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F. D. Saeva [a]

[a] Xerox Corporation Rochester Corporate Research Center, Webster, New York, 14580

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# A Novel Method for Determining the Existence and Chirality of Cholesteric Mesophases

F. D. SAEVA

Xerox Corporation
Rochester Corporate Research Center
Webster, New York 14580

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Cholesteric mesophases are normally identified by characteristic textures, sign of the birefringence which distinguishes between cholesteric (negative sign) and smectic or nematic mesophases (positive sign) and existence of a cholesteric pitch band. The chirality of the cholesteric mesophase can then be determined from the handedness of the reflected or transmitted light(1) from the pitch band using polarizing optics, or from the variation of optical rotation with wavelength according to the theoretical predictions of deVries.(2)

However, when the cholesteric pitch band is inaccessible and the Grandjean texture unstable, it may be difficult to establish with certainty the existence of a cholesteric mesophase. This difficulty is especially present in large pitch materials near perfect compensation.(3,4) It is the object of this note to describe a novel method for determining the existence and chirality of cholesteric mesophases which is independent of texture and wavelength $\lambda_0$ of the cholesteric pitch band.

It has been previously reported(5) that optically inactive compounds dissolved in cholesteric mesophases display induced circular dichroism (ICD) in their electronic transitions, the sign of which is generally opposite to that of the circular dichroism (CD) of the pitch band(6). Organic azo, arylazonaphthols, anils, and anthraquinone dyes all show this effect which is present whether the cholesteric mesophase is in the Grandjean or focal conic texture, unlike all the methods mentioned above. Since ICD exists only when a macroscopic helix is present, it is proposed that the existence of ICD be used to indicate the presence of a cholesteric mesophase, the sign of which specifies mesophase chirality.

The ICD is normally sufficiently large to allow semiquantitative information (i.e. handedness of preferential absorption of circular polarized light) to be obtained with a spectrophotometer in conjunction with circular polarizers, just as well as with a CD spectropolarimeter. The experimental results presented here were obtained using a Cary 14 spectrophotometer in which circular polarizers(7) were placed between the light source and sample. Figure 1 presents the absorption spectrum

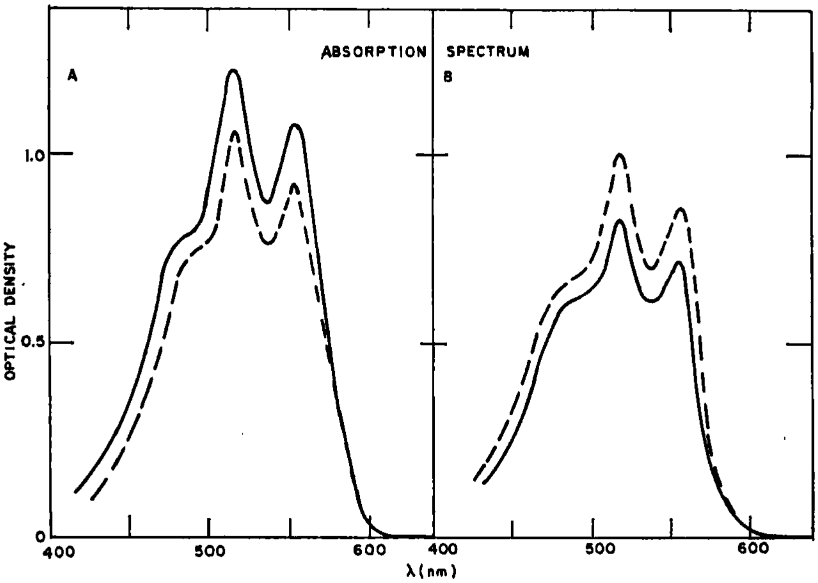

Figure 1. Absorption spectra of (A) 2% 1-Amino-2-phenoxy-4-hydroxyanthraquinone (1) in 51/49 wt % cholesteryl nonanoate (CN)/cholesteryl chloride (CC) [right-handed helix], and (B) 2% 1 in 64/36 wt % CC/CN [left-handed helix] using right (———) and left (- - - -) circularly polarized light.

using left and right circular polarized light (CPL) for an organic dye (1-amino-2-phenoxy-4-hydroxyanthraquinone) dissolved in cholesteric mesophases obtained from mixtures of cholesteryl chloride (CC) and cholesteryl nonanoate (CN) which are left- and right-handed helical structures. The organic dye in a right-handed helical cholesteric mesophase absorbs right CPL to a greater extent than left

CPL. The opposite is true for the same dye in a left-hand helicoidal cholesteric mesophase. Optical density variations between left and right CPL depend on the helical pitch, efficiency of the circular polarizers, optical density of the dye absorption and have been observed to be ~0.1 of an absorption unit.

All experimental observations thus far indicate that the cholesteric liquid crystal induced circular dichroism is a general phenomenon for dissolved molecules in cholesteric mesophases and appears to be independent of solute molecular structure.(5) However, it is recommended that an organic dye molecule with high extinction coefficient electronic transitions in the visible region of the spectrum, where the circular polarizer is effective, be used as the probing molecule. A control experiment, i.e. a dye in a known cholesteric mesophase, is also suggested, as well as adjustment of solute concentration and sample thickness so that the absorption is above 0.4 OD if the spectrophotometer method is employed. The temperature at which a liquid composition is at exact compensation(3,4) can also be accurately determined by monitoring the preferential absorption of CPL as a function of temperature. If difficulties are encountered in the spectrophotometer method, a CD spectropolarimeter can be employed where the concentration of the probing molecule is less important and results are always conclusive. Again, it is recommended that a control experiment be performed if new dye-cholesteric systems, other than described in this note, are involved.

Since solute molecules, e.g. dyes, show helical stacking preferences when dissolved in cholesteric mesophases(5) it is recommended that low dye concentrations (less than 0.5 wt%) be used for cholesteric materials of large pitch ($> 10\,\mu$) to minimize perturbation by the dye on the original cholesteric mesophase.

In summary, a novel method has been identified which utilizes the preferential absorption of left and right CPL by solute molecules in liquid crystals to indicate the existence and chirality of a cholesteric mesophase. The sense of preferred absorption indicates the sense of the helicoidal cholesteric structure (e.g. *preferred absorption of left CPL* indicates the existence of a *left-handed helical cholesteric mesophase*). The experimental conclusions obtained by this technique are independent of texture and $\lambda_0$ of the cholesteric pitch band.

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