation at ~ 500 nm as a function of concentration of chiral solute. It is concluded that the requirement that a cholesteric liquid crystal must obey the deVries equation should only be considered valid when there is a negligible contribution from LCICD.

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