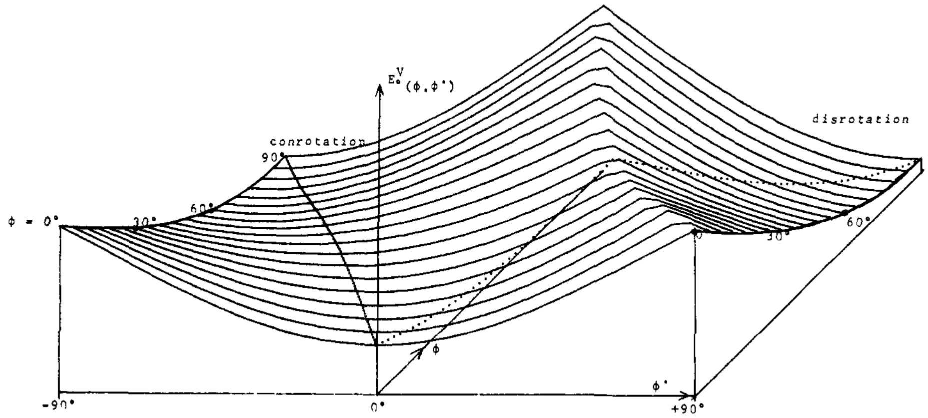

Figure 4. Energy surface (one-electron contributions) of the butadiene–cyclobutene ground configuration as a function of independent rotational angles ϕ and ϕ'. Dotted lines: $\phi = -\phi'$ conrotation, $\phi = +\phi'$ disrotation. (Note: $\phi' = +90°$ is electronically equivalent to $\phi' = -90°$ and the surface repeats periodically for angles outside the given range.)

path in this molecular state lies on a smooth energy slope, with no intervening energy maximum between the two paths. (This is true on either side of the peak value!) This in effect represents a highly unstable situation with strong restoring forces (negative derivatives of the energy with respect to the coordinates) directed toward $\phi' = -\phi$. Within this simplified model a synchronized disrotational motion appears therefore extremely improbable, not only on the grounds of a higher activation energy.

The energy difference between con- and disrotation is primarily controlled by the energy of the new σ bond. We expect therefore the same type of qualitative behavior in all reacting states with an appreciable value of the bond order: the energy minimum path is close to the predicted preferred rotation; the opposite rotation is energy wise unstable. The model supports the view of the concerted electrocyclic reaction as simultaneous rotations of the two reacting centers; along the minimum energy path, the rotations are, however, not in perfect synchronization. A twofold axis or a symmetry is then *not* retained during the reaction.

This observation detracts in no way from any previous conclusions as con- and disrotation refer to convenient, but not necessarily physically realized reference paths. It points, however, again to the fact that the bond order criterion is by its very nature a qualitative criterion for the prediction of rotations in electronically controlled electrocyclic reactions.

Cholesteric Liquid Crystal Induced Circular Dichroism (LCICD). V.[1] Some Mechanistic Aspects of LCICD

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Abstract: The influence of cholesteric liquid crystalline mesophase pitch (degree of helicity), temperature, texture, solute concentration, and cholesteric matrix on the intensity and sign of the cholesteric liquid crystal induced circular dichroism (LCICD) in pyrene was investigated. The spectroscopic information (polarizations of electronic transitions, detection of hidden transitions) provided by the LCICD spectra is also discussed. The LCICD intensity is dependent on pitch of the cholesteric mesophase, temperature, and texture. The sign of the LCICD is dependent on the position of λ_0 of the cholesteric pitch band relative to the wavelength of absorption, cholesteric matrix properties, as well as the chirality of the mesophase. The molecular ellipticity, $[\theta]$ (deg cm^2/dmol), for pyrene in a single cholesteric matrix is independent of solute concentration over a range in which the concentration was altered by two orders of magnitude. The concentration independence of $[\theta]$ indicates the lack of a mechanism change over the concentration range studied and that solute–solute interactions do not play an important role in the origin of LCICD for dilute solutions of solutes in cholesteric mesophases. Rotational strengths for pyrene in 70:30 (wt %) cholesteryl nonanoate–cholesteryl chloride are in the range of $1.0\text{–}3.0 \times 10^{-38}$ cgs depending on the pitch of the cholesteric mesophase.

In the past decade or so there have been several reports of induced optical activity and circular dichroism (CD) in chirally perturbed achiral molecules. Certain achiral molecules display extrinsic CD while complexed to polypeptides in an α-helical confor-

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[1] F. D. Saeva, *Mol. Cryst. Liquid Cryst.*, **18**, 375 (1972), and ref 2–4 are considered the first four in this series.

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[5] Rochester Institute of Technology Co-op.

mation,[6–9] when dissolved in chiral solvents,[10,11] or as aggregated dyes.[12] Extrinsic CD has also been observed in a small class of molecules (*e.g.*, urea[13] and benzil[14]) which are not optically active in solution but gain their optical activity from a special type of molecular organization in the crystalline solid state. Molecules in this unusual class of materials are arranged in a helical form in the crystal and can be translated from one to the other by a trigonal screw axis.[14]

We have recently reported[2] that achiral molecules dissolved in cholesteric liquid crystalline mesophases also display extrinsic circular dichroism. The extrinsic CD within the electronic transitions of dissolved molecules appears to be a result of: (a) the solute being exposed to a helical arrangement of solvent molecules and/or (b) a helical arrangement of solute molecules. It is felt that the relative importance of these two mechanisms contributing to the cholesteric liquid crystal induced circular dichroism (LCICD) varies with solute concentration, symmetry, electronic and magnetic properties, as well as the characteristics of the liquid-crystalline solvent. Extrinsic CD has also been observed for the intrinsically chiral molecules within the cholesteric mesophase.

The existence of a macroscopic helicoidal structure, known to exist in cholesteric mesophases, was found essential for the observation of LCICD, since transforming the helical cholesteric structure to a uniaxial nematic mesophase (*i.e.*, unwinding the helicoidal cholesteric structure by means of an electric field) results in the loss of LCICD.[2]

The sign of the LCICD has been found to be dependent on the macroscopic helix sense[15] of the cholesteric mesophase as well as the direction of the electronic transition moments of the solute.[3]

In this paper the magnitude and sign of LCICD are studied as a function of pitch of the cholesteric matrix, temperature, solute concentration, as well as cholesteric matrix properties. The experimental results are then discussed in terms of the mechanism and/or mechanisms contributing to LCICD. The spectroscopic information derived from the LCICD spectra of anthracene and pyrene is also discussed.

Experimental Section

Circular dichroism spectra were run on a Cary 61 spectropolarimeter. Samples consisted of thin films (10–25 μ) of the liquid crystal between 1 in. × 1/8 in. quartz discs. Cell thicknesses were determined, in those cases where Mylar spacers were not employed, by relating absorption spectral intensities in films of unknown thickness to films of known thickness. The texture of the cholesteric mesophase was the Grandjean in all samples. The temperature was 22°, unless otherwise specified, and molecular ellipticity, $[\theta]$, was calculated by means of the following equation

$$[\theta] = \theta \mathrm{MW}/10lc \ (\mathrm{deg\ cm^2/dmol})$$

where θ is the observed ellipticity in degrees, MW, molecular weight, l, path length in cm, and c, concentration in g/ml.

Rotational strengths (R_K) were calculated by means of the following expression

$$R_K \cong 1.23 \times 10^{-42}[\theta]\Delta K/\lambda_1$$

where $[\theta]$ is the molecular ellipticity, λ_1, $\lambda_{\max}$ in cm^{-1}, and ΔK. peak half-width in cm^{-1}.

Materials. Pyrene and anthracene employed in this study were purchased from Princeton Organics, Princeton, N. J., and were of Prinz quality (99.999 mol % purity). *p*-Methoxybenzylidene-*p'*-*n*-butylaniline (nematic range of 22–48°) was also purchased from Princeton Organics and possessed a resistivity of 5 × 10^{10} ohm cm (25°). Cholesteryl chloride (mp 96°) and cholesteryl nonanoate (cholesteric range 78–92°) were purchased from Eastman Kodak Co., Rochester, N. Y., and were recrystallized twice from *n*-propyl alcohol prior to use.

Electric field experiments involved the application of a dc voltage across liquid crystal films between 1 × 1/8 in. SnO coated quartz disks utilizing 1 mil Mylar spacers.

Results and Discussion

Initial experiments designed to provide mechanistic information concerning the LCICD phenomenon dealt with a study of the dependence of LCICD sign and intensity on the pitch of the cholesteric helical structure. The LCICD sign was observed to be dependent on the position of λ_0 of the cholesteric pitch band relative to the wavelength of absorption. For a right-handed helical cholesteric mesophase composed of cholesteryl chloride–cholesteryl esters the LCICD sign for a transition moment with a preferred orientation parallel with the long axis of the liquid crystal molecules is summarized in Table I. The variation of solute LCICD sign with the position of λ_0 of the cholesteric pitch band is in agreement with the theoretical calculations of Holzwarth and Holzwarth.[16] The theoretical study extends the theory of electromagnetic radiation in nonabsorbing cholesteric liquid crystals to the absorbing case by adding a frequency dependent complex distribution to the spiraling dielectric tensor of the liquid crystal itself.

Table I. Sign of LCICD as a Function of λ_0

Helix sense	λ_0/λ_{ab}[a]	LCICD sign[b]
Right-handed	>1	−
	<1	+
Left-handed	>1	+
	<1	−

[a] λ_{ab} = wavelength of absorption; λ_0 = reflective wavelength of the cholesteric pitch band. [b] May change with a variation in the cholesteric matrix.

The pitch of the cholesteric mesophase was then altered by means of a dc electric field while mesophase texture, composition, temperature, and solute concentration were held constant. The LCICD intensity of pyrene in a 70:30 (wt %) cholesteryl nonanoate (CN)–cholesteryl chloride (CC) supercooled cholesteric mesophase was monitored as λ_0 was varied between 6378 and 5979 Å, and the experimental

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(15) The chirality of the cholesteric mesophase is that indicated by the handedness of circular polarized light transmitted in the region of the pitch band (*i.e.*, a cholesteric mesophase that selectively transmits left-handed circular polarized light in the region of the pitch band is a left-handed helix).

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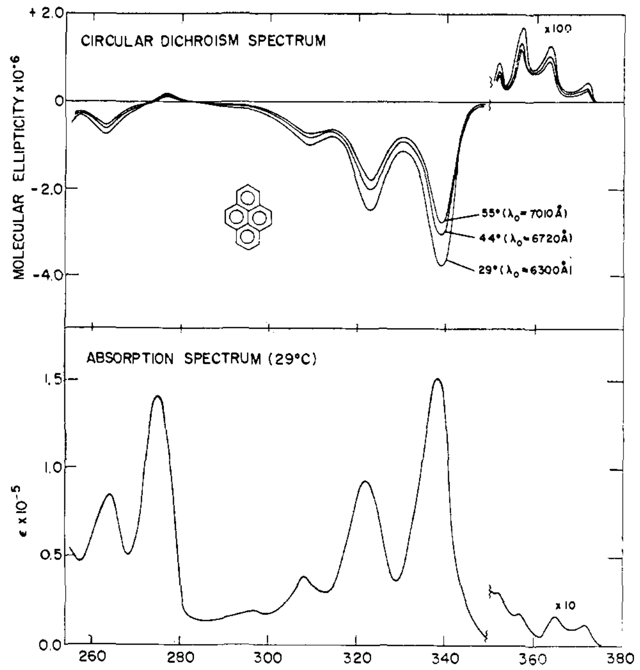

Figure 1. Circular dichroism and absorption spectrum of pyrene in 70:30 (wt %) cholesteryl nonanoate–cholesteryl chloride as a function of temperature.

Table II. Liquid Crystal Induced Circular Dichroism (LCICD) of Pyrene as a Function of Pitch of the Cholesteric Mesophase

$10^{-5}[\theta]^a$	λ_0,[b] Å	Applied voltage[c]
2.93	6378	0
2.90	6360	10
2.88	6339	20
2.82	6279	30
2.66	6168	40
2.07	5979	50

[a] Molecular ellipticity in units of deg cm²/dmol. [b] Pitch (p) of the helicoidal cholesteric helix can be obtained by using the following expression: $\lambda_0 = np$ where refractive index $n \simeq 1.5$ and λ_0 = reflective wavelength of the cholesteric pitch band. [c] Voltage applied to a 1 mil film of 2.85×10^{-3} M pyrene in 70:30 (wt %) cholesteryl nonanoate–cholesteryl chloride.

results are presented in Table II. A decrease in pitch results from an increase in the angle between the "nematic-like" layers in the cholesteric mesophase. The molecular ellipticity, $[\theta]$, of pyrene was found to be a hyperbolic function of pitch of the cholesteric mesophase over the range of pitches studied, and the intensity of the LCICD decreased as the helix pitch decreased. The dependence of LCICD intensity on pitch is in agreement with previous suggestions[2] and theoretical calculations.[17] The variation of the LCICD intensity with pitch was studied over a limited range of pitches and as the pitch increases to infinity the circular dichroism must decrease and eventually reach zero intensity.[2]

The combined influence of temperature and pitch on the LCICD intensity of pyrene in 70:30 wt % CN–CC was then studied. The experimental results are presented in Figure 1. The LCICD of pyrene was found to decrease in a nonlinear fashion as the temperature was increased from 29 to 55°. A movement of λ_0 of the cholesteric pitch band to longer wavelength also resulted from the change in temperature. From the previous discussion of the pitch dependence on LCICD, where LCICD intensity decreased with decreasing pitch, it can be seen that the temperature dependence of LCICD dominates over the pitch dependence. The observed decrease of LCICD intensity with an increase in temperature is presumably a result of a randomization of the solute within the mesophase or possibly a consequence of an alteration of electric and/or magnetic interactions[18] between the solute and liquid crystal molecules.

The LCICD spectrum of pyrene (Figure 1) presents some spectroscopically significant information concerning the polarizations of the electronic transitions. The 0–0 bands for the ^1L_b, ^1L_a, and ^1B_b transitions occur at 372, 339, and 277 nm, respectively. The 0–0 bands of the ^1L_b and ^1B_b transitions, which are known to be transversely polarized (short axis in-plane),[19,20] show positive circular dichroism (*i.e.*, $\epsilon_L > \epsilon_R$) in a right-handed helicoidal cholesteric mesophase consisting of 70:30 (wt %) CN–CC. 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 mixed of polarization[21,22] 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)[19,20] and shows negative circular dichroism. The signs of the LCICD bands and transition moment polarization are in agreement with the previously proposed quadrant rule[3] and with experimental results on 2-carbomethoxy pyrene.[17]

A mixing of molecular states provides the electric and/or magnetic transition dipoles which are required for optical activity. Such a mixing of states requires that interacting chromophores (intra- or intermolecular) not be widely separated in space.[18] In view of the above requirement for the observation of CD the influence of solute–solute interactions on the origin of LCICD was investigated as a function of pyrene concentration between 8.38×10^{-4} and 9.64×10^{-6} g/ml in eight incremental steps. The pitch of the cholesteric mesophase was independent of the solute concentration over this range and the temperature was held constant. The calculated molecular ellipticity for each of the eight samples was found to be identical within experimental error (~5%). The concentration independence of the molecular ellipticity indicates that the mechanism does not change over the concentration range studied and that solute–solute interactions do not play an important role in the origin of LCICD.

Cholesteric mesophases may exist in either the Grandjean (helix axes parallel to the optic axis) or focal conic textures (helix axes perpendicular to the optic axis) or as combinations of the two textures depending on the conditions used for sample preparation. Since there is a 90° difference in molecular orientation between the two textures, we decided to investigate the intensity of LCICD of pyrene in 40:60 CN–CC as a function of

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the texture of the cholesteric mesophase to determine the extent of change of LCICD with texture. As the Grandjean is transformed into the focal conic texture by means of an electric field, the LCICD intensity decreased for a longitudinally polarized electronic transition, as one would expect for such a change in molecular orientation if the solute molecules were parallel to those comprising the mesophase. Since the intensity of LCICD was found to be dependent on texture of the cholesteric mesophase we have attempted to work with the Grandjean (planar) texture exclusively.

The sign of the LCICD of *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) has been previously found to be dependent on the helix sense of the cholesteric mesophase, composed of two different ratios of cholesteryl chloride and cholesteryl nonanoate.[2] The LCICD sign for the 300-nm transition in MBBA was found to be *opposite* to the sign of the reflective circular dichroism of the pitch band in samples where low concentrations of MBBA in cholesteryl cholesterics were employed. We have recently observed the LCICD sign of the 300-nm transition in MBBA to be the *same* as the reflective circular dichroism of the pitch band in a cholesteric mesophase prepared from nematic MBBA by the addition of 5 wt % *l*-menthol.[23] The signs of both pitch band reflective circular dichroism and MBBA (300 nm) CD were found to be positive.[23] Thus, for two cholesteric matrices of the same chirality (right-handed helix) different signs of the LCICD for a single achiral material have been observed. This experimental observation, we feel, demonstrates the importance of the cholesteric matrix to the origin of LCICD and may reflect the difference between identical and nonidentical interacting chromophores.

Figure 2 presents the circular dichroism and absorption spectrum for anthracene in 40:60 (wt %) CN–CC. The ^1L_a transition in anthracene (0–0 at 379 nm) is transversely polarized[24] (short axis in-plane), and gives rise to positive circular dichroism. The relative intensities of the LCICD bands in anthracene (between 300 and 400 nm) do not follow its absorption spectrum. This may be a result of mixed polarization within the ^1L_a transition or an overlapping with the normally unobserved ^1L_b transition which is predicted to be longitudinally (long axis in-plane) polarized[24] and should show negative circular dichroism following the experimental observations with pyrene.

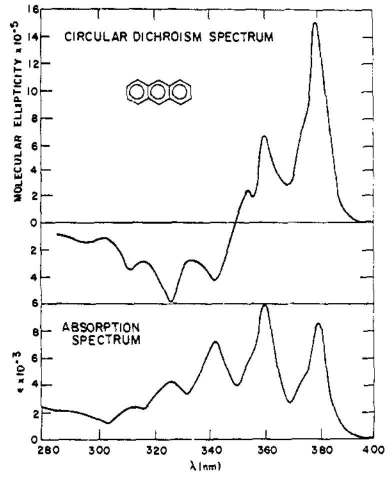

Figure 2. Circular dichroism and absorption spectrum of anthracene in 40:60 (wt %) cholesteryl nonanoate–cholesteryl chloride ($\lambda_0 = 10\ \mu$).

Conclusion

The LCICD intensity (*e.g.*, in pyrene and anthracene) is dependent on pitch of the cholesteric helix, temperature, cholesteric matrix properties, wavelength, and texture. The molecular ellipticity, on the other hand, is independent of the solute concentration over a limited concentration range. These experimental observations are consistent with previous theoretical studies[16,17] which attribute the origin of LCICD primarily to the chiral organization of the solute (mechanism b) within the cholesteric mesophase. As the concentration of the solute is increased so that it can be considered the solvent, as in the case of *l*-menthol in MBBA, LCICD appears to arise from the interaction of identical chromophores which are helically oriented. Further experiments are in progress to elucidate the detailed aspects of the origin of LCICD. Since θ, the observed ellipticity, is linearly proportional to the concentration of solute (c) dissolved in the cholesteric mesophase as well as sample thickness (l), *i.e.* $\theta \alpha c l$, and the proportionality constant, $[\theta]$, is a function of temperature, pitch, texture, wavelength, and cholesteric matrix, the preceding variables must be specified in any quantitative determination of LCICD.

Acknowledgment. Stimulating discussions with J. J. Wysocki and Drs. W. H. H. Gunther, G. Johnson, J. E. Kuder, and H. Scheraga are gratefully acknowledged.

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