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Infrared Rotatory Dispersion Studies of Induced Cholesteric Mesophases in Electric Fields II. DC Field Induced Texture Changes in Mesophases with Positive and Negative Dielectric Anisotropy

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Infrared Rotatory Dispersion Studies of Induced Cholesteric Mesophases in Electric Fields
II. DC Field Induced Texture Changes in Mesophases with Positive and Negative Dielectric Anisotropy

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The reflection Cotton effect in the infrared rotatory dispersion spectra of induced cholesteric mesophases (with positive and negative dielectric anisotropies) vanishes under the influence of a dc electric field applied parallel to the helical axis. The field interval between the threshold and full disappearance of the reflection Cotton effect for mesophases with negative dielectric anisotropy is twice as large as that for systems with positive dielectric anisotropy. A bathochromic shift of the reflection Cotton effect for the cholesteric mesophase of ZLI 1083 under the influence of a dc electric field was observed.

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

INTRODUCTION

Following the pioneering investigations[1,2] of the cholesteric–nematic phase transition caused by applied electric fields and the subsequent theoretical treatments,[3,4] an intensive study began on the threshold field, the electric field-induced reorientation of the helical axis,[1,7] and the changes in helical pitch and color.[5–9] In the latter case both a decrease[5,6] and an increase[7,8] of the pitch (as indicated by the corresponding color changes) have been observed experimentally. A blue to red color change was observed with increasing electric field applied normal to the helical axis,[7] whereas for fields applied parallel to the helical axis, a red to blue color change was observed,[5,9] accompanied by a 90° reorientation of the helical axis.[1,7]

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The influence of frequency upon the threshold voltage was found to depend largely on the sign of the dielectric anisotropy.[1]

It is well known that the dissolution of a chiral compound in a nematic liquid crystal leads to a cholesteric mesophase.[10] The optical properties of the latter are nearly identical to those of pure cholesteric mesophases[11]; the principal difference is the larger pitch, and hence the selective reflection and the related reflection Cotton (R-Cotton) effect are usually found to appear in the infrared rather than in the visible.

In a previous paper[12] we presented a new way of studying the influence of a dc electric field on an induced cholesteric mesophase by means of infrared spectroscopy. In the present work, infrared rotatory dispersion (IR-ORD) was used to study the influence of a dc electric field applied parallel to the helical axis on several induced cholesteric mesophases of both positive and negative dielectric anisotropy.

EXPERIMENTAL

Details of the preparation of the induced cholesteric mesophases and the measurement of the IR-ORD spectra were as described in a previous paper.[12]

The following nematic liquid crystal hosts were used: ZLI 1083 (Merck), a mixture of 4-cyano-*trans*-4′-alkylcyclohexylbenzenes; ZLI 1695 (Merck), a mixture of 4-alkyl-*trans*,*trans*-bicyclohexyl-4′-carbonitriles; ZLI 1052 (Merck), a mixture of 4-*n*-pentyl 4-alkyloxyphenylbenzoates; Licristal 4 (Merck), 4-methoxy-4′-butylazoxybenzene; MBBA (Riedel-de Haen), *N*-4-methoxybenzylidene-4′-*n*-butylaniline and a 50% MBBA/EBBA mixture.

As chiral guest compounds (inducing the helical twist) (+)-2-phenylpropanoic acid (Merck) **1**, 1.5 wt%–4.5 wt%, and cholesteryl chloride (Merck) **2**, 4.5 wt%–8.5 wt% were used. All the materials were obtained commercially and used as supplied.

RESULTS AND DISCUSSION

As previously observed,[12,13] the wavenumbers, and to some extent the amplitudes, of the R-Cotton effect in the IR-ORD spectra of all the systems studied, increase with increasing guest concentration and decreasing temperature.

Under the influence of the applied dc electric field, the amplitude of the R-Cotton effect remains unchanged up to a particular threshold voltage, beyond which it rapidly decreases to zero. The values of the central wavenumber of the R-Cotton effect, $\tilde{\nu}_R$, and the threshold field, E_{th}, measured in the IR-ORD spectra are listed in Table I.

The electric field interval over which the R-Cotton effect disappears for mesophases with positive dielectric anisotropy is about 2000 V cm^{-1}. This band is about half as broad as those for mesophases with negative anisotropy (about 4000 V cm^{-1}).

As an example, Figure 1 shows the way in which the relative amplitude of the

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TABLE I

Central wavenumber of the reflection Cotton effect ($\tilde{\nu}_R$) and dc threshold field (E_{th}) of the induced cholesteric mesophases studied

Nematic Phase	Dielectric Anisotropy	Chiral Guest Compound (Concentration, wt%)	$\tilde{\nu}_R/cm^{-1}$	E_{th}/Vcm^{-1}	Shift $\Delta\tilde{\nu}_R/cm^{-1}$
ZLI 1083	+10.1	**1**, 4.0	4300	4000	bathochrom 200
ZLI 1695	+4.2	**1**, 4.5	4630	6000	without
ZLI 1051	+0.1	**2**, 5.1	2400	8000	without
Licristal 4	−0.2	**2**, 8.5	3200	15000	hypsochrom 200
MBBA EBBA	−0.5	**1**, 1.75	1600	5000	hypsochrom 300
MBBA	−0.7	**1**, 1.58	1900	5200	hypsochrom 400

R-Cotton effect of the system ZLI 1083 doped with (+)-2-phenylpropanoic acid varies with the applied dc electric field.

The values for the threshold fields for the induced cholesteric mesophase of ZLI 1083 calculated using the Helfrich equation[4]

$$E_{th} = 2\pi \left(\frac{(2k_{22}k_{33})^{1/2} n \tilde{\nu}_R}{\varepsilon_0 \Delta\varepsilon d} \right)^{1/2}$$

are in good agreement with the experimental values.

Thus, using the changes of the R-Cotton effect in the IR-ORD spectra we were able to detect the dielectric instability which is a transitional state before reorientation of the helix.

When the electric field is decreased or switched off, the R-Cotton effect appears at the same wavenumber again, showing that the induced cholesteric mesophase has returned to a state identical to that before the transformation. The recovery speed is however inversely proportional to the time of application of the electric field.

The data in Table I for mesophases with positive dielectric anisotropy, as well as those from our previous investigation,[12] show that in most cases, the wavenumber of the R-Cotton effect is not affected by the strength of the electric field. However for the induced cholesteric phase of ZLI-1083, the disappearance of the R-Cotton effect is accompanied by a field-induced bathochromic shift of 200 cm^{-1}. The plot of this shift *vs.* applied field is given in Figure 2. We have not found any mention of this kind of red shift in the literature for cholesteric liquid crystals of positive dielectric anisotropy. Since the IR-ORD spectra taken with electric fields above

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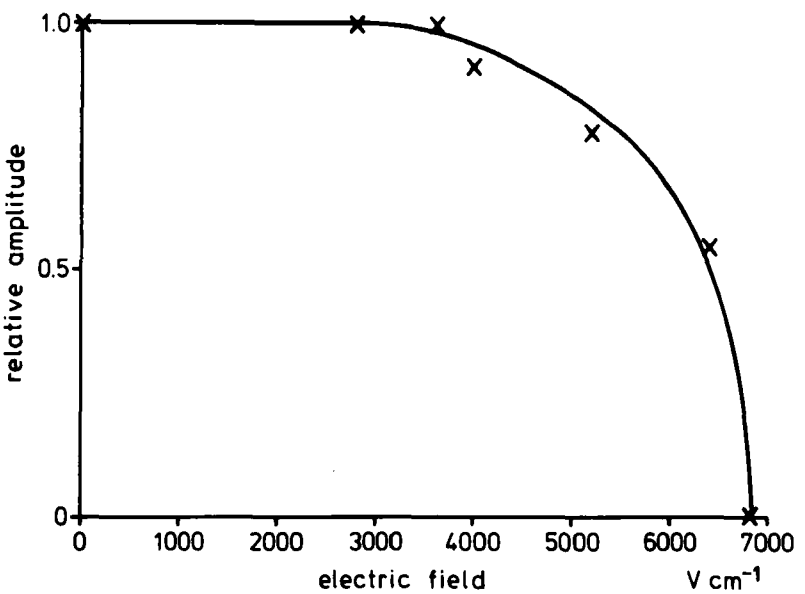

FIGURE 1 Relative amplitude (A_R) of the R-Cotton effect of the induced cholesteric mesophase ZLI 1083 (chiral guest compound (+)-2-phenylpropanoic acid) *vs.* applied electric field.

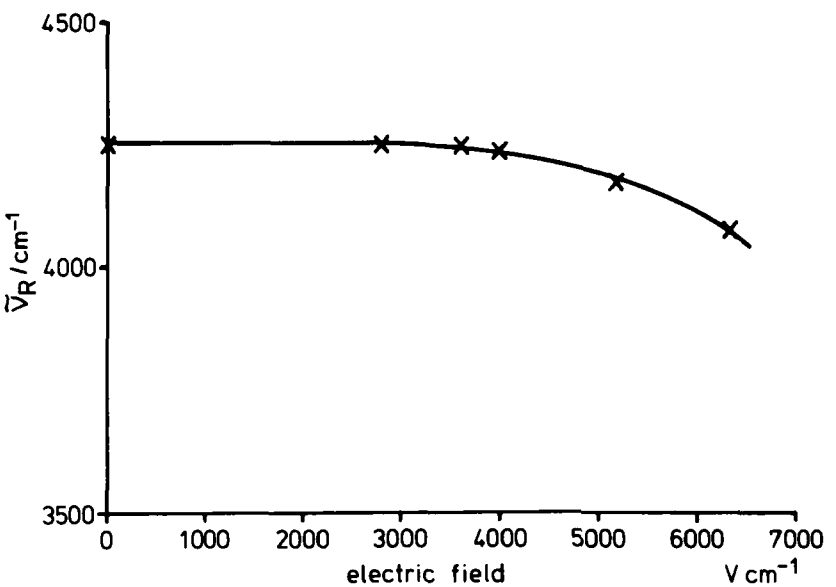

FIGURE 2 Change of the position of the R-Cotton effect of the induced cholesteric mesophase of ZLI 1083 (chiral guest compound (+)-2-phenylpropanoic acid) *vs.* applied electric field.

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the threshold value did not show a reduced transmission intensity, we exclude the possibility of dynamic scattering in this case.

Under the influence of a dc electric field parallel to the helical axis, the amplitude of the R-Cotton effect of the three cholesteric mesophases with negative dielectric anisotropy remains unchanged up to the threshold voltage. Above this voltage, two changes of the R-Cotton effect appear: the amplitude falls to zero and there is a hypsochromic shift. The data for the R-cotton effect position, the threshold fields and the observed hypsochromic shifts are given in Table I.

This hypsochromic effect is rather surprising, since one would expect that cholesteric liquid crystals with negative dielectric anisotropy would be in a so called 'stable state' for fields applied parallel to the helical axis.[14] An explanation of the observed phenomenon could be the conductivity of the samples.[15] Investigations are in progress on the same system under the influence of an ac electric field which should clarify this problem.

CONCLUSION

The influence of a dc electric field on induced cholesteric mesophases with both positive and negative dielectric anisotropy was studied by means of infrared rotatory dispersion. The observed R-cotton effect was found to vanish in both cases under the influence of the applied electric field because of texture changes. The full disappearance of the R-Cotton effect for mesophases with positive dielectric anisotropy occurs over a field interval of about 2.10^3 V cm^{-1}, whereas for those with negative dielectric anisotropy, the field interval is twice as large. The calculated and experimental threshold fields for the induced cholesteric mesophase of ZLI 1083 are in good agreement. Together with the disappearance of the R-Cotton effect, a bathochromic shift of 200 cm^{-1} was observed for this system.

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