Investigation of ordering of the mesophase of cholesteric liquid crystals on basis of their optical parameters

Yu. V. Denisov, V. A. Kizel', and E. P. Sukhenko

Moscow Physico-Technical Institute

(Submitted January 30, 1976)
Zh. Eksp. Teor. Fiz. **71**, 679–690 (August 1976)

The dispersion of optical rotation, circular dichroism, intensity, and half-width of the selective reflection band of a number of cholesteric liquid crystals are measured as functions of layer thickness in the electronic absorption range as well as in the selective reflection range. These quantities are shown to depend on the thickness in a complex manner and some conclusions regarding the nature of ordering of the mesophase are drawn on this basis. The results are compared with the theory. The layer structures near the wall and in the bulk of the sample are considered. Some assumptions are made concerning the mechanism and degree of orientation and the causes of appearance of strong gyrotropy. The measurements are performed with a number of cholesterine derivatives in the mesophase and in the vitrified mesophase. It is pointed out that the electronic absorption region, which hitherto has not been studied in detail, appears to be of special interest.

PACS numbers: 61.30.+w, 78.20.Nw

The main distinguishing optical properties of cholesteric liquid crystals (CLC) are the onset of Bragg maxima of the selective reflection (SR) far from the absorption bands, and the strong rotation of the plane of polarization of the light. The latter exceeds the rotation in the isotropic phase (which is usual for organic compounds) by 3–4 orders of magnitude, both in the reflection region and in the absorption region. All these phenomena are most clearly observed in the presence of a definite type of order and, as shown by the theory, depends on the thickness of the object. The indicated ordering is inherent in the mesophase of CLC, but to establish it fully it is necessary to have some external action. Obviously, the determination of the character of this ordering and of the actually existing structure should precede the investigation of any property of the mesophase.

In the ordinary investigation methods, using thin cells and the simplest setup, use is made of the orienting influence of the walls; there are also more complicated procedures. Without considering for the time being the molecule-orientation mechanisms, we note only that in this case one should expect the presence of layers near the boundary, which are subject to the direct influence of the walls and have special properties; the thicknesses of these layers should be of the order of the effective radius of the wall forces. At larger cell thicknesses there appear regions where the influence of the walls, both direct and via intermediate particles, already vanishes and the structure should become somewhat disordered. Since the investigations are carried out usually in cells on the order of 20–40 μ and thinner, in addition to the indicated phenomenon there should be observed all those macroscopic phenomena which appear when light passes through a thin layer adjacent to a dielectric wall. The simplest analysis, assuming homogeneity of the layer, is given in the papers of Tolmachev and Sonin[1] and Tur,[2] but the real picture, of course, is more complicated.

It follows from all the foregoing that the dependence of all the optical parameters of the CLC on the thickness of the layers should be complicated, and that an investigation of this dependence can yield very valuable information on the details of the ordering of the CLC mesophase. For reasons presented below, it appears that most information can be obtained in the little-studied region of electronic absorption. In this paper we investigate the dependence of the optical parameters on the thickness for certain CLC in the planar texture of the mesophase, which is most convenient and interesting for study.

EXPERIMENTAL TECHNIQUE

General information on the structure and properties of the investigated substances and on the details of the experimental procedures were given in our earlier papers.[3,4] The substances were purified by recrystallization from methanol, although for the described investigations the degree of individuality of the substances is of no importance. The substances were investigated in thermostatically controlled (±0.01°) quartz cells with gaps, the thicknesses of which were strictly fixed and were measured by interference methods, with multiple conditioning by melting in the liquid phase and subsequent cooling. The presence of a planar texture of the working area and the absence of birefringence were monitored beforehand also *in situ* by a polarization microscope; the best of several samples was chosen, and the measurements were performed on several such samples.

The measurements of the dispersion of the optical rotation (DOR) were made on polarimeters for the ultraviolet, visible, and infrared regions,[5] the circular dichroism (CD) was measured with a Russel–Juan SD-185 dichrograph and by a procedure described earlier,[3,4] the transmission was measured with a Hitachi EPS-3 spectrophotometer and an SF-8 spectrophotometer, while the reflection was measured with the reflexometer of our Institute. We used MDI-3 and DFS-12 monochromators.

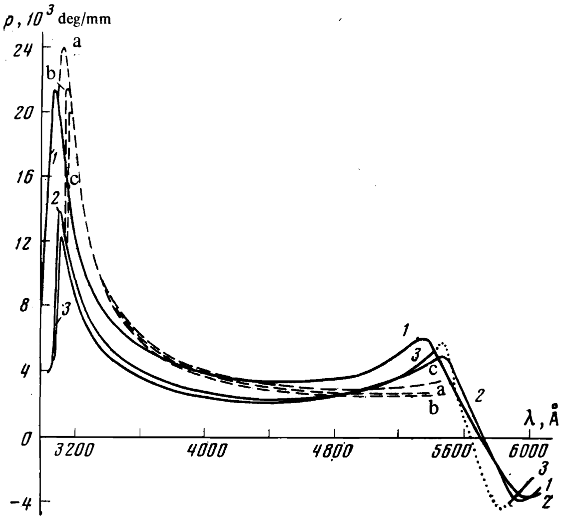

FIG. 1. Dependence of the dispersion of the optical rotation ρ(λ) (per mm of path) on the thickness of the liquid-crystal layer for cholesteryl cinnamate at $T = 157.5\,^{\circ}\mathrm{C}$—solid lines (1—thickness 1.2 μ, 2—3.1 μ, 3—4.8 μ); for cholesteryl-n-chlorcinnamate at $T = 171.5\,^{\circ}\mathrm{C}$—dashed lines (a—1.2 μ, b—3.1 μ, c—4.8 μ).

RESULTS AND DISCUSSIONS

Figures 1 and 2 show the general picture of the phenomena, which is needed for the analysis of the subsequent data. The electron-absorption bands of the investigated substances lie in the regions indicated in Table I. Absorption in the region of the electron bands is so large (Fig. 2) that it is possible to obtain only the edge of the band.1) Figure 3 shows its structure with the aid of the CD curves. Since the absorption, as for all molecular crystals, changes little on going to the isotropic phase or to the solution, the structure of the bands can be assessed also from Fig. 4.

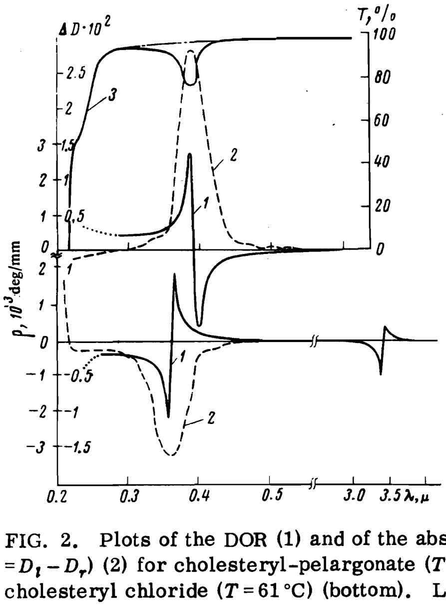

FIG. 2. Plots of the DOR (1) and of the absolute CD($\Delta D = D_l - D_r$) (2) for cholesteryl-pelargonate ($T = 80\,^{\circ}\mathrm{C}$) (top) and for cholesteryl chloride ($T = 61\,^{\circ}\mathrm{C}$) (bottom). Layer thickness 1.2 μ. Curve 3—transmission of pelargonate under the same conditions.

TABLE I.

Substance	Long-wave edge of electron absorption band in the mesophase, A	Pitch of helix, p, A
Cholesteryl-cinnamate	3050	3100–4000
Cholesteryl-4-chlorcinnamate	3200	3700–4500
Cholesteryl pelargonate	2150	2400–3200
Cholesteryl chloride	2180	2400–2800
Cholesteryl-4-methylcinnamate	3200	5700–6500
"Licrystal" compound (Merck 10217)	2150	~4200

In the visible region, the decrease of the transmission (an example is shown in Fig. 2) is due to the selected reflection (in cholesteryl-n-chlorcinnamate the SR band lies in the longer-wavelength region). All substances have also optically active bands of vibrational origin[6] in the frequency region of the cholesterine base (Fig. 2).

The dependences of the parameters on the layer thickness (cell thickness) are given in Figs. 1, 3, 5, and 6–9 (averaged over several samples for each value of the thickness). Before we proceed to analyze the results, we must analyze thoroughly the experimental situation. The required flat texture was established by us in the usual manner[7–10]—by moving the cover glass of the cell in a definite direction; we used for this purpose a cell of special shape, and the operation was carried out inside the thermostat without removing or moving the cell. For the cholesteric structures experiment has shown that, rubbing the glass surface or producing scratches on it (which gives a clearly pronounced result for nematic phases[7,8]) is ineffective.[7,9] Epitaxial effects can hardly be expected for fused quartz (they were observed by us only when covers of calcite with different axis orientations were used, but were weak), and movement is essential.[10]

It appears that the main orienting action should be ascribed to the dragging of the surface layers of the CLC as a result of the strong friction between the glass and the CLC and the viscosity of the latter; this gives rise to mechanical orientation. If we assume this mechanism, then the role of the front and rear (immobile) walls become significantly non-equivalent, and the or-

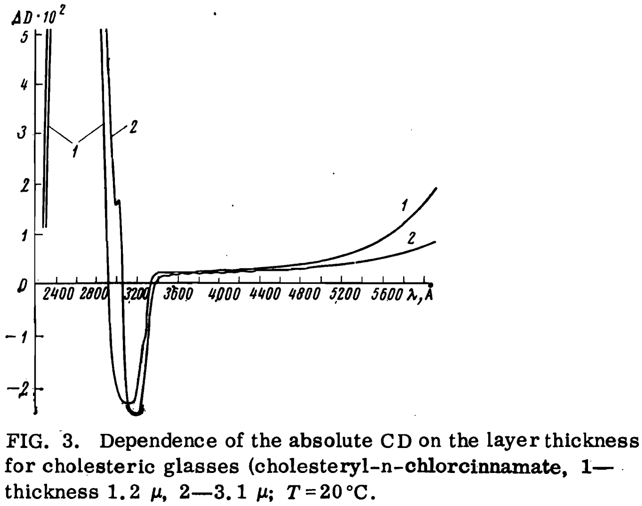

FIG. 3. Dependence of the absolute CD on the layer thickness for cholesteric glasses (cholesteryl-n-chlorcinnamate, 1—thickness 1.2 μ, 2—3.1 μ; $T = 20\,^{\circ}\mathrm{C}$.

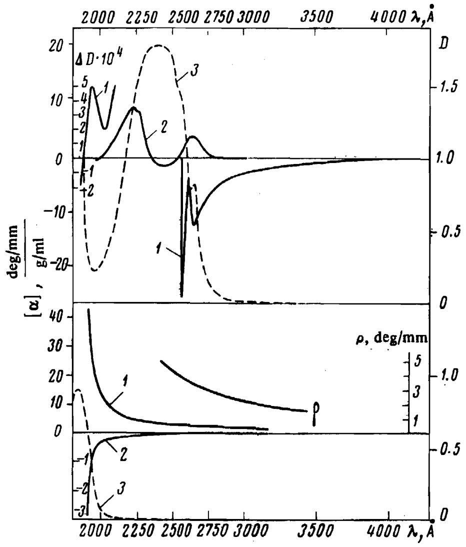

FIG. 4. 1) Specific optical rotation of the solutions [α], 2) their absolute circular dichroism ΔD, 3) absorption spectrum of solutions—optical density D for cholesteryl-chloride (bottom, concentration 4.9×10^{-3} g/ml) and for cholesteryl-p-chlorcinnamate (top, concentration 8×10^{-4} g/ml). Curve ρ—optical rotation of the chloride melt.

dering becomes unilateral. In this connection, the usual assumption made in the interpretation of the Grosjean bands[11] that the number of rotations of the helix between the walls is an integer is not obligatory under the present situation (see below).

We note next that a CLC with a flat texture is a uniaxial anisotropic medium, where the optical axis is perpendicular to the planes of the layers, and thus coincides with the direction of propagation of the light. In the region of the maximal absorption, the light traveling inside the medium along the axis is polarized, strictly speaking, elliptically, and the axis of the ellipse rotates in a complicated manner as the beam propagates, since the "rotation" is in this case not additive with the birefringence. Therefore the position of the inversion point can shift, depending on the thickness (in the course of propagation).

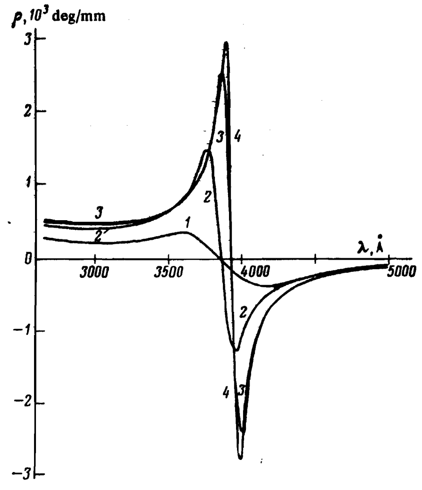

FIG. 5. DOR of cholesteryl-pelargonate for different layer thicknesses: 1—1.2 μ; 2—3.1 μ; 3—4.8 μ; 4—12.0 μ; $T = 79.9$ °C.

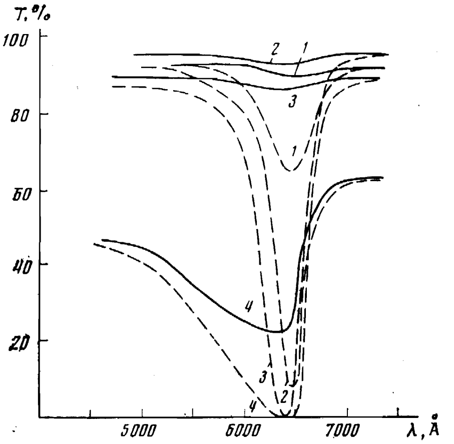

FIG. 6. Selective transmission T of "Licrystal" compound (Merck 10217); solid line—right hand polarization, dashed—left-hand. 1—thickness 4.8 μ; 2—19.5 μ; 3—50 μ; 4—203 μ.

We consider the first the region of selective reflection. Figures 5 and 6 show a typical variation of certain parameters with changing thickness. According to the existing theories (see, e.g.,[12-14]), the position of the maximum λ_{max} of the SR is connected with the pitch p of the cholesteric helix by the relation $\lambda_{max} = \bar{n}p$, where $\bar{n}$ is the average refractive index. By calculating from the previously obtained data[3] the value of p, we can find the number of revolutions of the spiral in the cell, $m = d/p$ (see the table).[2)] Figures 7–9 show plots of the parameters against m; we have compared here substances that differ most in the pitch of the helix. It is seen that the curves are quite similar (qualitatively)

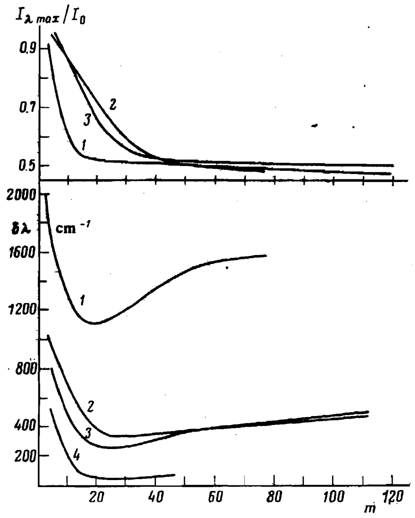

FIG. 7. Dependence of the relative intensity $I_{\lambda,max}/I_0$ and of the half-width $\delta\lambda$ of the selective-transmission band on the number of periods of the structure, m, for different substances: 1—cholesteryl-n-methylcinnamate, $T = 160.4$ °C; 2—"Licrystal" (Merck-10217), $T = 20$ °C; 3—cholesteryl pelargonate, $T = 79.9$ °C; for comparison, curve 4 shows the half-width of the DOR curve in the SR region in accordance with Fig. 5 for cholesteryl pelargonate at $T = 79.9$ °C.

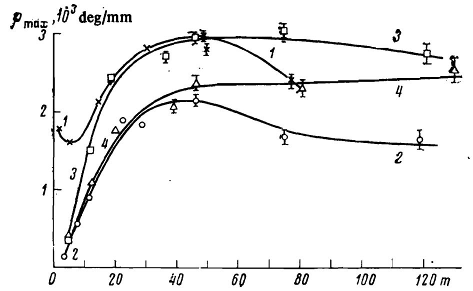

FIG. 8. Dependence of the maximum positive amplitude of the DOR curve, ρ_{max} in the SR region on the number m of the periods of the structure for different substances: 1—cholesteryl-p-methyl cinnamate, $p \approx 6470$ Å, $T = 160.4$ °C; 2—"Licrystal" (Merck 10217) $p \approx 4200$ Å, $T = 20$ °C; 3—cholesteryl pelargonate $p \approx 2600$ Å, $T = 79.9$ °C; 4—cholesteryl chloride, $p \approx 2400$ Å, $T = 61$ °C.

for substances having substantially different chemical structures and substantially different values of p.

The selective reflection (just as the anomalous DOR in this region) is the result of Bragg diffraction by the cholesteric spiral structure. As is well known, to obtain a distinct diffraction maximum it is necessary to have reflection from several layers; with increasing number of layers, and consequently with increasing number of interfering rays, the maxima become narrower and their intensity increases. This is precisely the behavior shown in Fig. 7 for transmission and in Fig. 8 for the rotation due to the same causes. An increase of the thickness above 10–20 layers produces already slight changes in the interference results, but on the other hand the orientation in the deep layers, far from the wall and its orienting action, becomes somewhat less ordered.[3)] In these layers, the optical axis lies already not strictly along the ray, but at a certain angle; there is, of course, a certain statistical scatter of the angles, and the average angle depends on the degree of ordering. This leads to a shift of λ_{max} for these layers into the short-wave region[15] and, as a result, to an inhomogeneous broadening of the selective transmission curve towards the short-wave side (Fig. 6). In principle, the degree of asymmetry of these curves can serve as a measure of the disorder of the deep layers of the structure. For the same reason, a slight decrease of the value of the rotation takes place at $m > 40$ (Fig. 8).

Dreher[16] has shown that the aperiodic deformation of the structure also shifts λ_{max} towards the short-wave side; similar deformations, at the given method of orientation, can also occur. A comparison with the theory[14,17] shows that the theoretical shapes of the curves $I = I(d)$ and $\rho = \rho(d)$ are qualitatively closest (a numerical comparison is impossible because of the difference between the calculated parameters) to curve 4 of Fig. 8, and then the agreement becomes worse on going in succession to curves 4, 3, 2, and 1. The values of p of these substances are arranged in the same sequence, namely 2400, 2600, 4200, and 6470 Å respectively at the temperatures of the experiments—this means that in this series, for the same value of m, the number of molecular layers in the cell increases.

If we accept the assumption made concerning the deviation from the normal to the sample surface of the local optical axis of the sections of the microstructure, located far from the (displaced) surface, then it is obvious that these deviations should increase with increasing number of molecular layers, and actually one should expect a worse agreement with the theory based on the assumption of a structure that is ideally ordered in the entire volume. In addition, the curves were taken at different temperatures, which increase in the order 4, 3, 1 (the compound 2 is a mixture for which p is practically independent of the temperature), and this also favors our assumptions.[4)]

According to Tolmachev and Sonin[1] and Kassubeck and Meier,[11] the change of thickness can be accompanied by oscillations of the pitch p within a single revolution. At a relatively small assortment of the thicknesses, it is difficult to draw a judgment concerning the presence of these oscillations—they will yield only an apparent scatter of the points. But these oscillations, as indicated above, can exist, if at all, only in the case of an ideal orientation in the entire cell and if both walls exert the same orienting action. In experiments with smooth variation of the temperature, causing a smooth change in the pitch, in the ordinary case of plane-parallel cells, as performed by many workers (see, e.g.,[3,15,18]) no such oscillations were ever observed, and the obtained temperature dependence of the parameters was monotonic. It is seen that the general character of the curves for the SR and the DOR is somewhat different; this is natural if it recognized that surface and volume effects are being compared; the DOR curve flattens out later on, as expected, and its agreement with the theory[14,17] is worse, as is also natural.

We proceed to the region of electronic absorption bands. The extrema in the region 3100 Å on Fig. 1 obviously constitute long-wave parts of the curves of the anomalous DOR, corresponding to the band with the longest wavelength. The capabilities of the instruments

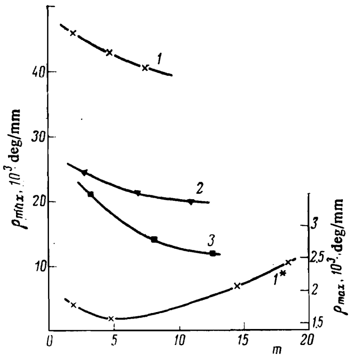

FIG. 9. Dependence of the maximum positive amplitude of the DOR curve, λ_{max}, in the region of the electronic absorption bands, on the number of periods of the structure, m, for different substances (left-hand scale): 1—cholesteryl-p-methyl cinnamate ($T = 160.4$ °C); 2—cholesteryl-p-chlorcinnamate ($T = 171.5$ °C); 3—cholesteryl cinnamate ($T = 157.5$ °C). Curve 1* (right-hand scale)—magnified segment of the curve for substance 1 in the SR region from Fig. 8.

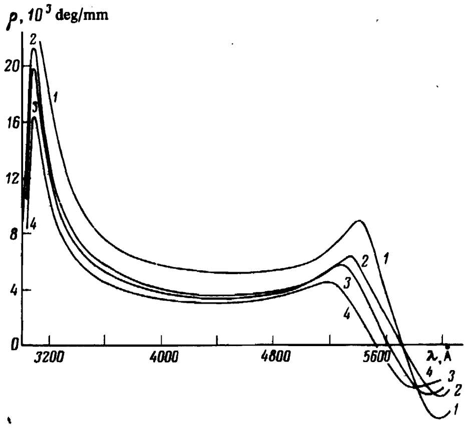

FIG. 10. Temperature dependence of optical rotation for cholesteryl cinnamate in the mesophase (1—T=152.0 °C; 2—157.6 °C; 3—163.7 °C; 4—171.5 °C). Sample thickness 1.2 μ.

(large optical density and ellipticity) do not make it possible to obtain short-wave parts. Figures 1 and 3 show the variation of the parameters with thickness, while Fig. 9 shows the dependence on m. The amplitude of the DOR curves decreases here with increasing thickness, in contrast to the SR region. This is natural, since the interference factor is absent here, and the degree of ordering decreases with thickness (owing to the deep layers), and consequently the rotation also decreases (see the discussion below).

In view of these differences in behavior, it is necessary to note incidentally the following. In the analysis of the DOR phenomena in the SR region it is obviously necessary to take into account the superposition of the wings of the considered—stronger—bands which are connected with absorption. This influence is quite noticable, for example, on curve 1 of Fig. 8, which shows $\rho_{\max}=\rho_{\max}(m)$ in the SR region for methyl cinnamate, if they are compared with the curve that shows the same for the absorption band (Fig. 9, curves 1 and 1*). On curve 3 of Fig. 8, which shows the behavior of the phenomena for pelargonate, this influence is weaker because of the lower intensity of the electron band and its greater distance (Fig. 4). At larger thicknesses (approximately 5–10 periods) the course of the phenomena in the SR region is determined mainly already by the influence of the reflection, all the more since the contribution of the absorption bands (Fig. 9) decreases.

The course of the phenomena is substantially different also in other respects. It is seen from Fig. 10 that the dependence of the optical rotation on the temperature for the bands in the SR region and in the absorption region is also different. Whereas the SR band is strongly displaced over the spectrum (see also[3,4]), the electronic absorption band remains practically in place (as is customary for molecular crystals), even following supercooling and vitrification.

The difference in the behavior is due also to the difference in the character of the wave fields in the region of absorption and SR, a difference demonstrated theoretically in Stegmeyer's paper.[19]

It is seen from Figs. 1 and 2 that the signs of the bands in the electronic absorption region and in the SR region are different, as are also the CD signs: this is seen also from the figures for the pelargonate and chloride, even so only the initial sections of the curves could be obtained there. On going to the isotropic phase or to the solution (Fig. 4), where the helical structure and the SR vanish and only the optical activity of the molecules themselves comes into play, the signs of the bands connected with absorption remain the same for pelargonate and changes for the others.[5)] This shows that the signs of the bands in the mesophase are connected only indirectly with the configuration of the molecules (a change in the conformation of the molecules is not very likely); indeed, in the SR region the sign is governed by the relative arrangement of the molecules,[20] while in the absorption region it depends also on the orientation of the absorption oscillator, responsible for the gyrotropy, relative to the axes of the dielectric tensor.[21] We note incidentally that a comparison of the mesophase and the solution thus makes it possible to assess the mechanism of the phenomena.

Account must be taken here of the fact that the CLC molecules are chiral, and consequently they are active in the isotropic phase. A contribution to the activity is made by all types of interaction inside the molecules: electric dipole–electric dipole, electric dipole–magnetic dipole, etc. When summing the contributions of the individual molecules it turns out that if all the orientations are equally probable the contribution is made only by the electric dipole–magnetic dipole tensor, or more accurately by that part of this tensor which contains the scalar product of the moments. On the other hand, if the medium is subject to some disorder, then contributions are made also by all other terms and the combined gyrotropy can increase even within the framework of the model of the oriented gas by several orders of magnitude.[22–24] The rotational forces of the molecules themselves, as is well known, change little on going from a solid molecular crystal to a melt or to a solution, and therefore the very strong change in the magnitude (by 3–4 orders of magnitude) and in the sign of the rotation and CD of CLC on going from the isotropic phase to the mesophase indicate that the addition of the contributions of the individual molecules takes place essentially differently in these phases. Large values of the rotation in the mesophase are due precisely to another result of the addition of the molecular contributions of the molecules that are arranged in order (in helices of definite sign). The change of the conformations of the molecules, even if it does exist, cannot yield so strong an effect. Therefore to interpret the phenomena it is necessary first of all to calculate the indicated summary gyrotropy.

In addition, in the case of ordering we can expect the appearance of excitonic effects. The anisotropy of the external field can also produce an effect, consisting both in a manifestation of induced optical activity[25,26] and in a lowering of the symmetry of the molecules, causing an increase of their optical activity (see, e.g., [24]). However, the contribution of the last factors cannot be practically large. The existing theories of the optical rotation of the cholesteric structure do not consider the resonance region. Its influence in the SR region is taken into account so far only by an addition of a term of the Sellmeyer type (A/λ^2).

For a more complete interpretation of the behavior of the DOR in the absorption region it is obviously necessary to analyze the origin of the bands. From the foregoing material it is seen that the structure of the bands is complicated, they consist of several components, of which only some have circular dichroism, and furthermore differing in sign. The following preliminary remark can be made. An analysis of the spectra of a large number of related and isostructural compounds, carried out by us, shows that the saturation bands of the ethers (pelargonate and chloride) in the region 2050–2150 Å belong to the double bond of the cholesterin base ($\Delta^5\pi - \pi^*$ transition), whereas the long bands of the cinnamates in the region of 2800 Å are due to conjugation of chromophores in the ether chain (K band) and as a result should be much more sensitive to changes of the structure of the phase and the conformation of the chain; this affects particularly the CD and DOR.

It is seen from the figure that the dependences of the CD and DOR on the thickness for these two types of bands are indeed quite different. Whereas for the first (2100 Å) the CD per unit path length, as shown by our measurements, remains unchanged, for the latter (2800 Å) the absolute CD and the DOR remain approximately constant, i.e., when calculated per unit of path lengths, they decrease (Figs. 1, 3, 9); this is equivalent to assuming a lowering of the order in the deep layers, which turns out to be larger in the second bands which are more sensitive to the phase structure. It is probable that this is precisely the reason why in the SR region the behavior of the curves of Fig. 8 in the region $m > 50$ is different for the saturated ethers and for cinnamate. This leads to the (not original) statement that the description of the cholesteric helix by only the pitch parameter is too crude and does not take into account its conformation.

We note incidentally that SR effects of second order[10,27] can become superimposed on the effects connected with absorption. One could assume, on the other hand, that the band that varies little with thickness belongs to the molecules next to the well, while the band belonging to the molecules in the volume increases, naturally, the absolute CD with increasing cell thickness. This, however, is less probable, since one can hardly assume the absorption to produce so large a difference in the spectra.

At the present time, the proposed qualitative picture cannot be reinforced by some theoretical calculations, all the more since it is necessary to establish more accurately the nature of the bands located in the region difficult to investigate, and, by virtue of the large extinction, which lend themselves to an investigation only in solutions. There is no doubt, however, that a consistent comparison of the measurements in the mesophase in the isotropic phase and in the solution can yield the desired answer.

In any case, it can be stated that different bands can yield information on the different aspects of the phenomena, and that the CLC are of interest not only in themselves, but also as a model object for the solution of a number of general problems of crystal gyrotropy.

We are most grateful to Professor G. B. Sergeev for the possibility of performing the measurements with certain instruments and to V. D. Tishchenko and E. I. Kovshov for supplying some of our compounds.

---

1) In this spectral region and at the given density, none of the aforementioned instruments makes it possible to measure fully either the dispersion of the optical rotation or the circular dichroism.

2) It is possible to determine $\lambda_{\max}$ also from the midpoint of the curves of the anomalous DOR, inasmuch as the agreement is good (a determination from the inversion points is not valid, since the tail of the electron band is superimposed on the curve—see below).

3) A primitive and rough estimate[9] yields for the thickness of the ordered region a value of 20–60 helix pitches.

4) Figure 8 indicates the experimental errors; it is seen that they increase strongly with increasing m. This is natural from the point of view of the presented arguments. Small differences in the displacements of the inversion points on Figs. 1 and 5 are probably due to the strong ellipticity at the center of the band.

5) We have chosen the same signs of the rotation and the dichroism that are used in most papers on CLC in the theory of optical activity, the signs of the rotations are usually assumed to be opposite (against the ray direction).

---

[1] A. V. Tolmachev and A. S. Sonin, Fiz. Tverd. Tela (Leningrad) 17, 3096 (1975) [Sov. Phys. Solid State 17, 2052 (1975)].
[2] M. Tur, Mol. Cryst. Liq. Cryst. 29, 345 (1975).
[3] Yu. V. Denisov, V. A. Kizel', E. P. Sukhenko, and V. T. Tishchenko, Tr. MFTI Fizika, No. 6, 1975, p. 193.
[4] Yu. V. Denisov, V. A. Kizel', E. P. Sukhenko, and V. T. Tishchenko, Kristallografiya 21, 991 (1976) [Sov. Phys. Crystallogr. 21 (1976)].
[5] V. A. Kizel', Yu. I. Krasilov, and V. N. Shamraev, Prib. Tekh. Eksp. 1, 160 (1967).
[6] Yu. V. Denisov, V. A. Kisel', V. V. Mnev, and E. P. Sukhenko, Pis'ma Zh. Eksp. Teor. Fiz. 22, 242 (1975) [JETP Lett. 22, 112 (1975)].
[7] F. Kahn, and G. Taylor, H. Schouhorn, Proc. IEEE 61, 28 (1973) [Russ. transl.].
[8] L. M. Blinov, V. A. Kiesel, V. Rumyantsev, and V. V. Titov, J. Phys. (Paris) 36, Suppl. N 3, C 1 (1975), p. 69.
[9] F. Price and Bak Chan S., Mol. Cryst. Liq. Cryst. 29, 225 (1975).
[10] D. Berreman and T. Scheffer, Mol. Cryst. Liq. Cryst. 13, 223 (1975).
[11] P. Kassubek and O. Meier, Mol. Cryst. Liq. Cryst. 8, 305 (1969).
[12] S. Chandrasekhar and G. Ranganath, Mol. Cryst. Liq. Cryst. 25, 195 (1974).
[13] E. I. Kats, Zh. Eksp. Teor. Fiz. 59, 1854 (1970); 65, 2487 (1973) [Sov. Phys. JETP 32, 1004 (1971); 38, 1242 (1974)].
[14] S. Chandrasekhar, and J. Prasad, Mol. Cryst. Liq. Cryst. 14, 115 (1971); S. Chandrasekhar, Mol. Cryst. Liq. Cryst. 19, 556 (1972).
[15] J. Fergason, Appl. Opt. 7, 1729 (1968).
[16] R. Dreher, Solid State Commun. 12, 519 (1973).
[17] M. Aihara and H. Inaba, Opt. Commun. 3, 77 (1971).
[18] A. S. Sonin, A. V. Tolmachev, V. G. Tishchenko, and V. G. Rak, Zh. Eksp. Teor. Fiz. 68, 1960 (1975) [Sov. Phys. JETP 41, 981 (1975)]; T. Harad and P. Crooker, Mol. Cryst. Liq. 30, 79 (1975).

[19] M. Stegemeyer, Ber. Bunsenges. Phys. Chem. 78, 860 (1974).
[20] H. Raessler and M. Labes, J. Chem. Phys. 52, 631 (1970).
[21] G. Holzwarth and N. Holzwarth, J. Opt. Soc. Am. 63, 324 (1973).
[22] H. Hameka, J. Chem. Phys. 36, 2540; 38, 2090 (1963).
[23] Ying-Nan Chiu, J. Chem. Phys. 50, 5336 (1969); 52, 1042 (1970).
[24] V. A. Kizel', Yu. I. Krasilov, and V. I. Burkov, Usp. Fiz. Nauk 114, 295 (1974) [Sov. Phys. Usp. 17, 745 (1975)].
[25] P. Shipper, Chem. Phys. Lett. 30, 323 (1975); D. Graig, E. Power, and T. Thirunachamandran, Phys. Lett. 27, 149 (1974).
[26] S. Mason and R. Peacock, Chem. Commun. 19, 712 (1973); S. Mason, Chem. Phys. Lett. 32, 201 (1975).
[27] V. E. Dmitrienko and V. A. Belyakov, Fiz. Tverd. Tela (Leningrad) 15, 3540 (1973) [Sov. Phys. Solid State 15, 2365 (1974)].

Translated by J. G. Adashko

Temperature dependence of the heat capacity of the nematic liquid crystal MBBA on going into the isotropic phase

B. I. Ostrovskiĭ, S. A. Taraskin, B. A. Strukov, and A. S. Sonin

All-Union Research Institute of Optical-Physical Measurements

(Submitted February 5, 1976)
Zh. Eksp. Teor. Fiz. 71, 692–699 (August 1976)

Results are given of the measurement of the heat capacity and latent heat of transition to the isotropic phase for the liquid crystal MBBA (*n*-methoxybenzylidene-*n*'-butylaniline. Values of the critical exponents *a* and *a*' are obtained. The anomaly of the heat capacity is found to be pronounced in a narrow temperature range $|T-T_c|> 1$°C in the vicinity of the phase transition. The experimental data are discussed on the basis of the Landau phenomenological theory with allowance for spatially inhomogeneous fluctuations of the characteristic transition parameter. It is shown that the theory cannot describe the anomaly of the heat capacity in the isotropic phase in the case $|T-T_c|< 1$°C.

PACS numbers: 61.30.+w, 65.40.Hq, 64.70.Ew

INTRODUCTION

Critical phenomena in phase transitions in liquid crystals, accompanied by the vanishing of long-range orientation order in the locations of the long axes of the molecules, have been insufficiently studied to date. The existing experimental data[1,2] indicate that, as the isotropic-nematic phase transition point is approached, the light scattering intensity increases, and the magnetic double refraction, which plays a role of a generalized susceptibility, becomes larger. There are also indications of the presence of characteristic anomalies in the temperature dependence of the heat capacity,[3,4] which can be connected with the spatially-inhomogeneous fluctuations of the characteristic parameter of the phase transition. In the Landau theory, the effect of correlation of the fluctuations is taken into account by the introduction of small corrections to the thermodynamic potential.[5,6] A similar approach has been fruitful in the case of ferroelectrics[7]; however, there are practically no experimental data which could be used for quantitative estimates in liquid crystals.

In the present work, we have attempted to carry out quantitative analysis of the possibility of the application of the Landau theory for the description of critical anomalies in the region of the phase transition from the nematic to the isotropic phase. This analysis is carried out on the basis of accurate measurements of the heat capacity of the liquid crystal MBBA (*n*-methoxyl benzylidene *n*'-butylaniline).

METHODOLOGY AND EXPERIMENTAL RESULTS

The heat capacity C_p and the latent heat of transition $\Delta q(T_c)$ of the liquid crystal MBBA were measured in an adiabatic calorimeter of the Strelkov construction.[8] The liquid crystal of MBBA, synthesized according to the usual method, was subjected to systematic purification: vacuum distillation, recrystallization from absolute ethanol, and drying in a vacuum desiccator in the presence of P_2O_5. The temperature of transition to the isotropic phase amounted to 42.49 °C, according to our measurements of the heat capacity.

The calorimetric cell consisted of a cylindrical thin-walled (wall thickness ≈ 0.5 mm) glass ampoule with a copper-silver coating and an axial opening for the insertion of a thermometer and a heater. The liquid crystal, whose mass amounted to ~6 g, was placed in a cylindrical gap of thickness 3 mm. After the liquid crystal was put in the calorimetric cell, the latter was sealed shut. During the entire time of the experiment (6 months), the temperature of the phase transition, which corresponds to the maximum in the heat capacity, did not change. The temperature was measured by a platinum resistance thermometer TSPN-1 (100 ohm) with an accuracy to within 0.001 °C (in the proper scale