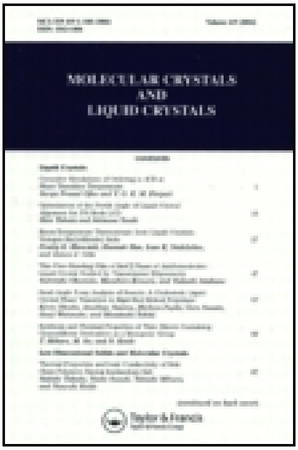

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Utilization of the Cholesteric → Nematic Phase Transition for the Evaluation of Polarization Spectra with Unpolarized Light

F. D. Saeva [a] & G. R. Olln [a]

[a] Xerox Corporation. Webster Research Center, 800 Phillips Road, Webster, New York, 14580

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Utilization of the Cholesteric→Nematic Phase Transition for the Evaluation of Polarization Spectra with Unpolarized Light

F. D. SAEVA and G. R. OLIN

Xerox Corporation, Webster Research Center, 800 Phillips Road, Webster, New York 14580

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A spectroscopic technique for the determination of optical polarization spectra is described where the anisotropic sample serves as its own polarizer. The molecular alignment of solute molecules is converted from a helical cholesteric to a uniaxial nematic structure by means of an electric field. The variation in the absorption of incident unpolarized light by an aligned solute in the two states provides the polarization of the optical transition of interest.

Optical polarization studies are extremely important in the investigation of the symmetry and vibrationally induced mixing of excited molecular states as well as being sensitive to low intensity optical transitions of polarization opposite to more intense overlying bands. The primary requirement for direct polarization measurements is that the molecules be at least partly oriented. The chromophores of interest may be oriented in a host crystal,[1,2] in strong electric fields,[3,4] in stretched polymer films,[5,6,7] and in liquid crystals.[8,9] Relative polarization directions can be found by the method of photoselection which is achieved by irradiating the molecules under investigation, embedded in a rigid glass, with polarized light.[10–14]

All of the above techniques employ the use of polarizing optics. Recently, however, it has been reported that unpolarized light may be employed where the anisotropic sample serves as its own polarizer.[15,16]

In this letter we describe the measurement of polarization spectra, without the use of polarized light, for ordered solutes in cholesteric liquid crystalline mesophases, directly from the difference in the absorption spectra for the solute in two different molecular orientations.

Anisotropic solute molecules become oriented in liquid crystalline mesophases such that they align their long molecular axis parallel to the long molecular axis of the rod-shaped liquid crystal molecules. It has been suggested that dispersion forces are primarily responsible for solute alignment, in cases where specific interactions such as hydrogen bonding, and permanent electric dipole moments are of minor importance.[17,18] In this study anthracene was used to demonstrate the spectroscopic method because it possesses both long axis in-plane and short axis in-plane polarized electronic transitions in a readily accessible region of the spectrum.[19,20]

Anthracene (1.5 mg) was dissolved in 160 mg. of a 60/40 (wt %) mixture of cholesteryl chloride (CC)/cholesteryl nonanoate (CN) which forms a right-handed helical super-cooled cholesteric mesophase at room temperature

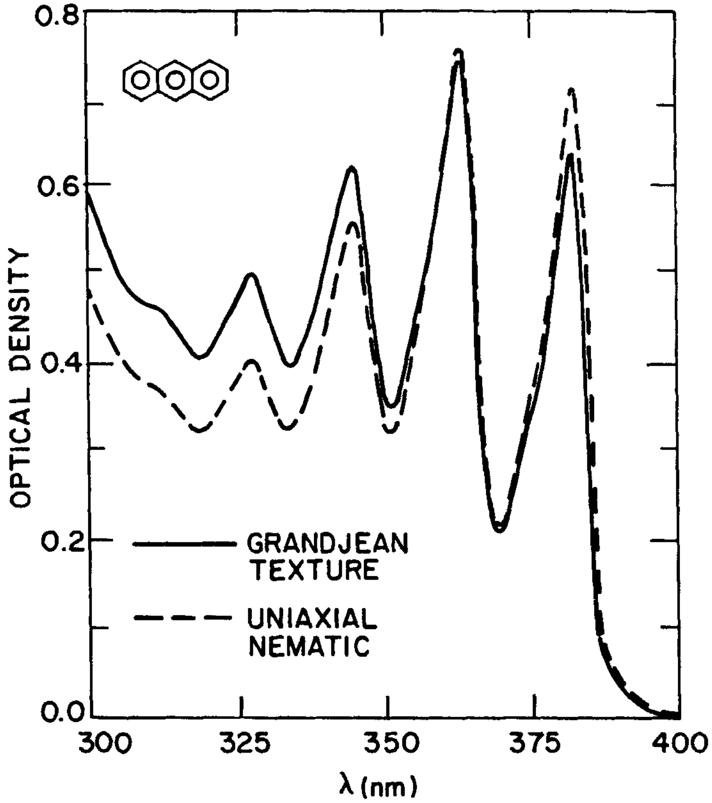
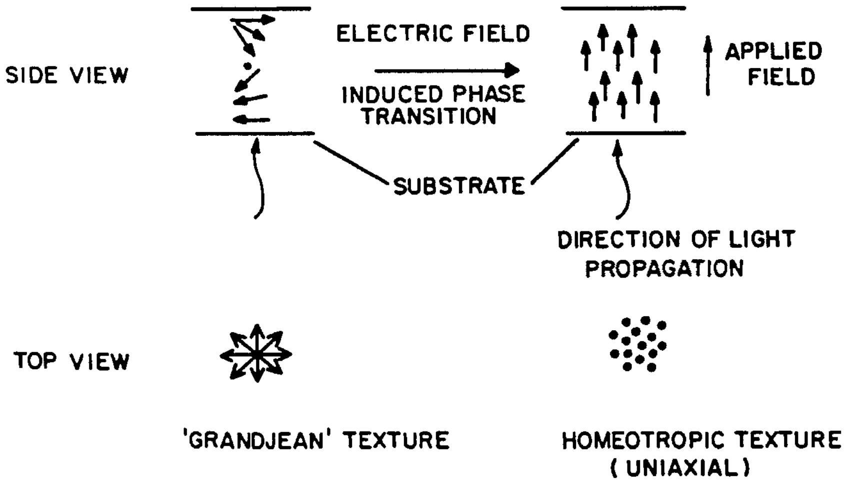


FIGURE 1 Anisotropic absorption spectrum of anthracene in 60/40 (wt %) cholesteryl chloride/cholesteryl nonanoate.

with a helical pitch of 0.74 μm. The overall liquid crystal composition possesses a positive dielectric anisotropy and readily undergoes the cholesteric → uniaxial nematic phase transition upon the application of an electric field.[21] The liquid crystal composition was placed between SnO coated quartz discs (1″ × 1/16″) using a 1 mil mylar® spacer. The disturbed (Grandjean) texture was obtained by a small displacement of the two discs and the absorption spectrum for anthracene recorded between 300 – 450 nm on a Cary 15 spectrophotometer *without any polarizing optics.* A dc electric field (~ 100V/mil) was then applied across the liquid crystal film to induce the cholesteric-nematic phase transition producing the uniaxial nematic mesophase and the absorption for anthracene was recorded again. The difference in the absorption spectra provides directly the effective polarization spectrum for (see Figure 1) anthracene. The direction of light propagation is normal to the substrate.

The molecular organization in both the "Grandjean" texture and the uniaxial phase is schematically described below:



In the Grandjean texture the long molecular axis of anthracene is oriented normal and isotropically about the helix axis when sample thickness is larger than the pitch of the cholesteric mesophase. Optical transitions longitudinally (x) polarized, i.e. 311, 323, 342 nm bands will show maximum absorption in this texture. The transversely (y) polarized bands at 350 and 378 nm will show slightly *less* than maximum absorption due to the possibility of molecular rotation about the long axis in which the short-axis in-plane transitions may lie along the direction of light propagation as well

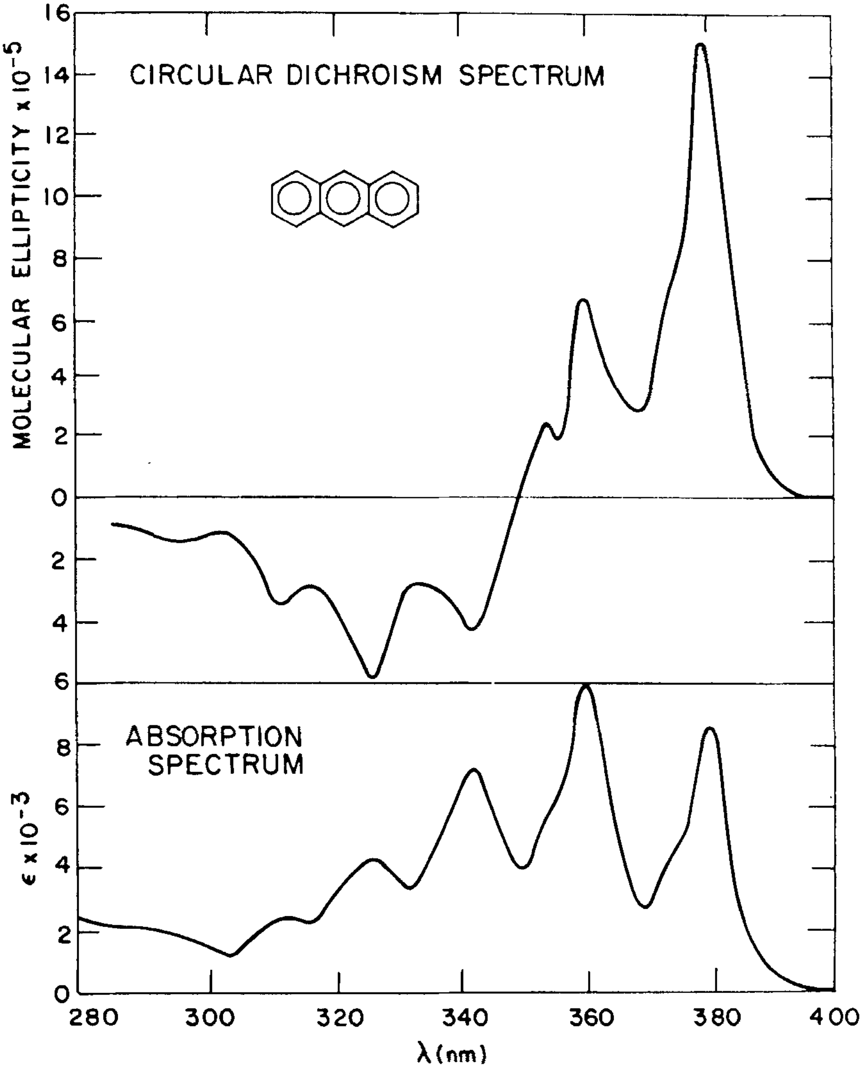
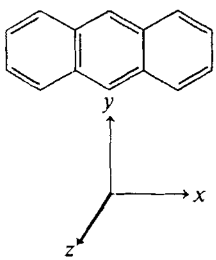


FIGURE 2 Circular dichroism spectrum of anthracene in 60/40 (wt %) cholesteryl chloride/cholesteryl nonanoate.



Optical transition (nm)	Polarization direction
311	x
323	x
342	x
350	y
378	y

as normal to it. In the electric field induced uniaxial phase, however, anthracene is aligned preferentially such that its long molecular axis lies parallel to the direction of applied electric field as well as the direction of light propagation. In this alignment the short axis in-plane polarized transitions will show *maximum* absorption. In contrast the long axis polarized bands will exhibit *minimum* absorption in this case. The polarization information provided in Figure 1 is entirely consistent with that obtained from the liquid crystal induced circular dichroism (LCICD) measurements (see Figure 2) in the same cholesteric matrix as used throughout this study.[22] The spectroscopic technique has been applied to many other molecules, e.g., azo, anil, and quinone dyes, and experimental observations were consistent with the previous discussion.

Cholesteric liquid crystals behave like a uniaxial crystal where the optic axis corresponds to the helix axis. In the Grandjean texture then light is propagating down the optic axis as is the case in the homeotropic state. As a consequence, one need not correct or account for the polarization properties of the spectrophotometer photomultiplier in this method as is required by many other polarization techniques.[15]

In summary, we describe a simple method for determining linear dichroism spectra for solutes in cholesteric mesophases by the use of conventional spectrophotometers without the use of polarizing optics. The detailed interpretation of the polarization spectra for unknown molecules depends, as do all the previous mentioned direct polarization methods, on the alignment within the liquid crystal.

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References

1. D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954).
2. R. M. Hochstrasser, *ibid*, **33**, 459 (1960).
3. H. Labhart, *Adv. Chem. Phys.*, **13**, 179 (1967).
4. W. Liptay, *Angew Chem.*, **81**, 195 (1969).

5. A. Jablonski, *Acta Phys. Pol.*, **3**, 421 (1934).
6. E. W. Thulstrup, J. Michl, and J. H. Eggers, *J. Phys. Chem.*, **74**, 3868 (1970); **74**, 3878 (1970).
7. E. W. Thulstrup and J. H. Eggers, *Chem. Phys. Lett.*, **1**, 690 (1968).
8. E. Sackmann, *J. Am. Chem. Soc.*, **90**, 3569 (1968).
9. E. Sackmann and H. Möhwald, *J. Chem. Phys.*, **58**, 5407 (1973).
10. G. Weber, *J. Biochem.*, **51**, 145 (1952).
11. A. C. Albrecht, *J. Mol. Spectrosc.*, **6**, 84 (1961).
12. F. Dorr, *Angew Chem.*, **78**, 457 (1966).
13. F. Dorr, *Creation and Detection of the Excited State*, edited by A. A. Lamola (Dekker, New York 1971), Vol. 1.
14. G. E. Johnson, *J. Phys. Chem.*, **78**, 1512 (1974).
15. A. Yogev, L. Margulies, J. Sagiv, and Y. Mazur, *Chem. Phys. Lett.*, **23**, 178 (1973).
16. H. Kelker, R. Hatx, and G. Wirzing, *Z. Anal. Chem.*, **267**, 161 (1973).
17. A. Saupe, *Mol. Cryst.*, **1**, 527 (1966).
18. A. Saupe, *Mol. Cryst., Liquid Cryst.*, **16**, 87 (1972).
19. J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, London, 1969, pp. 7, 54, 56, 70 and 526.
20. G. P. Ceasar and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 191 (1969).
21. J. J. Wysocki, J. Adams, and W. Haas, *Phys. Rev. Lett.*, **20**, 1024 (1968).
22. F. D. Saeva, P. E. Sharpe, and G. R. Olin, *J. Amer. Chem. Soc.*, **95**, 7656 (1973).