Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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Version of record first published: 21 Mar 2007.

To cite this article: H. Baessler , P. A. G. Malya , W. R. Nes & M. M. Labes (1969): The Absence of Helical Inversion in Single Component Cholesteric Liquid Crystals, Molecular Crystals, 6:3-4, 329-338

To link to this article: http://dx.doi.org/10.1080/15421407008083470

Molecular Crystals and Liquid Crystals. 1970. Vol. 6, pp. 329–338

The Absence of Helical Inversion in Single Component Cholesteric Liquid Crystals‡

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Received July 11, 1969; *in revised form September*, 17, 1969

Abstract—Since a thermally induced helical inversion has been observed in cholesteryl 2-(2 ethoxyethoxy) ethyl carbonate (CEC), it has been the view that compensation of the helical structure of cholesteric liquid crystals does not require the presence of two compounds which separately form a right and a left handed helix. The present investigation demonstrates that the material used in the previous investigation was probably a compensated mixture because it contained an impurity in a rather high concentration. Pure CEC forms a right handed helix with a pitch of 6000 Å at room temperature, and with no indication of a thermally induced helical inversion. It is further shown that in general the sense of the helical screw is not necessarily identical with the sign of the optical rotation of the constituent molecules.

Introduction

In cholesteric liquid crystals formed from one component, the pitch of the helix can be varied thermally. The sense of the helical screw, however, which is often assumed to correspond to the sign of the optical rotation of the constituent molecules,[1] remains unchanged. The only system which has been reported to *not* behave in this manner is cholesteryl 2-(2 ethoxyethoxy)

‡ The support of the National Aeronautics and Space Administration under Grant No. NGR 39–004–015 and of the National Institutes of Health under Grant No. AM 12172 are gratefully acknowledged.

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ethyl carbonate (CEC), in which an inversion of sign was observed at approximately 30°.[2] Normally such a thermally induced inversion is only found in compensated mixtures of compounds separately forming a right and a left handed helix such as cholesteryl chloride-cholesteryl myristate in a 1.75 to 1 ratio where it occurs at approximately 42°.[3] The problem is of importance to an understanding of the cholesteric structure, and the possibility of impurity effects being responsible for the behavior of CEC had not been eliminated.

The possibility that impurities might play an important role in CEC was suggested by a paper by Durand and Lee[4] reporting that CEC contains crystalline leaflets which gradually melt above room temperature and which are responsible for second harmonic generation of light.[5] These authors, however, claimed that the leaflets were *not* impurities but ordinary crystallites of CEC. The present investigation shows that this is not the case: the crystallites consist in the main of an impurity which is also responsible for the observation of helical compensation.

Purification of CEC

CEC was obtained from the same source (Distillation Products Ind.) as that which Durand and Lee[2,4] had used. It was found by visual examination that it consists of a viscous liquid and a small amount of crystalline material. As a thin film, the well stirred mixture showed strong carbonyl absorption at 5.77μ and weak carbonyl absorption at 5.66μ. When submitted to thin layer chromatography (silica gel G, acetone in methylene chloride, 1/9, v/v, visualized with I_2 vapor), several components were observed with R_F values of 0.27, 0.51 and 0.81–0.89.

Another sample of CEC (200 mg) was chromatographed on a column of (20 g) silica gel G deactivated with 3% water (w/v). Fractions of 50 ml each were collected using n-hexane-benzene, 8/2 (fractions 1–4), n-hexane-benzene, 1/1 (fractions 5–9), benzene (fractions 10–14), benzene-ether, 3/1 (fractions 15–19), benzene-ether, 1/1 (fractions 20–24), and ether (fractions 25–29). Fractions

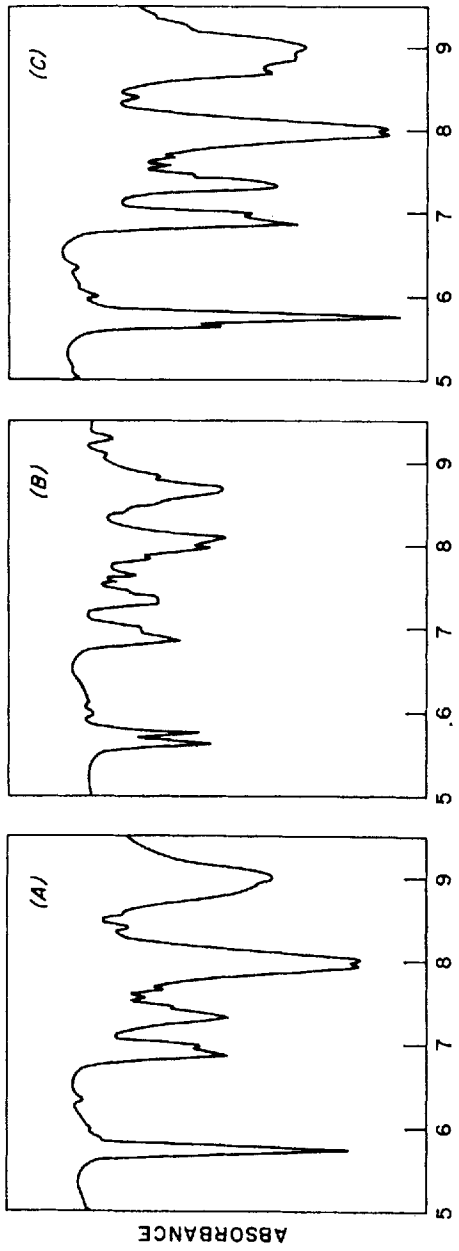

Figure 1. Infrared Spectra of CEC Samples in the Carbonyl and C-O Vibration Region. (A) Pure CEC; (B) Major Impurity; (C) Commercial CEC.

2–4 yielded a colorless crystalline material; fractions 11–14 contained a substance with the same R_F as cholesterol; and fraction 15 contained the oily ester (142 mg). Repetition of the chromatography with an additional 400 mg of crude ester yielded an additional 285 mg of pure ester. The R_F of the pure ester was 0.57, and as a thin film on sodium chloride it showed a single peak for carbonyl absorption at 5.75μ (Fig. 1A).

The major impurity was collected as fractions 2–4 (45 mg from 200 mg CEC), and melted at 152–161°, with softening at 99°. Its infrared spectrum showed two carbonyl peaks at 5.66 and 5.77μ (Fig. 1B). It (2.0 mg) was not soluble in 50 ml boiling ethanol. It was, however, soluble in cyclohexane, and in this solvent exhibited no absorption in the UV. These data exclude the possibility of hydrocarbon impurities which could arise during preparation of the ester, viz., Δ^6-3,5-cyclocholestene, $\Delta^{3,5}$-cholestadiene, and $\Delta^{4,6}$-cholestadiene. A possible structure is dicholesteryl carbonate, m.p.[6] 176°, clears at 248°, but insufficient data are available in the literature to make an exact comparison.[7] This impurity is clearly present in commercial CEC as evidenced by the infrared spectra (Fig. 1C). Its concentration is so high that it precipitates at room temperature and forms crystallites floating in the bulk material mainly consisting of CEC. Upon heating, the solubility in CEC increases. This accounts for the slow melting process of the crystalline leaflets which extends over a temperature range of nearly 100° depending on the heating rate. These observations disprove Durand and Lee's[4] assignment that the leaflets are ordinary crystallites of CEC.

Experimental Measurements

The optical rotatory power (OR) was used as a probe for the determination of the sense of the cholesteric helical structure. It was measured polarimetrically at a wavelength of 5893 Å as previously described.[8] The sample was sandwiched between quartz discs held apart by a 10μ mylar spacer. In order to determine the dispersion curve of OR, the rotation angle was measured

with a polarizing microscope, using interference filters to select certain wavelength bands in the range 4000 to 7000 Å. The texture of the cholesteric phases and the transition temperatures were checked microscopically.

Results and Discussions

Pure CEC has a reversible cholesteric-isotropic transition temperature $T_{is\rightarrow chol} = 31.0 \pm 0.5°$. Upon slowly cooling, solidification occurs at 15°. However, if the sample is allowed to stand at room temperature for a few days $T_{chol\rightarrow s} = 24.5°$. The solid-cholesteric transition temperature is $T_{s\rightarrow chol} = 24.5°$. The values are in disagreement with Durand's data.[2] The isotropic and cholesteric phases are homogeneous with no evidence for partial crystallization. The cholesteric phase shows positive optical rotation (Fig. 2, curve 1) and the data are well reproducible on heating and cooling. For $T > T_{is\rightarrow chol}$ and $T < T_{chol\rightarrow s}$ the OR vanishes abruptly. Clearly no change in sign of the OR occurs which could indicate a change in the sense of the helix.

The correlation between the sense of the helical screw and the sign of the resulting OR is given by de Vries' formula:[9]

$$r = 360/8Z \cdot \alpha^2/\lambda'^2(1-\lambda'^2) \tag{1}$$

r is the specific rotation in deg cm^{-1}. Z is the pitch of the helix, $\alpha = \Delta n/\bar{n}$ is the relative birefringence of the layers constituting the cholesteric structure, $\bar{n}$ is the mean refractive index and $\lambda' = \lambda/\bar{n}Z$ where λ is the wavelength of the analyzing light. $\bar{n}Z$ is the wavelength of maximum reflection. The definition of the sign is such that a right handed helix, defined by $Z > 0$ rotates the plane of plane polarized light moving towards an observer clockwise ($r > 0$). Two limiting cases have to be considered:

$$r = 360Z/8\lambda^2 \cdot \alpha^2\bar{n}^2 \quad \text{for} \quad \lambda \ll \bar{n}Z \tag{2}$$

and

$$r = -360/8\lambda^4 \cdot Z^3\bar{n}^4\alpha^2 \quad \text{for} \quad \lambda \gg \bar{n}Z \tag{3}$$

In order to determine the sign of Z from the sign of r, it is therefore

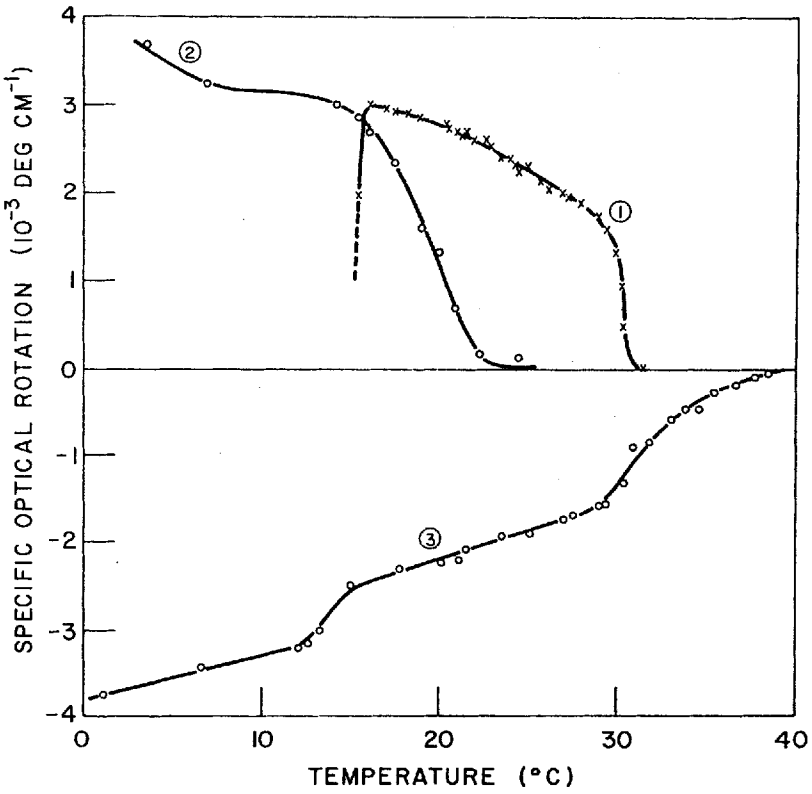

Figure 2. Specific Optical Rotation as a Function of Temperature of CEC Samples. Curve 1, Pure CEC; Curve 2, Commercial CEC from which crystallite impurity has sedimented; Curve 3, well-stirred commercial CEC.

necessary to know whether one is on the short or long wavelength side of the reflection band. For that purpose the dispersion curve of OR in pure CEC displaying the plane texture was measured (see Table 1). The experimental data can be fitted to Eq. 1 if one makes the following choice for the parameter values:

$$\lambda_0 = \bar{n}Z = 9000\,\text{Å} \quad \text{and} \quad \alpha = 3.07 \times 10^{-2}.$$

The value for λ_0 was confirmed by a measurement of the distance of neighboring Grandjean lines in a wedge-type

TABLE 1 Experimental and Calculated Value for the Rotation Angle of a 25.4μ CEC Sample at Room Temperature.

$\lambda_{[\text{Å}]}$	ϕ_{exp} (deg) error $\pm 0.5°$	ϕ_{calc} (deg)
4000	12.0	11.5
4330	10.0	10.3
4660	9.0	9.1
5000	8.0	8.4
5330	7.5	7.9
5660	7.5	7.5
6000	7.0	7.1
6330	7.0	7.2
6660	7.5	7.3
7000	7.5	7.4

sample[10,11] which provides a direct determination of the pitch. The result was $Z = 6000 \pm 300$ Å at room temperature yielding $\lambda_0 = 9000 \pm 500$ Å by using the experimental value $\bar{n} = 1.503$ for the mean refractive index. These results show that pure CEC forms a right handed cholesteric structure which does not undergo helical inversion.

In order to probe the influence of impurities on the results obtained with commercial CEC, two samples of unpurified CEC were examined. Both were taken from material stored in a bottle which had been allowed to stand for 4 months. Because the specific weight of the crystallites present in commercial CEC is slightly higher than that of the bulk material, they are subject to sedimentation. A sample (referred to as No. 2) prepared from material from the top of the bottle therefore contained only very few crystalline leaflets. Its behavior was similar to that of pure CEC. The optical rotation of the cholesteric phase is positive (Fig. 2, curve 2), the helix right handed. The transition temperatures, however, are shifted to lower values ($T_{is \rightarrow chol} = 22.5°$) indicating the presence of some impurities.

A completely different behavior is observed with a sample (No. 3) prepared from the thoroughly stirred contents of the

bottle. At room temperature roughly half of the sample consists of crystallites randomly distributed in the isotropic bulk material showing practically no OR. After melting the crystallites at higher temperatures and recooling, a homogeneous phase is formed which becomes cholesteric at $T_{is \rightarrow c} = 37.5°$ and can be supercooled to $-60°$ without solidification (observation time 2 hours). The optical rotation measured at the short wavelength side of the reflection band is negative indicating a left-handed cholesteric structure. The pitch must be of the order of 1μ. This suggests that dicholesteryl carbonate (DC), which is the most likely crystallite impurity, tends to form a left-handed and tightly wound cholesteric structure.[12] Mixing two compounds one of which is capable of forming a right-handed and the other a left-handed structure can produce helical compensation as has been shown by a number of investigations.[3,8,13] If, for example, the relative concentration of the "right handed" species has a critical value C_{ro}, the resulting structure is nematic. For $C_r > C_{ro}$ a right-handed and for $C_r < C_{ro}$ a left-handed cholesteric phase is formed. In the " well stirred " sample of CEC obviously the concentration of CEC was below its critical value, so that DC dominated helix formation. Upon lowering the DC-concentration, one must pass through a mixing ratio at which the nematic phase exists at a temperature which is within the mesomorphic range. Durand[2] must have observed this phenomena.

It therefore appears that no single component material is known which displays a thermally induced helical inversion, and that impurities can play an important role in the properties of liquid crystalline systems.

Correlation Between Molecular Optical Activity and Helical Sense

Dissolution of an optically active cholesteryl ester in the nematic phase of *p*-azoxyanisole or *p*-azoxyphenetole[14] leads to the formation of a cholesteric mesophase with a pitch inversely proportional to the solute concentration. This result, and the fact that all cholesteric mesophases which are known so far are

composed of optically active compounds, led to the conclusion that optical activity is a necessary condition for the twisted cholesteric structure becoming energetically stable. In addition, there is some support for the assumption that the sense of the helical screw is identical with the sign of the optical rotatory power of the constituting molecules: (1) a racemic mixture of *p,p'*-diactive amyloxyazoxybenzene mixed with *p,p'*-di-*n*-hexyloxyazoxybenzene does not form a cholesteric phase but the optically active compound does;[15] (2) dextro-rotatory amyl *p*-(4-cyanobenzylideneamino)cinnamate forms a right handed helix, laevo-rotatory cholesteryl benzoate a left-handed helix and a mixture of both gives a compensated structure at an appropriate mixing ratio.[13] The present investigations, however, show that the sense of the helical screw and of the specific optical rotation do not always agree (see Table 2). Both pure CEC and cholesteryl

TABLE 2 Comparison Between Specific Optical Rotation (Measured in Chloroform Solution at Room Temperature) and Sense of the Helix

Compound	Specific optical rotation α_D	Helix sense
cholesteryl 2-(2 ethoxyethoxy) ethyl carbonate (CEC)	−22.0	right-handed
dicholesteryl carbonate (DC)	<0	left-handed[12]
cholesteryl chloride (C)	−30.8[14]	right-handed[13]
cholesteryl myristate (M)	−26.5	left-handed[13]
C:M = 1.75:1.00	−28.8	compensated at $T = 42°$

chloride are laevo-rotatory on a molecular basis but form a right handed helix. Both compounds can be mixed with a laevo-rotatory compound, which alone produces a left handed helix, to form a compensated structure. In particular, a 1.75:1.00 weight mixture of cholesteryl chloride and cholesteryl myristate is not racemic. It gives rise, however, to a compensated helical structure. With molecules containing more than one asymmetric carbon

site, the relationship between molecular optical activity and the helical sense which they can establish either as a pure mesophase or as solutes in a nematic phase is therefore rather complex. Further investigations of the nature of this relationship are in progress.

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