Optical activity of the planar texture of a number of cholesterol esters

A. S. Sonin, A. V. Tolmachev, V. G. Tishchenko, and V. G. Rak

Khar'kov State University

(Submitted December 14, 1974)
Zh. Eksp. Teor. Fiz. **68**, 1951–1959 (May 1975)

The temperature dependence of the optical-rotation dispersion of the planar texture of six cholesterol esters (valerate, pelargonate, caprynate, laurate, myristate and palmitate) is investigated. The measurements are carried out throughout the complete cholesteric mesophase, near phase transitions to an isotropic liquid and fusion and for a transition from the smectic to cholesteric state. The results are discussed in accordance with the phenomenological theory of optical properties and structure of liquid crystals. The temperature dependence of the optical anisotropy parameter for a plane texture is derived on basis of the experimental data. The peculiarities of the behavior of the optical characteristics thus obtained are ascribed to ordering of molecules in a layer of mesomorphic matter.

PACS numbers: 81.55.

1. INTRODUCTION

The optical activity (natural rotation of the polarization plane of linearly polarized light) of cholesteric liquid crystals, together with selective scattering and circular dichroism, is one of the methods of spectral investigation of the structure and properties of this class of organic compounds. As a rule, pure cholesterine esters, to which this paper is devoted, form two types of structure, confocal and planar.[1] The transition to the planar texture is realized during the course of predominant orientation of the twist axes of the local ordered regions in the volume of the sample, relative to a certain solid angle whose axis is normal to the surface of the layer. At fixed external conditions, the planar texture is stable enough and has optical properties analogous to those of a uniaxial optically-negative crystal. The temperature dependence of the optical properties of cholesteric liquid crystals yields valuable information on the dynamics of the variation of the macroscopic parameters of the texture, namely the pitch of the helix, the components of the dielectric tensor, and the optical-anisotropy parameter.

The optical activity of cholesteric liquid crystals was investigated by various methods: by the method of classical polarimetry using the rotation angle of the analyzer,[2-6] by the prism method, which makes it possible to separate and measure the refractive indices of right- and left-circularly polarized light,[7,8] and by the method of polarization microscopy.[9] Most published papers are devoted to the study of compositions, i.e., mixtures of cholesteric or cholesteric and nematic liquid crystals, which form in comparison with pure esters a more stable and homogeneous planar texture. However, the physical interpretation of these results is very complicated, since the mechanism of the intermolecular interaction in a multicomponent system is not clear. On the other hand, the experimental data on the optical activity of pure cholesterine in wide spectral and temperature intervals, with the exception of an earlier work by Mathieu[2], are extremely scanty. Therefore an investigation of questions of this kind seems most timely to us.

2. EXPERIMENTAL PROCEDURE AND RESULTS

We have investigated the temperature dependence of the dispersion of the optical rotation of cholesterine esters of moncarbonic acids of the fatty series–valerate, pelargonate, caprynate, laurate, myristate, and palmitate. The criterion for the choice of the substance was its ability to wet the cover glasses, a particularly important factor at the chosen sample thickness ~10 μ. We have established experimentally that the high-temperature homologs of the series, the mesophase existence region of which lies above 100°C (e.g., butyrate), wet the glasses much less effectively and form thin layers with thin air bubbles.

To obtain a planar texture, the substances were melted between fused-quartz substrates. The sample thickness was fixed by a liner of aluminum foil and was monitored prior to the start of the measurements by an interference method. The sample was placed in a thermostatically controlled cell and installed in the cuvette section of the SPU-M spectropolarimeter. The cell

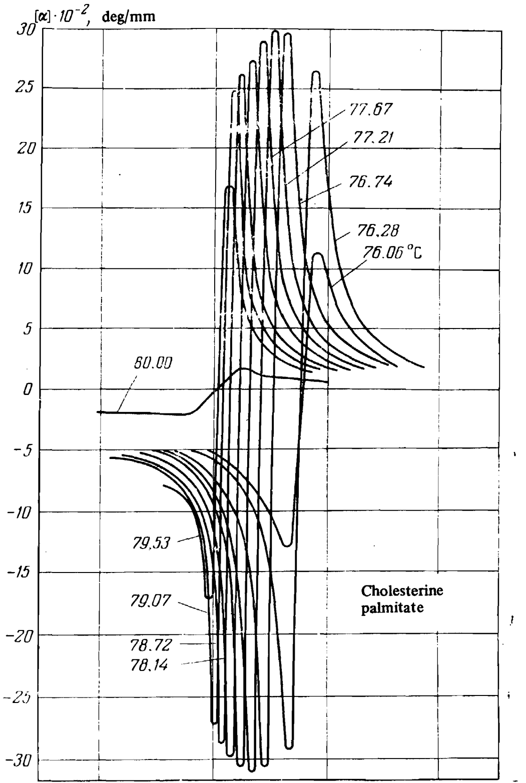

FIG. 1. Dispersion of the optical activity of palmitate.

temperature was thermostatically maintained in the interval 60–120°C within ±0.05°C. The sample temperature was measured with a differential copper-constantan thermocouple accurate to ±0.01°C. The error in the measurement of the rotation of the plane of polarization of linearly polarized light passing through a layer of the liquid crystal, using the SPU-M instrument, did not exceed ±0.025°.

The measurement procedure consisted in the following. The cell temperature was set approximately at the midpoint of the interval of the cholesteric mesophase and maintained for some time. Then, by varying the temperature in succession in steps of 0.3–0.4°C, the samples were thermostatically controlled for the measurement of the dispersion of the optical rotation. The temperature was first decreased to the lower limit T_0 of the cholesteric mesophase, and was then increased to the initial values, step by step, to the bleaching point T_c of the transformation into an isotropic liquid. The temperature interval near T_c was investigated only at rising temperature, for when the isotropic melt was cooled below T_c a homotropic state was produced and changed, following a shift of the glases, into a planar structure but with a mesophase region that differed somewhat in temperature. For each substance the optical activity measurement was repeated in the entire temperature interval not less than five times with new prepared samples. The described procedure made it possible to obtain sufficiently good reproducibility of the experimental data, namely, not worse than 5% in the ''peak–valley'' region of the optical-rotation anomalous dispersion curve, and ~0.1% in the region of normal dispersion.

Figures 1 and 2 show typical families of the specific-rotation curves $[\alpha]$ for two homologs, palmitate and valerate. The curves were plotted by points over the wavelength in steps of 2 nm. In Fig. 3, the quantity a (in relative units) is the normalized amplitude of the optical-activity curve, a/a_{max}, where $a = [\alpha]_{peak} - [\alpha]_{valley}$. The values of the maximum amplitude are indicated for all six substances. The wavelength λ_0 corresponds to the inversion point of the anomalous specific-rotation curve. For all the investigated substances, the temperature dependence of $[\alpha]$ has a common tendency–with increasing temperature the amplitude a of the optical activity reaches a certain maximum value, and then decreases (Fig. 3a).

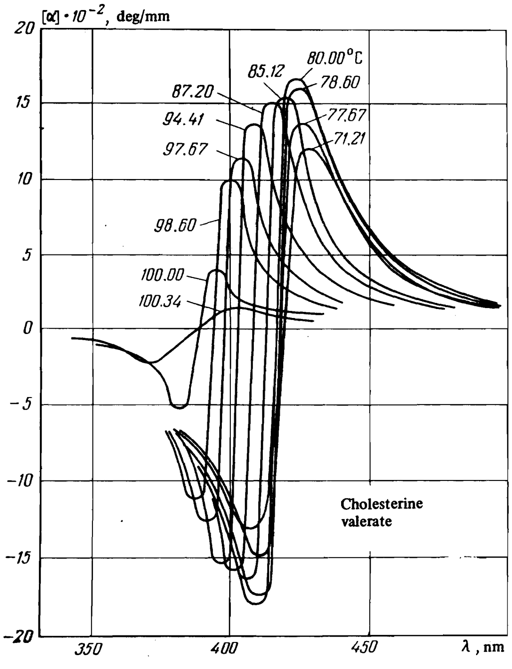

FIG. 2. Dispersion of the optical activity of valerate.

3. DISCUSSION OF EXPERIMENTAL DATA

We can extract from the experimental data the values of the dielectric anisotropy δ and the helix pitch P, which enter in the general theory of the properties of cholesteric crystals.[11,12]

To this end it is convenient to use the formulas obtained earlier in[13], even though these formulas pertained to an ideally-ordered layer of a cholesteric liquid crystal. In fact, the planar structure of a pure cholesterine ester is polycrystalline, in which no clear-cut stratification over the thickness is observed. Using in the analysis of the experimental results the information on the idealized model, we are considering by the same token the structure and the properties of an abstract single-domain sample with averaged characteristics of a planar structure. Since our problem concerns the connection between the molecular structure of a liquid-crystal layer and its optical properties, rather than the exact measurement of the macroscopic texture parameters, this approximation is perfectly permissible. All our subsequent reasoning will be based on the assumption that the temperature governs the ordering of the moelcules in the cholesteric mesophase, and a measure of this ordering is provided by the singularities of the observed optical characteristic.

The anisotropy parameter δ was calculated with a computer from the experimental values of the optical activity at concrete P and λ for each value of the temperature. When determining the anisotropy parameter by the method of fitting the $[\alpha]$ curve to four points, the discrepancy in its value did not exceed 15%. Valerate and palmitate (see Fig. 4) are different in that for the former, in the entire region of the cholesteric mesophase, the amplitude $[\alpha]$ varies smoothly at an almost constant pitch, whereas for the latter these quantities change quite strongly. The variation of the pitch with temperature follows from data on the change of the length of the inversion wave λ_0, Fig. 3b. The quantities λ_0 and P are connected by the relation $\lambda_0 = P\bar{\epsilon}^{-1/2}$, where $\bar{\epsilon}$ is the average dielectric constant of the liquid crystal. Taking into account its weak dispersion and temperature dependences, we can assume its average value to be 2.25.

It is expedient to consider two temperature regions: 1) from the temperature T_0 of the lower limit of the cholesteric mesophase to the point corresponding to the maximum amplitude $[\alpha]$, and 2) from the temperature a_{max} to T_c.

1) In this temperature interval, the changes in the properties and structure of a layer of cholestric liquid crystal can be treated on the basis of the general laws of pre-crystallization processes in ordered alloys, which are connected with the formation, in the melt, of a solid crystal with the cooling of the molecular aggregates (clusters) whose local structure differs both from

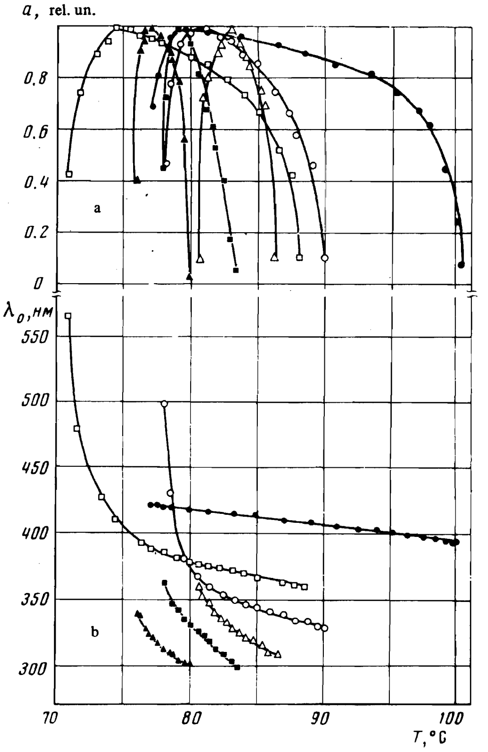

FIG. 3. Temperature dependence of the amplitude [α] in relative units (a) and of the wavelength of the inversion point of the curve [α] (b) for valerate (●), a_{max} = 3468°; palmitate (▲), a_{max} = 6089°; laurate (△), a_{max} = 5438°; myristate (■), a_{max} = 4815°; caprynate (○), a_{max} = 3882°; pelargonate (□), a_{max} = 2623°.

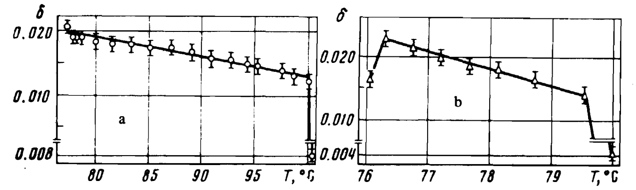

FIG. 4. Variation of the anisotropy parameter of the planar structure of valerate (a) and palmitate (b) in the region of the cholesteric-mesopase temperatures.

that of the solid crystal and from the medium in which formation of the clusters begins.[14] We have in mind here the so-called noncrystallizing clusters, the thermodynamic stability of which in a certain temperature interval near T_0 is sufficient to prevent spontaneous crystallization. In those cases when the long-chain molecules are rigid,$^{1)}$ such effects can become clearly pronounced in the pre-crystallization period several degrees before the crystallization point, in the form of denser packing of the molecules.

Starting with the ideas of Keating[15] and Böttcher[16] that the nonlinearity of the vibrations of the asymmetric molecules of cholesteric liquid crystals are the cause of their helical ordering, it can be assumed that the compacting of the molecules can lead to a decrease in the forces of the short-range intermolecular interaction, i.e., in final analysis to an increase in the pitch in terms of the scale of the entire sample, with an accompanying decrease of the degree of helical orientation. In addition, cluster formation with decreasing temperature should contribute to an increase of adsorption on the part of the cover glasses, and the thickness of the coundary regions, whose molecules are most susceptible to such an influence, increases. On the other hand, the dimensions of the volume in which the molecules still retain the ordering peculiar to the mesophase and which, strictly speaking, indeed exhibits the observed dispersion of the optical rotation, becomes smaller. Thus, the change of the amplitude [α] as the temperature is lowered to T_0 may be due to the increase of the pitch and to the decrease of the effective length of the optically-active layer. Similar arguments hold also for cholestric liquid crystals having a smectic phase (a noticeable decrease of the anisotropy parameter for palmitate, see Fig. 4). In this case the appearance of ("denser" molecule groupings can be regarded as a "clustering" process on going to a more ordered (smectic) phase with larger viscosity and with less freedom of molecule motion.

2) With increasing temperature, the amplitude [α] and the texture anisotropy parameter begin to decrease. As the temperature rises, the shorter molecule axes, which previously had only one degree of freedom and were capable of executing rotational motion about the long axis, become unbound. At temperatures close to T_c, the predominant direction of the orientation in the texture, can in practice no longer be separated against the background of the predominant random thermal vibrations. In the region of the phase transition into an isotropic liquid, the texture, as a form of ordering of the molecules, becomes completely disorganized. The optical activity decreases sharply, and a jumplike decrease takes place in the anisotropy parameter (Fig. 4). Above the temperature point T_c, the liquid-crystal layer becomes optically isotropic. The optical rotation is due to the intrinsic optical activity of the molecules, the dispersion of [α] is a smooth positive curve and does not exceed in magnitude several degrees per millimeter.

The results of our optical measurements agree with the results of thermodynamic investigations of cholesteric liquid crystals with respect to the parameters characterizing the kinetics of the formation of the cholesteric mesophase near the phase transitions between the solid and liquid crystals and between the liquid crystal and an isotropic liquid, namely, the surface energy σ of the phase separation boundary[17] and the specific volume V_0.[18] According to the data of these references, the interphase energy on the boundaries between the solid and liquid-crystal phases agrees in magnitude with the analogous parameters of many organic solutions (betol, antipyrene), and amounts, e.g., for caprynate, to 14.13 erg/cm^2. Therefore the values of σ in the phase transition from the smectic or cholesteric state to the solid-crystal state should be of approximately the same order of magnitude. The fact that the ratio of the interphase energy to the surface energy of the solid phase of liquid crystals is quite high, on the order of several tenths,[17] leads to the conclusion that a gradual transition takes place into the solid-crystal state, lasting up to several dozen minutes. Naturally, some inertia in the orientation processes in the melt should appear also near T_0. In our case this is manifest for example for a compound having only a cholesteric phase (valerate), in a smooth decrease of the amplitude [α] with temperature, Fig. 3a. Also typical is the behavior of the anisotropy parameter and of the pitch, which is proportional to $\lambda_0(T)$, of a planar structure of monotropic valerate, which undergo no abrupt changes near T_0 (see Figs. 4 and 3b).

No. of homolog, N	Name	K, rel. un.	No. of homolog, N	Name	K, rel. un.
5	Valerate	3.7	12	Laurate	~57.3
9	Pelargonate	40.9	14	Myristate	~57.3
10	Caprynate	52.1	16	Palmitate	~57.3

The strongest change occurs in the optical characteristics of palmitate, myristate, and laurate near the transition from the cholesteric to the smectic phase. Thus, for palmitate in the interval 76.0–76.3°C and myristate in the interval 78.2–78.6°C the specific rotation is decreased by more than a factor of 2.5, and for laurate in the range 80.7–80.9°C it decreases by a factor of almost 8. The coefficient K, which is proportional to the slope of the plot of a(T) against temperature and characterizes the rate of decrease of the amplitude of the specific rotation with temperature near T_0, is exceedingly large in the transition between the liquid-crystal modifications, including valerate, and gradually decreases with decreasing number $N = n + 1$ of the homolog, where n is the number of carbon atoms in the alkyl chain of the ester (see the table). Sharply pronounced changes of the optical properties of cholesteric liquid crystal on the "cholesteric–smectic" transition boundary are due entirely to the transformation of the texture within the limits of one liquid-crystal phase state. This is evidenced, in particular, by the smooth character of the temperature dependence of the specific volume in the entire region of the mesophase of caprynate.[18] For caprynate and pelargonate, as the temperature decreases to T_0, in spite of the presence of a smectic state, we observed no jumplike decrease of the amplitude $[\alpha]$, although the slope of the $\alpha(T)$ curve for these homologs is quite appreciable. Obviously, in the vicinity of T_0 the mechanism of the intermolecular interaction is determined in this case to a greater degree by the forces present in the cholesteric phase, which is much more strongly pronounced than in the first three compounds.

Measurements of the specific volume near the bleaching temperature T_C offers evidence of a negligible change of V_0 on going from the isotropic-liquid to the liquid-crystal state. For caprynate and pelargonate, this change amounts to 5×10^{-6} and 7×10^{-6} m^3/kg, respectively.[18] In this case we can expect small values of the heat of transition and of the interphase energy, i.e., the disordering of the liquid-crystal phase at the transition point should take place instantaneously, as is indeed confirmed by the jumplike decrease of δ, Fig. 4.

Thus, a careful measurement of the optical properties of cholesteric liquid crystals makes it possible to describe the mechanism whereby the molecules of the substance become ordered near the phase transitions, in the mesophase itself, and in transition within the mesophase from one liquid-crystal modification to another.

It should be noted in conclusion that our interpretation of the observed phenomena is not exhaustive. The discussion will be more fruitful when more experimental results are available on the structure of cholesteric liquid crystals in thin layers, primarily near the crystallization point, and on the temperatures of the intermediate transitions within the mesomorphic state.

---

[1] The case of cholesteric liquid crystals.

---

[1] G. W. Gray, Molecular structure and the properties of liquid crystals, Academic Press, N. Y. (1962).
[2] J. P. Mathieu, Bull. Soc. franc. Minér. Crist., 61, 174 (1938).
[3] V. N. Aleksandrov and I. G. Chistyakov, Kristallografiya **14**, 520 (1969) [Sov. Phys.-Crystallogr. **14**, 431 (1969)].
[4] S. Chandrasekhar and J. S. Prasad, Mol. Cryst. Liq. Cryst., **14**, 115 (1971).
[5] J. Teucher, K. Ko, and M. M. Labes, J. Chem. Phys. **56**, 7, 3308 (1972).
[6] J. S. Prasad and M. S. Madhava, Mol. Cryst. Liq. Cryst. **22**, 165 (1973).
[7] P. Chatelain and J. C. Martin, C. R. Acad. Sci. **C268**, 758 (1969).
[8] J. C. Martin and R. Cano, C. R. Acad. Sci. **B278**, 219 (1974).
[9] M. Brunet-Germain, Acta Cryst. **A26**, 595 (1970).
[10] G. M. Gray, J. Chem. Soc. **10**, 3733 (1956).
[11] H. de Vries, Acta Cryst. **4**, 219 (1951).
[12] E. I. Kats, Zh. Eksp. Teor. Fiz. **59**, 1864 (1970) [Sov. Phys.-JETP **32**, 1004 (1971)].
[13] A. S. Sonin, V. G. Rak, A. V. Tolmachev, and V. M. Kuz'michev, Tezisy dokl. III Vsesoyuznoĭ konferentsii po zhidkim kristallam (Abstr. of Papers, 3rd All-Union Conf. on Liquid Crystals), Ivanovo, 1974.
[14] A. R. Ubbelohde, Melting and Crystal Structure, Oxford, 1965.
[15] P. N. Keating, Mol. Cryst. Liq. Cryst. **8**, 315 (1969).
[16] B. Böttcher, Chem. Ztg. **96**, 214 (1972).
[17] F. K. Gorskii and N. M. Sakevich, Kristallografiya **12**, 674 (1967) [Sov. Phys.-Crystallogr. **12**, (1968)].
[18] N. M. Sakevich, Zh. Fiz. Khim. **42**, 2930 (1968).

Translated by J. G. Adashko
209