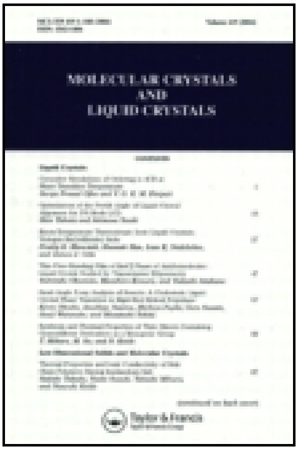

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Infrared Rotatory Dispersion Studies of Induced Cholesteric Mesophases in Electric Fields I. Texture Change Induced by a DC Electric Field

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Infrared Rotatory Dispersion Studies of Induced Cholesteric Mesophases in Electric Fields I. Texture Change Induced by a DC Electric Field

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The influence of a dc electric field on induced cholesteric mesophases was studied by infrared rotatory dispersion. The reflection Cotton effect was found to vanish above a threshold field of strength about 5.10^3 V/cm because of a field-induced texture change. The frequency of the reflection Cotton effect is independent of the applied voltage.

Keywords: I. R. spectroscopy, optical rotatory dispersion, cholesteric liquid crystal, electric field

INTRODUCTION

The effect of electric fields on the structure of cholesteric liquid crystals has received much attention during the last two decades.[1] After the first publications on this topic,[2,3] interest was focused on the cholesteric–nematic phase transition. Both theoretical[4,5] and experimental[2,3,7–9] work indicated that the helical structure of a cholesteric liquid crystal can be deformed and ultimately destroyed (unwound) by an applied electric field. The threshold field for this transformation has been studied as a function of sample thickness, temperature and composition.[7] Special attention has been paid to the electric field-induced color change and pitch dilation.[3,6,8,9] The main experimental techniques used in these investigations were optical microscopy and reflection spectroscopy in the visible region.

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It is well known that a cholesteric twist can be induced in a nematic host phase by introducing a chiral guest species which can be either mesogenic or non-mesogenic.[10] The optical properties of these induced cholesteric solutions are nearly identical to those of pure cholesteric phases and show selective reflection and the related reflection Cotton effect (R-Cotton effect); the principal difference is that, because of their longer pitches, induced cholesteric phases tend to show these effects in the infrared region rather than in the visible.[11]

Bearing in mind the practical importance of such induced cholesteric phases in different electronic devices[12] and their possible use in other applications,[13] we have studied the influence of a dc electric field on an induced cholesteric phase using infrared optical rotatory dispersion (IR-ORD).

To our knowledge, the field-induced change of the R-Cotton effect in induced cholesteric liquid crystals has not been studied previously by this technique.

EXPERIMENTAL

The IR-ORD spectra were recorded using a computer-controlled Fourier transform infrared spectrophotometer (Nicolet 7199) equipped with two wire grid polarizers (Oriel), set at 45°. The scheme of measurement has been described previously.[14]

For these measurements, a modification of the conventional IR sample cell with silicon plates was used. The positive electrode for the applied dc electric field was an amalgamated copper plate directly attached to one of the silicon plates. The negative electrode was the thermostatted box, as shown in Figure 1. The spacing between the plates was adjusted to about 25 μm by a teflon spacer. The silicon plates were rubbed with tissue paper in one direction to obtain a uniform planar alignment of the induced cholesteric phases.

We have investigated the induced cholesteric phases formed by (+)-2-phenylpropanoic acid (Merck) and the nematic mixture E1 (BDH) (a eutectic mixture of 4-alkyl-4′-cyanobiphenyls), over the concentration range 1.5 wt% to 5 wt%. The materials were obtained commercially and were used as supplied. The solutions were prepared by mixing the components in the isotropic phase above the clearing point. The cells were filled with the solutions in the cholesteric phase. All measurements, except those connected with determining the temperature dependences, were carried out at 20°C. The sample temperature was controlled by a thermostat to an accuracy of ±0.1°C.

Because of the interference between the silicon plates, interference patterns on the base line as well as on the R-Cotton curve were observed.

RESULTS AND DISCUSSION

Under the experimental conditions described, the chiral (+)-2-phenylpropanoic acid induces a cholesteric twist in the nematic liquid crystal E1 and a planar cholesteric structure is obtained. In the IR-ORD spectrum a large R-Cotton effect is

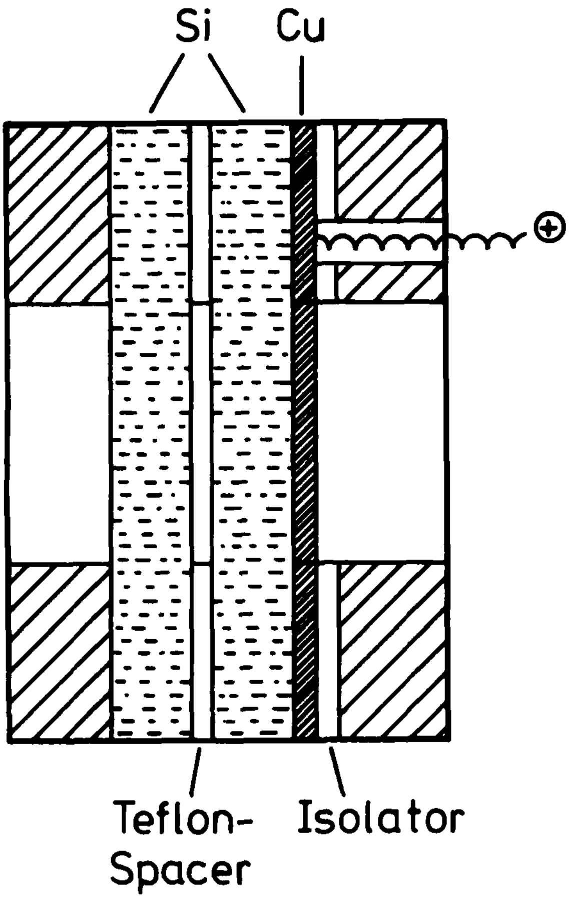

FIGURE 1 Schematic drawing of the cell.

observed due to selective reflection (Figure 2). The wavelength of the R-Cotton effect, λ_R, is related to the pitch, z, of the helix by

$$\lambda_R/n = z, \quad \text{(in wavenumbers: } 1/(n\bar{\nu}_R) = z)$$

where n is the mean refractive index, and depends on guest concentration and temperature.[15] The sign of the R-Cotton effect indicates a right-handed structure.

The data in Table I show that the position of the R-Cotton effect, as indicated by its central wavenumber, for the induced cholesteric phases varies linearly with the concentration of guest species. With increasing applied dc electric field, the amplitude of the R-Cotton effect remains unchanged until a given threshold voltage is reached. In order to deform the cholesteric structure, electric energy is required to overcome the elastic energy between the molecules. This means that there is a threshold value of the electric field at which the electric energy is balanced by the elastic energy. Above this threshold field strength the amplitude began to decrease

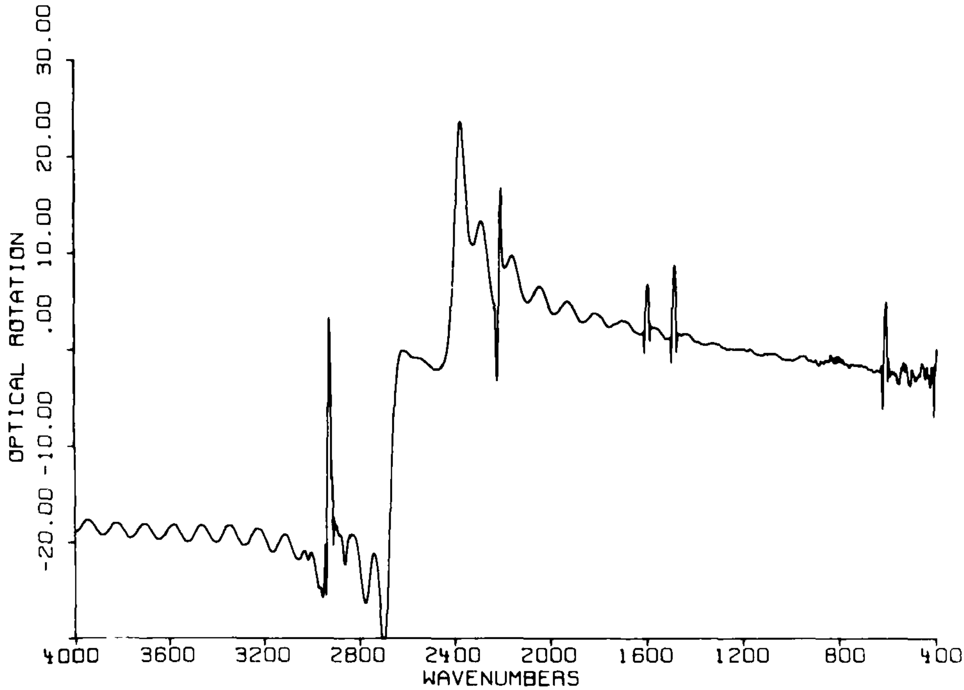

FIGURE 2 IR-ORD spectrum of an induced cholesteric mesophase: 3 wt% (+)-2-phenylpropanoic acid in E1.

(Figure 3), and the R-Cotton effect vanished when the electric field was 10–20% above the threshold value. This threshold field depends on the guest concentration.

Figure 3 shows the relative amplitude of the R-Cotton effect *vs.* the applied field strength. As can be seen, the amplitude disappears over an interval of the field strength of about 1000 V/cm. After switching off the field, a restoration of the R-Cotton effect is observed in reverse order. However, the longer an electric field of strength above the threshold value is applied, the more time is required for the relaxation. The position of the R-Cotton effect remains practically unchanged over the range of applied voltages studied (we observed less than 10 cm^{-1} hypsochromic shift near the threshold).

The data in Table I show an enhancement of the threshold field with increasing guest concentration.

TABLE I

Position of R-Cotton effect ($\tilde{\nu}_R$) and threshold field (E_{th}) at different concentrations of chiral guest molecule

Concentration/wt.%	$\tilde{\nu}_R$/cm^{-1}	E_{th}/Vcm^{-1}	sign(ACE)
1.78	1660	4000	−
3.00	2540	4600	+
4.20	3490	5600	+
5.04	4186	6400	+

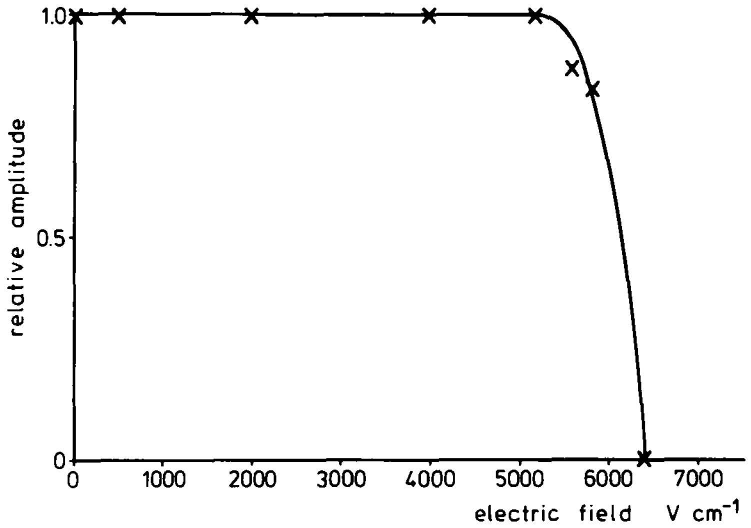

FIGURE 3 Relative amplitude of the R-Cotton effect *vs.* electric field.

It was found that the application of an electric field parallel to the helical axis of a cholesteric liquid crystal with positive dielectric anisotropy leads to a dielectric instability.[5] Using the Helfrich equation[5]:

$$E_{\text{th}} = 2\pi \left[\frac{(2k_{22}k_{33})^{1/2}\, n\bar{\nu}_{\text{R}}}{\varepsilon_0 \Delta\varepsilon d} \right]^{1/2}$$

we found an agreement between the theoretical and experimental threshold fields observed for the induced cholesteric mesophase under study. Therefore we conclude that, in this case, we have observed a dielectric instability, followed by a 90° reorientation of the helical axis. The appearance of dynamic scattering, due to impurities, can be excluded because the spectra taken with electric fields above the threshold do not show any reduction in the transmitted intensity.

In order to study the influence of temperature on the threshold field, we measured the IR-ORD spectra of the same induced cholesteric solution at different temperatures (Table II). The threshold field was found to decrease with increasing temperature from 4600 V/cm at 19.6°C to 4400 V/cm and 3800 V/cm at 24.6°C and

TABLE II

Influence of temperature on the amplitude (A_{R}) and position ($\bar{\nu}_{\text{R}}$) of the R-Cotton effect and threshold voltage (E_{th}) at 3 wt% guest concentration

t/°C	A_{R}	$\bar{\nu}_{\text{R}}$/cm^{-1}	E_{th}/Vcm^{-1}
19.6	100	2485	4600
24.6	90	2478	4400
19.6	100	2529	4600
29.5	55	2530	3800

29.5°C, respectively. The relative amplitude of the R-Cotton effect decreases with temperature increase in accordance with previous observations.[15] These had been explained in terms of an increase in the average angle between the molecular long axis and the director with increasing thermal motion. The absorption Cotton effect (ACE) of the nitrile group at 2230 cm^{-1} shows a change of sign with relative change of the R-Cotton effect position at different concentrations.

CONCLUSION

The influence of an electric field on induced cholesteric phases has been studied for the first time by means of infrared rotatory dispersion spectra. The magnitudes of the observed threshold fields are in agreement with the theoretical values, calculated using the Helfrich equation. The helical pitch is independent of the field strength and the amplitude of the R-Cotton effect becomes zero for fields above a threshold value. This threshold value decreases with increasing temperature and decreasing guest concentration, whereas the pitch of the cholesteric helix remains practically unchanged over the temperature range studied.

Acknowledgments

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