THE OPTICAL PROPERTIES OF ANISOTROPICALLY ORDERED SOLUTES IN CHOLESTERIC LIQUID CRYSTALLINE MESOPHASES

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ABSTRACT

Liquid crystalline mesophases may be either thermally (thermotropic) or solvent (lyotropic) induced. The anisotropic ordering of molecules within each of these classes may then be of the smectic, nematic or cholesteric type.

The present work deals solely with liquid crystalline mesophases of the cholesteric type where one of the many requirements for the formation of cholesteric mesophases is the existence of chiral single molecules. The chiral molecules may be derivatives of cholesterol or certain polypeptides, e.g., poly-γ-benzyl-L-glutamate (PBLG) in helix supporting solvents. We have previously observed that achiral solutes display circular dichroism (CD) in thermotropic cholesteric liquid crystalline mesophases. This extrinsic liquid crystal induced circular dichroism (LCICD) has been more recently observed in lyotropic cholesteric mesophases and employed to probe the internal molecular organization of both classes of cholesteric mesophases, as well as to provide spectroscopic and conformational information concerning the interaction of solutes in liquid crystalline mesophases in general.

Distinct differences have been observed between the LCICD of anthracene in thermotropic cholesteric mesophases composed of cholesteryl derivatives and lyotropic (PBLG) systems. The results of these LCICD studies will be discussed in terms of the following mechanisms: (a) helical organization of solute molecules, and (b) solute molecules exposed to a helical organization of liquid crystal molecules.

INTRODUCTION

In recent years there has been a resurgence of interest in liquid crystals since the early studies by Friedel in the 1920s. Presumably, this recent interest is a result of the development of new instrumental techniques for characterizing the properties of these intriguing materials, the realization of their importance in biological systems, as well as their use in novel device applications

The purpose of this contribution is to compare the optical properties of achiral solutes in thermotropic and lyotropic cholesteric mesophases and to indicate the information that is provided both about the solute as well as the internal structure of these mesophases from circular dichroism (CD) studies. A brief review of liquid crystal classes and mesophase types is provided along

with the known spectroscopic applications of liquid crystals with the object of placing the subject matter of this contribution into the proper perspective.

Brief description of liquid crystals

Liquid crystals, commonly referred to as the fourth state of matter, exhibit strong birefringence as a result of the anisotropic organization of associated single molecules. Liquid crystals may be divided into the following two main classes: (1) thermotropic (thermally induced), and (2) lyotropic (solvent induced).

Thermotropic liquid crystals are the most widely studied and normally consist of organic molecules which are fairly rigid and rod-like in structure and possess at least one polarizable group. Lyotropic mesophases, on the other hand, generally contain both hydrophobic and hydrophilic groups within a single molecule. A variety of substances, e.g. 9-bromo-phenanthrene-3-sulphonic acid[1], long chained fatty acids[2], certain ionic dyes[3] as well as concentrated solutions of a variety of synthetic polypeptides such as poly-γ-benzyl-L-glutamate[4], exhibit lyotropic liquid crystalline behaviour in various solvent systems.

Each of the liquid crystal types may be further characterized as being either smectic, nematic or cholesteric. For an up-to-date review of the

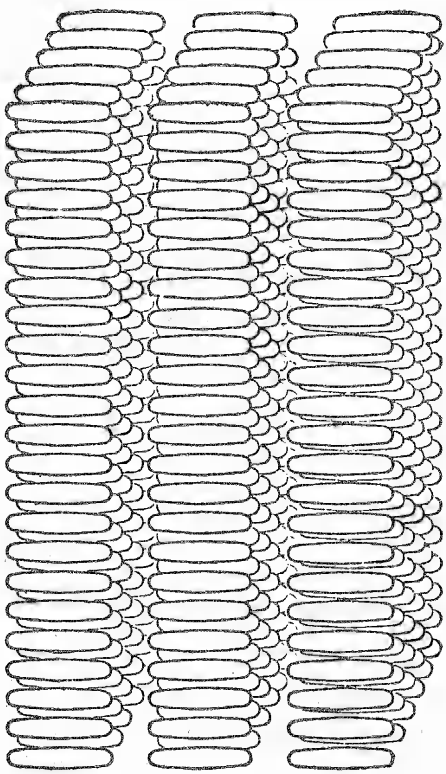


Figure 1. Schematic drawing of a smectic A mesophase

structure and physical properties of liquid crystals see the review article by Brown. Doane and Neff[5].

The smetic mesophase is the most highly structured of the three classes. Molecules in smectic mesophases are stratified in layers where there is a preferred directionality of the long molecular axis. As a consequence of the two dimensional order found in smectics they tend to be the most highly

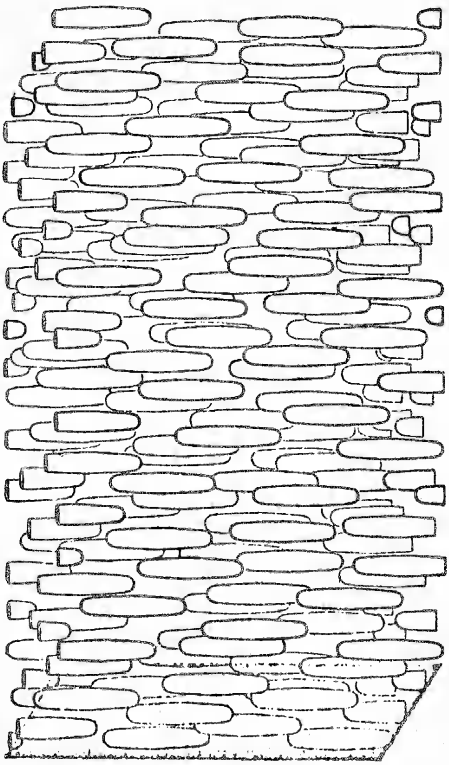


Figure 2. Schematic drawing of a nematic mesophase

viscous of the three classes. Various types of smectic mesophases have been observed each with a slightly different molecular arrangement. See *Figure 1* for a schematic drawing of the smectic A mesophase type.

Nematics, on the other hand, contain molecules with uniaxial molecular alignment (one dimensional order), described schematically in *Figure 2*, within randomly distributed groups of molecules and behave optically like uniaxial crystals. Nematic mesophases are normally of lower viscosity than smectic mesophases reflecting the weaker intermolecular interactions between molecules.

Cholestic mesophases are a special type of liquid crystal in that they require the existence of a centre of chirality within the single molecules of which the mesophase is composed[6]. Cholesteric compositions may also be obtained by the addition of chiral solutes. which may not be liquid crystalline

themselves, to nematic structures[7]. Resolution into enantiomers of a nematogenic compound possessing a racemic centre also has been shown to result in a cholesteric material[8]. The molecular organization within this phase is such that there is a unidirectional alignment of molecules within single layers. The single layers are stacked so that the direction of the long axes of the molecules in one layer is displaced slightly from the direction in the adjacent layer tracing out a helical structure as shown schematically in *Figure 3*. The helical structure may be either left- or right-handed depending on nature of the cholesteric material. The pitch (p) of the cholesteric helix can be determined from the wavelength (λ_0) of the selective reflection of circular polarized light (CPL) either from absorption or circular dichroism (CD) measurements by means of the following expression $p = \lambda_0/n$ if n, the

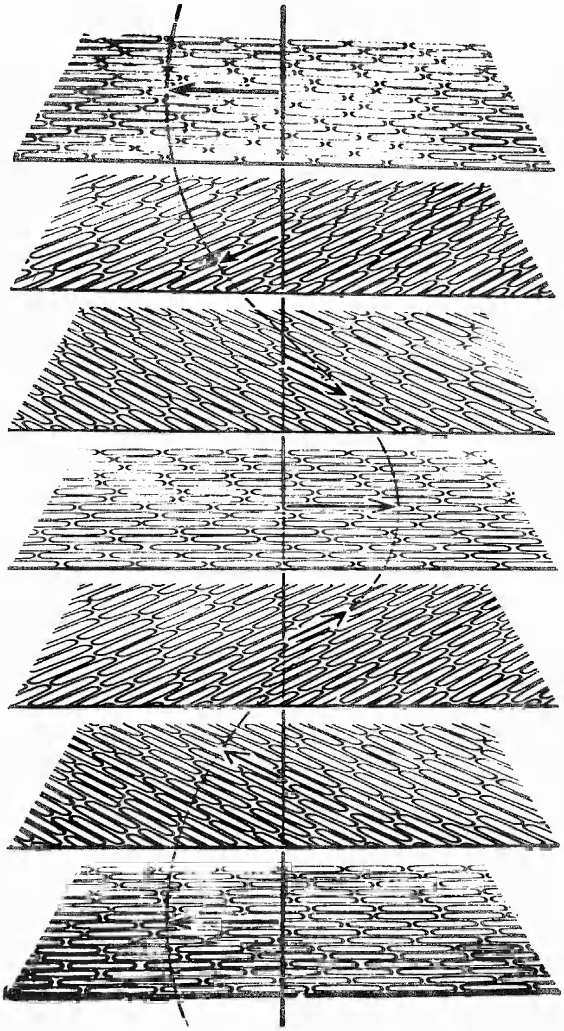
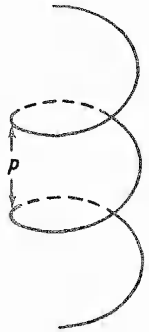


Figure 3. Schematic drawing of a cholesteric mesophase

refractive index of the mesophase. is known. Cholesteric mesophases are best known for the beautiful iridescent colours they exhibit as a result of the selective reflection of visible light when pitch values lie within a certain range.



Spectroscopic applications of liquid crystals

Polarization data for electronic transitions have been obtained by orienting solute molecules in aligned nematic[9] and cholesteric mesophases[10]. The observed polarization data are related to the extinction coefficients along molecular fixed axes, ε_x, ε_y, ε_z through the following expression.

$$\varepsilon_{\parallel} - \varepsilon_{\perp} = S_x\varepsilon_x + S_y\varepsilon_y + S_z\varepsilon_z$$

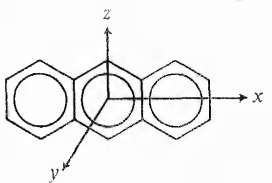
The quantities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the extinction coefficients measured with the electric vector of light parallel and perpendicular, respectively, to the direction of alignment of the long axis of the liquid crystal molecules. S_i is a parameter which describes the orientation of the solute in the liquid crystal matrix and is defined as

$$S_i = (3\cos^2\theta_i - 1)/2$$

where θ_i is the angle which the ith molecular axis makes with the long axis of the liquid crystal molecules, and may be derived from liquid crystal n.m.r. studies[11—13].

From polarization and n.m.r. studies in liquid crystals it was concluded that solute molecules align in the best packing arrangement from steric considerations, e.g. planar molecules orient their long axis parallel to the long axis of the liquid crystal molecules.

A positive S-value indicates that the corresponding axis is preferentially oriented parallel to the magnetic field, which is the same as the molecular axis of the liquid crystal molecules of positive dimagnetic anisotropy. A maximum value of $+1$ would correspond to perfect alignment of axis, while a negative S-value (maximum-$\frac{1}{2}$) indicates that the corresponding axis is preferentially oriented perpendicular to the magnetic field direction. S_x for anthracene, for example, normally has a positive value.



The optical properties of solutes in liquid crystals provide both spectroscopic information about the solute as well as preferred conformation of the solute in the liquid crystal. These studies, however, provide little information concerning the internal molecular structure in the liquid crystal matrix.

CHOLESTERIC LIQUID CRYSTAL INDUCED CIRCULAR DICHROISM (LCICD)

CICD in Thermotropic cholesterics

Recently achiral molecules dissolved in thermotropic cholesteric liquid crystals have been observed to exhibit enormous CD in the region of their absorption bands whose sign is dependent on the sense (chirality) of the cholesteric helix[14]. *Figure 4* shows the CD and absorption spectrum of a left- and right-handed helical cholesteric mesophase in which *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (I) has been dissolved. Selective reflection of circular polarized light from the cholesteric matrix[15] occurs between 500 and 600 nm while (I) absorbs between 230 and 390 nm. The helical structure of the cholesteric mesophase was found essential for the observation of extrinsic CD. This was shown by the loss of liquid crystal induced circular dichroism by the conversion of the helicoidal cholesteric mesophase into a unaxial nematic, i.e. unwinding the cholesteric helix, by means of an electric field[14, 16].

Further CD studies have shown the sign of the LCICD to be dependent on the polarization of the electronic transition within the solute as well as the

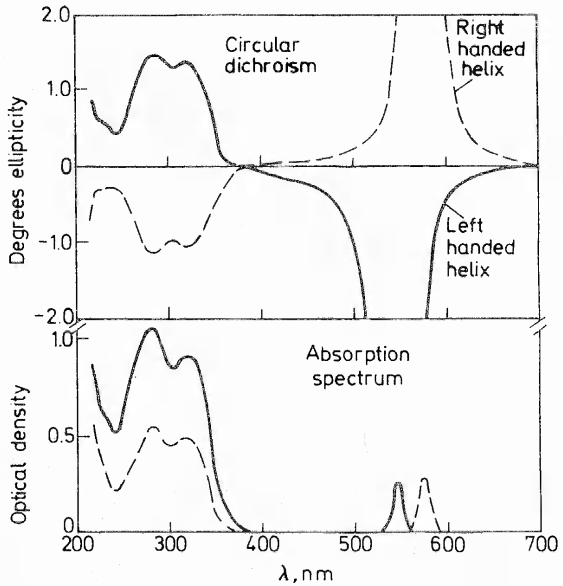


Figure 4. Circular dichroism (upper) and absorption spectrum (lower); – – – –, 6.3 μm film of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (*1*) (52.5 mg) in 10.0 g of 27.7:72.3 wt% cholesteryl chloride (*2*)–cholesteryl nonanoate (*3*) (right-handed helix); ———, 11.7 μm film of 1 (63.2 mg) in 10.0 g of 90.6/9.4 wt% 2:3 (left-handed helix)

chirality of the cholesteric helix[17]. *Figure 5* presents the LCICD and absorption spectrum of pyrene which is known to possess $\pi \rightarrow \pi^*$ electronic transition moments at wavelengths > 200 nm, polarized along different molecular axes[18, 19].

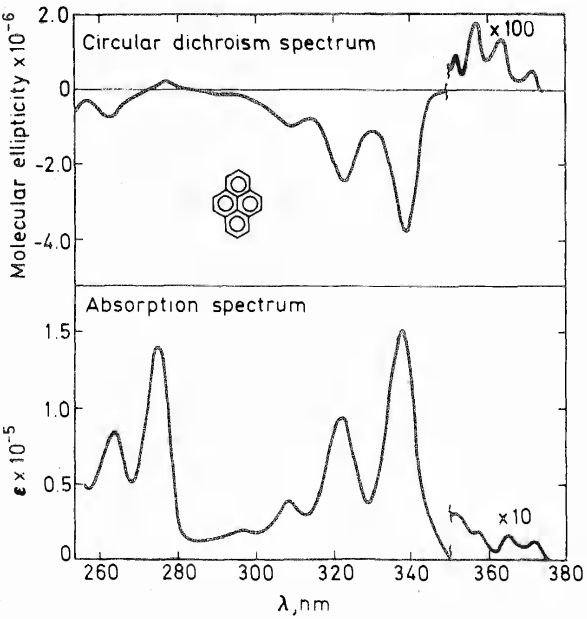
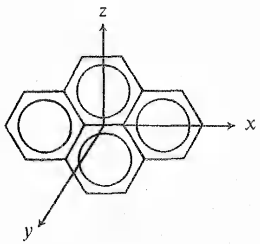


Figure 5. Circular dichroism and absorption spectrum of pyrene in 70/30 wt% cholesteryl chloride/cholesteryl nonanoate (λ_0 = 630 nm, T = 29°C)

The LCICD spectrum of pyrene (*Figure 5*) presents some spectroscopically significant information concerning the polarizations of the electronic transitions. The O–O bands for the ^1L_b, ^1L_a and ^1B_b pyrene transitions occur at 372, 339 and 277 nm, respectively. The transversely polarized (short axis) in-plane O–O band of the ^1L_b and ^1B_b transitions show positive CD (i.e. $\varepsilon_L > \varepsilon_R$) in a right-handed helicoidal cholestric mesophase consisting of 70/30 wt% cholesteryl nonanoate/cholesteryl chloride. All the vibrational bands within the ^1L_b transition appear to be of the same polarization in contrast to the ^1B_b transition which appears to be of mixed polarization[20, 21] or may contain overlapping transitions which are of opposite CD signs as indicated by the lack of match between the absorption and LCICD spectra. The ^1L_a transition, on the other hand, is longitudinally polarized (long axis in-plane) and shows negative CD.



O–O transition (nm)	Polarization
372	*z*
339	*x*
277	*z*

More recently the LCICD sign has been observed to be dependent on the position of λ_0 of the cholesteric pitch band relative to the wavelength of the absorption band[22]. For right-handed cholesteric mesophases composed of cholesteryl chloride–cholesteryl nonanoate mixtures the LCICD sign for a transition moment with a preferred orientation parallel to the long axis of the liquid crystal molecules is summarized in *Table 1.*

Table 1. Sign of LCICD as function of λ_0

Helix sense	λ_0/λ_{ab}*	LCICD sign
Right-handed	>1	−
	<1	+
Left-handed	>1	+
	<1	−

* λ_{ab} denotes wavelength of absorption.

The intensity of solute LCICD is a linear function of solute concentration over a limited range[22] and of sample thickness, and non-linear functions of temperature and pitch.

Experimentally, then, the LCICD sign for ordered solutes is dependent on the following: (*i*) the chirality of the cholesteric helix; (*ii*) polarization of absorption bands within a solute; (*iii*) preferred conformation of the solute with respect to the long molecular axis of the liquid crystal molecules, and (*iv*) the position of λ_{ab} relative to λ_0.

The LCICD intensity, on the other hand, is a function of: (i) pitch of the cholesteric helix, and (ii) temperature.

The preceding experimental observations for low concentration of solute agree with recent theoretical studies[23, 24] that extend the theory of electromagnetic radiation in non-absorbing cholesteric liquid crystal to the absorbing situation by adding a frequency dependent complex distribution to the spiralling dielectric tensor of the liquid crystal itself. The experimental sign of the CD depends upon the direction of polarization of the absorption band with respect to the background birefringence. Related studies including infrared CD investigations of the thermotropic cholesteric liquid crystals themselves have been recently reported[24–27].

LCICD in lyotropic cholesterics

Certain synthetic polypeptides. e.g. poly-γ-benzyl-L-glutamate (PBLG). are known to exist in an α-helical conformation in a variety of solvents[28]. Extrinsic circular dichroism has been observed within the electronic transitions of certain dyes[29, 30], such as acridine orange, complexed to isotropically oriented polypeptide molecules while in an α-helical conformation. Concentrated solutions of these polypeptides, in helix supporting solvents, have been found by Elliott and Ambrose[31] to form birefringent phases. Robinson[4] subsequently characterized these birefringent phases as cholesteric liquid crystalline mesophases, where the helical polypeptide is analogous to the cholesteryl derivative in thermotropic cholesteric systems.

Achiral molecules, such as anthracene and pyrene, which do not exhibit induced circular dichroism in dilute or concentrated isotropic solutions of PBLG, do indeed exhibit LCICD in the anisotropic birefringent lyotropic cholesteric mesophases formed by PBLG in helix supporting solvents such as chloroform, methylene chloride and dioxane.

LCICD has been observed for a number of achiral molecules dissolved in birefringent concentrated solutions of PBLG in helix supporting solvents. We believe this induced effect to be quite general and independent of chemical structure of the solute in contrast to rigid requirements for solutes that complex to isotropically oriented helical polypeptides[29,30]. The extrinsic CD of the achiral solute is associated with the formation of a birefringent cholesteric mesophase and disappears when the α-helical molecules of PBLB become randomly oriented by means of small changes in concentration of PBLG while the relative concentration of anthracene to PBLG is held constant. In other words, the extrinsic CD of anthracene in PBLG–dioxane mixtures is associated only with the lyotropic cholesteric mesophase.

The observed LCICD for anthracene in lyotropic cholesteric mesophases formed by PBLG in dioxane are distinctly different from that observed in thermotropic cholesteryl mesophases composed of cholesteryl derivatives[22]. *Figure 6* presents the LCICD and electronic spectra of anthracene dissolved in a thermotropic and a lyotropic cholesteric mesophase. The LCICD spectrum of anthracene in 18/82 wt% PBLG/dioxane follows its absorption spectrum quite closely, and the CD for the pitch band and anthracene absorption bands are both of negative sign. The chirality of the cholesteric helix is then left-handed, i.e. of opposite chirality† to the helicity of the polypeptide[33,34]. The LCICD spectrum of anthracene, on the other hand, in a thermotropic cholesteric mesophase composed of 60/40 wt% cholesteryl chloride/cholesteryl nonanoate shows CD bands of both positive and negative sign whose relative intensity does not follow its absorption spectrum.

The variation in the LCICD of anthracene between the two cholesteric systems is attributed to the difference in ability of the mesophases to physically order the solute. In the thermotropic system the most preferred conformation of the anthracene involves alignment of its long axis with the long axis of the liquid crystal molecules. In the lyotropic system, however, alignment of the long or short axes of anthracene perpendicular to the long axis of the liquid crystal molecules seems to be equally preferred. This conclusion is consistent with the relative sizes of the solute anthracene ($\sim$10 Å) and PBLG molecules ($\sim$850 Å for MW = 125000)[35]. The ordering of solute molecules by the liquid crystal would be most efficient for solutes of comparable size and shape to the liquid crystal molecules. The small variation in pitch between the two cholesteric mesophases was found not to be the cause of the difference in the LCICD spectra for anthracene presented in *Figure 6*.

Enantiomeric lyotropic cholesteric mesophases are produced by PBLG and PBDG in dioxane solvent as indicated by the LCICD spectra for anthracene in *Figure 7*. The chirality of the cholesteric helix in the lyotropic mesophase can be established by determining the sign of the CD in the region of the reflective wavelength of the cholesteric pitch band†. Once a correlation

† See Ref. 32.

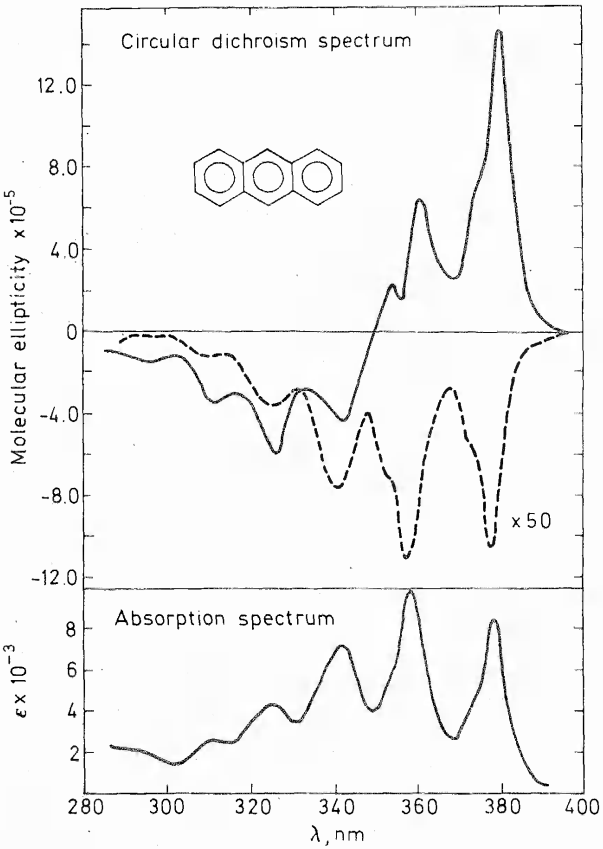


Figure 6. Circular dichroism and absorption spectrum of anthracene in
(——) 1. A thermotropic cholesteric mesophase composed of 60/40 (wt%) cholesteryl chloride/cholesteryl nonanoate (pitch ≃ 9 μm)
(– – – –) 2. A lyotropic cholesteric mesophase composed of 18/82 (wt%) PBLG/dioxane (MW PBLG = 125000, pitch ≃ 18 μm)

between the sign of the CD for the pitch band and a LCICD band has been made the chirality of the cholesteric helix may be determined simply from the sign of LCICD[33]. The chirality of the cholesteric helix formed by PBLG and PBDG in dioxane (described in *Figure* 7) are left- and right-handed respectively. The difference in LCICD intensity of anthracene in the PBLG and PBDG cholesteric mesophase is attributed to the variation in pitch between the two systems.

Molecular ellipticity values for anthracene in PBLG of differing molecular weight, i.e. 46000, 125000 were *identical* within experimental error for samples of virtually *identical* pitch. The lower MW sample relaxed from the 'Grandjean' to the focal conic texture in one or two hours while the higher MW samples took 24–30 hours to relax.

LCICD has also been observed within the electronic transitions of the polypeptide itself. Rotational strengths for the polypeptide absorption bands

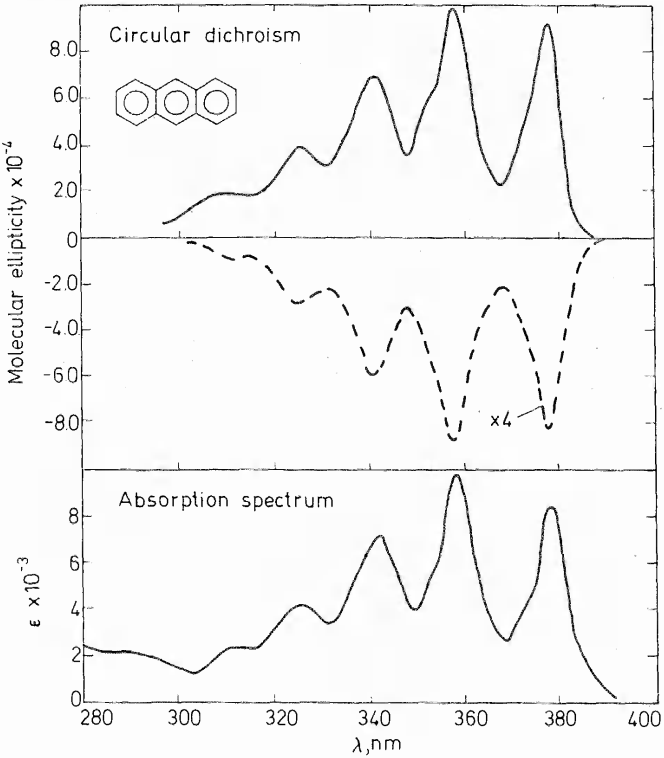


Figure 7. Circular dichroism and absorption spectrum of anthracene in
(– – – –) 1. A lyotropic cholesteric mesophase composed of 18/82 (wt%) PBLG/dioxane (MW PBLG = 125000, pitch ≃ 18 μm)
(— —) 2. A lyotropic cholesteric mesophase composed of 20/80 (wt%) PBDG/dioxane (MW PBDG = 120000, pitch ≃ 21 μm)

are approximately 10^2–10^3 larger in the cholesteric mesophase than in isotropic solution. The ^1L_b electronic transition of the benzyl group in PBLG shows large positive CD for a left-handed cholesteric mesophase.

CONCLUSION

Liquid crystal induced circular dichroism has been observed in achiral noncomplexing solutes in lyotropic cholesteric mesophases. The sign of the LCICD in both lyotropic and thermotropic cholesterics provides: (i) The chirality of the cholesteric helix (provided the region of λ_0 is known), and (ii) the preferred orientation of the solute with respect to the long molecular axis of the liquid crystal molecules.

The intensity of LCICD provides information about the pitch of the cholesteric mesophase.

In lyotropic cholesteric systems small molecules such as anthracene are not ordered to the extent they are in thermotropic systems composed of cholesteryl derivatives.

It is concluded that LCICD arises primarily from the helical organization of the solute alone (mechanism a). It is suggested that LCICD will also exist for randomly distributed solute molecules (mechanism b).

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