Fluctuation effects during melting of the cholesteric mesophase of liquid crystals

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A nondissipative circular dichroism due to structural fluctuations was observed in the isotropic phase of chiral liquid crystals near the melting point. It was found that these effects were similar for different chiral substances and were independent of the nature of the transition, thermal history, and orienting factors. The optical probe method was used. A dissipative circular dichroism in an absorption band of an impurity in the isotropic phase was also found. The nondissipative dichroism was attributed to fluctuations of a planar helix mode, whereas the dissipative dichroism included contributions from the planar helix mode and a conical helix mode.

INTRODUCTION

The numerous phases and phase transitions exhibited by each liquid crystal[1] make these crystals convenient objects for investigating, on the one hand, the specific intermolecular forces responsible for the formation of the mesophase and, on the other, a number of general aspects of the theory of phase transitions and of pretransition processes. Chiral liquid crystals, typical representatives of which are cholesteric liquid crystals, are of considerable interest from this point of view.

This interest is due to the fact that in chiral liquid crystals with a sufficiently strong chirality there is formed, in a narrow range of temperatures near the melting point of the cholesteric mesophase, a series of intermediate phases which are known as the blue phases and have a distinctive structure.[2,3] Transitions between these phases as well as a transition to the isotropic phase during subsequent heating are of the first order and they have very low heats of transition, i.e., they are close to second-order transitions. Systems of this kind exhibit very strong fluctuations, manifested by changes in all the optical parameters and particularly large in the isotropic phase near the melting point.[4] Chiral liquid crystals are also convenient because the chiral asymmetry of their molecules and supramolecular structures imparts a right-left asymmetry to the fluctuations and it becomes possible to investigate these processes using the gyrotropy parameter which is highly sensitive to structural changes.

The transition from the cholesteric mesophase to the isotropic phase can be described satisfactorily by the theory of Landau and de Gennes,[2] although there are some discrepancies between the experimental and theoretical results. However, the published experimental investigations of this phase transition have so far been limited to determination of the optical rotation mainly at one wavelength and the results have been contradictory.[5–7] We used measurements of circular dichroism carried out by two different methods to study the phenomena occurring near the melting point in chiral liquid crystals of different types. This approach was first used in Ref. 8 to observe a transition from a blue phase III to the isotropic phase in cholesteryl nonanoate and the associated fluctuations. Above the melting point in the isotropic phase there was a considerable "structural" circular dichroism (see below) and it was found that there exist pronounced processes, observed only in a narrow range of temperatures ~1–1.5 °C near the melting point, associated with fluctuations of a "planar spiral mode" and described theoretically in Ref. 9, but not observed before.

We shall show that these effects occur both in the presence and absence of the blue phases; they are common to chiral liquid crystals and obey certain general relationships which are analyzed below.

EXPERIMENTAL METHOD

The samples were prepared and thermostated as described in Ref. 10. The absorption spectra were recorded using a Hitachi 330 spectrophotometer and the circular dichroism measurements were made using a Jobin Yvon Mark III dichrograph. The spectral range of the dichrograph extended from 200 nm to approximately 900 nm and the total optical density should not exceed ~1 to ensure an acceptable precision; this imposed certain restrictions on the absorption, thickness of the sample, and impurity concentration (as discussed below). In particular, the molecules of all the investigated liquid crystals had a strong absorption band at short wavelengths, which prevented measurements in this range.

Fused quartz cells were used. Special attention was given to careful cleaning of the cells and to the optical quality of their walls, because the latter affected strongly the homogeneity of a sample, particularly important for a clear observation of a transition. Cells with an internal gap of ~10 μ and an orienting coating were used in a study of structured cholesteric mesophases and of the blue phases I and II. It was shown in Ref. 11 that a sample thoroughly oriented over the whole of its volume could be obtained provided the thickness did not exceed 10–20 μ; when the thickness was 100 μ, there was practically no orientation in the bulk of the crystal. In the case of the blue phase III and the isotropic phase the internal gap in the cells ranged from 10 to 100 μ and there was no special surface treatment, because it was shown in Ref. 8 that in the case of these phases the layer thickness and the surface quality of the cell walls did not affect the investigated phenomena.

Our study was carried out on acene cholesterol esters, their binary mixtures, and several other chiral substances; these substances were purified by chromatography. A steady-state equilibrium structure was established (this was important in the vicinity of a transition) by holding a sample

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at each temperature for at least 1 h and sometimes up to 3–4 h. The quality and homogeneity of a sample were monitored *in situ* by a polarizing microscope.

RESULTS OF MEASUREMENTS ON PURE SUBSTANCES

We investigated in greatest detail cholesteryl nonanoate (CN) and cholesteryl chloride (CC), which had well spread absorption bands, and we also studied their mixtures. In the case of CN we observed all three blue phases and the transition from the blue phase III to the isotropic phase; an increase in the pitch of the helix was known to cause successive disappearance of the third, second, and first phases. In the case of mixtures for which the wavelength of the selective reflection peak in the cholesteric mesophase was located in the range $\lambda_c \gtrsim 800$ nm we observed a direct cholesteric–isotropic phase transition. The compositions of the mixtures were selected so as to ensure that all the variants of the transitions took place.

The results of the measurements are presented in Figs. 1–5 and in Table I. The spectra of the blue phases I and II were reported in Ref. 10; in the present study we concentrated on the spectra of the blue phase III and of the isotropic phase. For all these substances, the effects which occurred during melting were identical to those observed during freezing (in contrast to the blue phases I and II), i.e., the melting was completely reversible and its parameters were reproduced when it was repeated. As mentioned earlier, the phenomena observed in the blue phase III and in the melt were independent of the thickness and of the boundary conditions.

Figure 1 shows the circular dichroism (ΔD) spectra of the blue phase III. The spectra were structure-free under all conditions and shifted toward longer wavelengths on increase in the pitch of the helix. Figure 2a shows the circular dichroism spectra of the isotropic phase for one of the CN–CC mixtures (with the composition ratio 78:22) recorded at various temperatures T, whereas Fig. 3 gives the spectra obtained for various mixtures close to ($\sim$0.1 °C) the melting point of the preceding phase. Clearly, the nature of the circular dichroism spectra changed greatly as a result of melting, so that for different mixtures and different temperatures the spectra of the isotropic phase were qualitatively similar and for all the mixtures the spectrum of this phase did not shift as a result of a change in the pitch of the helix or a change in the nature of the preceding liquid crystal phase, which was in contrast to the spectra of the blue phase III and other liquid crystal phases. The inset in Fig. 3 shows the circular dichroism spectrum of CN at 125°C.

It is clear from Figs. 1 and 3 that the positive circular dichroism in the melt (isotropic phase) was approximately an order of magnitude less than that of the preceding liquid-crystal phase and it was observed only in a narrow temperature range extending over 1.5–2 °C near the melting point, whereas further heating showed no dichroism (within the limits of the experimental error amounting to $\Delta D \sim 5\times10^{-6}$): only a strong negative circular dichroism band remained in the range $\lambda \lesssim 220$ nm and this band was little affected by temperature or by phase transitions (we show only the beginning of this band, because further into the band the optical density became too high and it was not possible to measure the circular dichroism—see above). This band was observed also in a solution of a liquid crystal and was due to the optical activity of the liquid-crystal molecules, i.e., it was due to a dissipative molecular circular dichroism. It was fairly strong, but in the region of $\lambda > 220$ nm its wing rapidly decreased practically to zero. Some back-

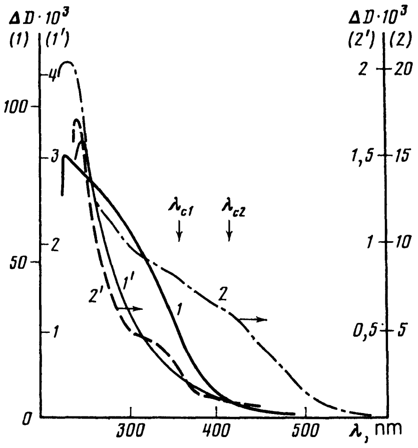

FIG. 1. Circular dichroism spectra of the blue phase III (1, 2) and of the isotropic phase (1′,2′) of CN (1,1′,$\lambda_c = 360$ nm) and of a CN–CC mixture in the ratio 84:16 (2,2′,$\lambda_c = 420$ nm) at the following temperatures: 1) 90.820 °C; 1′) 90.855 °C; 2) 84.955 °C; 2′) 85.030 °C. Thickness of the sample $L = 100\,\mu$.

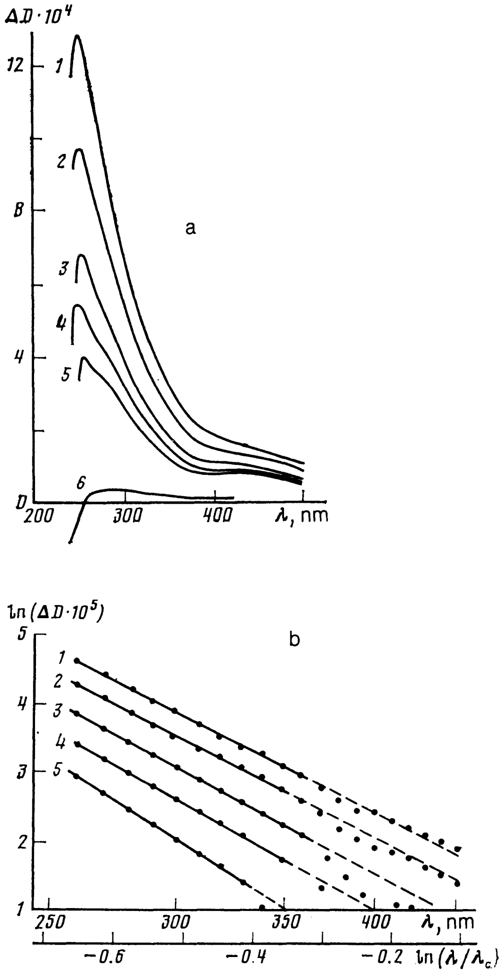

FIG. 2. a) Circular dichroism spectra of the isotropic phase of a CN–CC mixture with the composition 78:22 at the following temperatures: 1) 83.225 °C; 2) 83.330 °C; 3) 83.345 °C; 4) 83.755 °C; 5) 84.020 °C; 6) 84.500 °C ($T_c = 83.12$ °C, $L = 100\mu$). b) Same but in logarithmic coordinates.

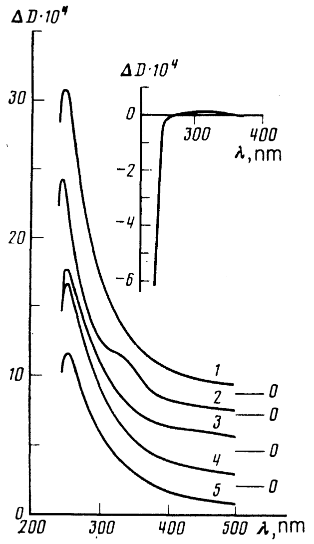

FIG. 3. Circular dichroism spectra of the isotropic phase obtained for different CN–CC mixtures: 1) 100:00, $T = 90.855$ °C ($T_c = 90.850$ °C); 2) 84:16, $T = 85.085$ °C ($T_c = 84.980$ °C); 3) 78:22, $T = 83.225$ °C ($T_c = 83.120$ °C); 4) 65:35, $T = 78.975$ °C ($T_c = 78.960$ °C); 5) 60:40, $T = 77.170$ °C ($T_c = 77.130$ °C). The inset shows a sample with the composition 100:00 at $T = 125$ °C.

ground circular dichroism, still one or two orders of magnitude less than the structural effect (Fig. 3), still remained. It was usually slightly above zero and was undoubtedly due to local defects, inclusions, local anisotropy, etc. The circular dichroism of the isotropic phase had the same sign as the helix in the cholesteric mesophase and was clearly due to structural features of the substance under the given conditions; it could be called structural circular dichroism.

Certain features of the effects should be stressed. In the case of the cholesteric mesophases and the following blue phases I and II we found that the period of the blue phase structure varied in proportion to the pitch of the helix of the initial cholesteric phase, with corresponding changes in the spectral positions of the reflections in the spectra of these phases.[10] In the case of the blue phase III, which did not have sharp peaks in the circular dichroism spectrum, the edge of a step which can be seen in Fig. 1 shifted proportionally to the pitch of the helix in the cholesteric mesophase; all this evidence indicated that the blue phase III had some structure with a period proportional to the pitch of the helix and, moreover, the structure was of the polydomain type. Since, in contrast to the liquid crystal phases, the circular dichroism spectrum of the isotropic phase did not vary with the pitch of the helix of the initial cholesteric phase and did not shift, we concluded that this was evidence of the absence of long-range order and that the microstructures and optical effects exhibited by the isotropic phase were of fluctuation origin.

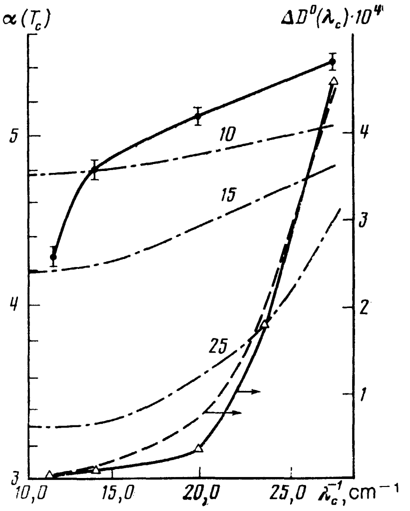

FIG. 4. Dependences of the power exponent α in Eq. (1) on λ_c^{-1} for CN–CC mixtures: ●) experimental results; the chain curves are calculated on the basis of Eq. (2) (the numbers alongside the curves gives the values of ξ_R in nanometers) and the dependence of ΔD^0 on λ_c^{-1} for the same mixture; △) experimental results; the dashed curves are calculated (see text).

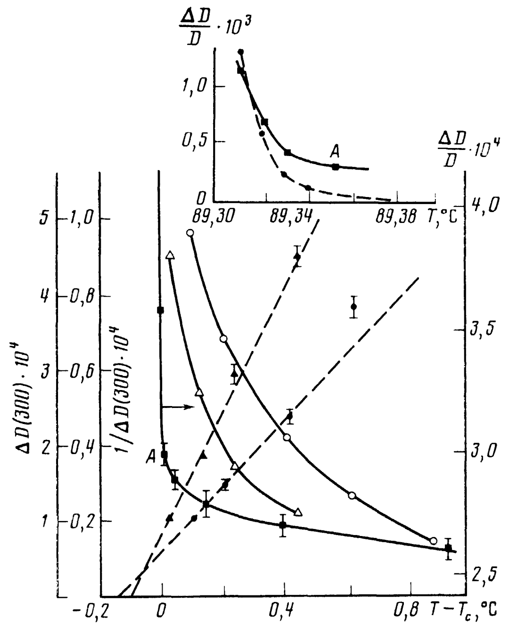

FIG. 5. Temperature dependences of the dichroism at $\lambda = 300$ nm for various mixtures (the scales are on the left): triangles represent CN–CC with the composition 78:22; the circles represent CN–nematic with the composition 50:50 (the open circles are the values of ΔD and the black dots give $1/\Delta D$), and the temperature dependences of the ratio $\Delta D/D$ for the absorption band of CB–CN with an admixture of 1% CB and a layer $L = 10\,\mu$ thick (squares). In the inset a part of this curve near the point A is compared with the behavior of the structural circular dichroism outside the band (the dashed curve corresponds to $\lambda = \lambda_c = 360$ nm).

In the limit when the wavelength was much greater than the characteristic size ξ_R of the fluctuations, $\lambda \gg 4\pi\xi_R n$ (n is the refractive index), which undoubtedly is true of our case, the spectral dependence usually obeyed a power law. For all the investigated substances we found that the circular dichroism spectra recorded in the range $\lambda > 220$ nm, i.e., outside an absorption band, was best described by an empirical dependence of the type (Fig. 2b)

$$\Delta D \approx \Delta D^0(\lambda_c, T)\,(\lambda/\lambda_c)^{-\alpha(\lambda_c, T)}, \qquad (1)$$

where λ_c is the wavelength of a selective reflection peak of a cholesteric mesophase. The results of the calculations carried out using this formula are presented in Figs. 4 and 5 and in Table I (T_c is the phase-transition temperature and T^* is the point of absolute instability of the isotropic liquid). When the temperature rise reached $\Delta T \gtrsim 1$ °C above the melting point or when the wavelengths were long ($\lambda \gtrsim 500$

TABLE I. Parameters of circular dichroism in isotropic phases of series of CN–CC mixtures.

$T°$, C	$T - T_c$	α	$\Delta D\cdot 10^5$, $\lambda = 300$ nm	$\Delta D\cdot 10^5$, $\lambda = \lambda_c$	Substance and its parameters
90.855	0.005	5.40	122	46	CN, blue phase III–isotropic phase $\lambda_c \approx 360\pm5$ nm $T_c \approx 90.85\pm0.01°$ C $T_c - T^* \approx 0.09\pm0.01°$ C
90.890	0.040	5.45	88	33	
90.930	0.080	5.45	70	27	
91.000	0.150	5.40	52	20	
83.225	0.100	5.10	48	3.5	CN–CC (78:22), blue phase II–isotropic phase $\lambda_c \approx 500\pm5$ nm $T_c \approx 83.12\pm0.02°$ C $T_c - T^* \approx 0.15\pm0.03°$ C
83.330	0.210	5.20	34	2.4	
83.545	0.420	5.40	21	1.40	
83.755	0.630	5.65	13	0.74	
84.020	0.900	6.35	7	0.29	
78.975	0.020	4.75	63	1.0	CN–CC (65:35), blue phase I–isotropic phase $\lambda_c \approx 720\pm5$ nm $T_c \simeq 78.955\pm0.01°$ C $T_c - T^* \simeq 0.1\pm0.02°$ C
79.080	0.105	5.25	36	0.36	
79.190	0.215	5.55	24	0.19	
77.170	0.045	4.25	57	0.54	CN–CC (60:40), cholesteric–isotropic phase $\lambda_c \approx 880\pm5$ nm $T_c \approx 77.125\pm0.01°$ C $T_c - T^* \approx 0.05\pm0.02°$ C
77.220	0.095	4.50	34	0.22	
77.275	0.150	4.55	26	0.16	
77.330	0.205	4.65	22	0.11	

nm), the circular dichroism became very small and it was not possible to determine reliably the parameters in the above empirical formula.

Clearly, α depended on the pitch of the cholesteric helix but its temperature dependence was weak: the value of this quantity rose slightly as a result of heating. The quantity ΔD^0 depended strongly on temperature; within the limits of the experimental error it decreased proportionally to $(T - T_i^*)^{-1}$ or even faster (see also below); T_i^* is the temperature of the absolute instability of a given mode.

In addition to mixtures of CN and CC, we observed similar effects also in the case of other substances such as cholesteryl myristate, a mixture of nematic N-805 (which itself is a mixture of hexacarboxylic acids) with CN (Fig. 5), a mixture of a nematic with a nonmesogenic chiral ("coiled") additive, which was a derivative of tigogenin. The effect was therefore common to all the chiral substances.

We shall now consider the physical interpretation of our results. In the first approximation of the Landau-de Gennes theory using a uniaxial nematic order parameter, we find that the contribution of fluctuations to the gyrotropy (more specifically the contribution to the rotation of the plane of polarization of light) has a temperature dependence of the $(T - T^*)^{-1}$ type. A more correct description of the processes in chiral liquid crystals requires the use of the results of Refs. 3–5 and 9 where a biaxial tensor order parameter $Q(\mathbf{r})$ is employed.[3] The free energy is considered using a Fourier expansion of $Q(\mathbf{r})$ and then an expansion of Q^τ into five components Q_m^τ (where $m = 0, \pm 1, \pm 2$) corresponding to irreducible representations of the rotation group.[3-5] Here, $m = \pm 1$ corresponds to a conical helix mode whereas $m = \pm 2$ corresponds to a planar spiral mode. The modes have different second-order phase transition temperatures T_c^* and T_p^*, and their relative contributions depend on the pitch of the spiral. When this pitch is large, the conical helix mode predominates, whereas in the case of substances with a shorter pitch where the blue phases can exist ($\lambda \lesssim 800$ nm) the theory predicts that fluctuations should be dominated by the modes with $m = \pm 2$.

Fluctuations in the isotropic phase near the transition to a cholesteric phase had been investigated experimentally only on the basis of the rotation of the plane of polarization at one wavelength.[5-7] This rotation is due to the conical helix mode and it exhibits a dependence on T of the type $(T - T_c^*)^{-1/2}$ and it is significant when the transition temperature is exceeded by ~ 10 °C or more. In the case of short-pitch chiral liquid crystals the anomalous behavior of the rotation of plane of polarization of light near the transition is attributed tentatively to the influence of the plane mode. The processes observed in our study can be regarded as fluctuations of the plane helix in its pure form. The value of ΔD for a mixture which is outside the range of existence of the blue phases (curve 5 in Fig. 3) should be, according to the above discussion, considerably less than for CN. Optical properties of fluctuations of this type have been considered theoretically in greatest detail in Ref. 9. The expression obtained there for the circular dichroism can be represented in the following form for the purposes of our discussion;

$$\Delta D = \frac{\pi k_B T L}{2n^2 \lambda_c^2 c_1 \ln 10} f(\eta, \tau), \tag{2}$$

where k_B is the Boltzmann constant; T is the temperature which in the investigated narrow interval can be regarded as constant; L is the thickness of the sample; c_1 is the Landau coefficient in front of the gradient term in the expansion of the free energy; $f(\eta,\tau)$ is a complicated function mainly governing the spectral and temperature dependences. Here, $\eta = \lambda_c/\lambda$ and $\tau = t/k^2$, where $t = (T - T^*)/(T_R - T^*)$ is the reduced temperature, T_R is the phase transition temperature for a racemic mixture, and $k = 4\pi\xi_R n/\lambda_c$ is known as the chirality.

The parameters of some typical liquid crystals (in particular $\xi_R \ll 15$ nm) were substituted in the above formula in Ref. 9 and estimates of ΔD were obtained for one wavelength $\lambda = \lambda_c$: they were in order-of-magnitude agreement with those obtained in our experiments. It would be of interest to consider in greater detail the agreement between the theory and experiment in the case of the spectral and temperature dependences of the specific substances that we investigated.

1. Spectral dependence. In the calculation of $f(\eta,\tau)$ and in rigorous calculations based on Eq. (2) we need to know exactly the dispersion of $n(\lambda)$ and the dispersion of the anisotropy of $n(\lambda)$, which are two parameters that influence significantly the calculations, particularly at short wavelengths. These parameters cannot be found in the literature and some of the other parameters are not known accurately. Therefore, in a quantitative comparison of the functional spectral dependence with the experimental results we used approximate estimates of n obtained in our previous investigation[10] and varied the parameters c_1, ξ_R, T_R, and T^* in Eq. (2) within limits of their typical values; we then calculated the $\Delta D(\lambda)$ dependence. The results of calculations in those spectral and temperature intervals where the measurements were carried out agreed well with the experimental dependences on λ.

2. Temperature dependence. This dependence was estimated using the experimental values of ΔD at $\lambda = 300$ nm, as this was still far from an absorption band and, on the other hand, the dichroism was still sufficiently high. An analysis of the changes in ΔD with temperature made it possible to determine T_p^*; this determination was independent of the selected wavelength. In view of the narrowness of the temperature interval (in practice less than 1 °C) an accurate value was difficult to obtain but we could reliably say that the circular dichroism decreased with temperature approximately as $(T - T_p)^{-1}$ or somewhat faster. Equation (2) predicts a somewhat more rapid fall which within the range of small fluctuations ($\xi_R \ll \lambda_c$) is proportional to $(T - T_p)^{-2}$, but in the immediate vicinity of the transition we can also have the dependence $(T - T_p)^{-1}$. In general, the temperature dependence may vary with the wavelength.

3. Influence of the pitch of the helix was estimated from the dependences of ΔD on λ_c for each mixture at a temperature close to the phase transition point. At the same temperature we estimated the exponent α. Next, the exponent was compared with the values given by Eq. (2); assuming that the coefficient c_1 was constant, we selected the value of t for the isotropic–cholesteric phase transition $\{t(T_c) = \frac{1}{2}[1 + k^2 + (1 + k^2/3)^{3/2}]\}$ for several typical values of ξ_R in the range of the pitches of the helix in the investigated substances. The results are compared in Fig. 4 [here $\Delta D^0(\lambda_c)$ is estimated to within a constant factor]. It should be pointed out that allowance for the dispersion would improve the agreement with the theory. We can see that ξ_R can vary from mixture to mixture. An estimate of the coefficient c_1 from the measured value of ΔD gives $c_1 \approx 6 \times 10^{-5}$ erg/cm for $\xi_R = 15$ nm.

We can summarize this qualitative analysis and the estimates by concluding that the observed structural circular dichroism is indeed associated with fluctuations of the planar spiral mode.

It would be of interest to estimate the correlation length ξ_R, using the calculation methods described above. If for each experimental spectral curve we calculate the parameter τ which ensures the best agreement between the theory and the experiment and then use approximate estimates of $n(\lambda)$ (Ref. 10), we find that the relationship for the correlation length of the plane helix mode $4\pi\xi_R = \lambda_c/(\tau - 1)^{1/2}$ gives the values $\xi_R \approx 10$–15 nm near the transition to the structured phase. The $\tau(T)$ dependence was found to be nonlinear for all substances and this was clearly due to the more rapid rise of ξ_R on approach to the transition point than that predicted theoretically (see Refs. 12 and 13). It is interesting to note that the circular dichroism spectrum of the blue phase III is also described by Eq. (2) with $\xi_R \approx 100$–150 nm.

INVESTIGATIONS BY THE OPTICAL PROBE METHOD

The method described above clearly allowed us to study the growth of fluctuations only in a narrow temperature interval and only for the planar spiral mode. Therefore, we also used the optical probe method suggested in Ref. 14 for the investigation of the blue phases.

It is known[15] that introduction of a linearly dichroic achiral impurity into the cholesteric phase of a liquid crystal in such a way that it is incorporated in the structure of this crystal, gives rise to a circular dichroism in the impurity absorption band because of the helical distribution of the impurity molecules. This circular dichroism is described, in accordance with approximate theoretical calculations,[15] by the relationship

$$\Delta D^{\text{circ}} \sim F(\lambda_m/\lambda_c)\,\delta_0\,\Delta D^{\text{lin}}, \tag{3}$$

where λ_c is the wavelength of the selective reflection maximum of the liquid crystal, λ_m is the wavelength of the maximum of the absorption band of the impurity, δ_0 is the permittivity anisotropy, and ΔD^{lin} is the effective linear dichroism of the impurity molecules distributed in the liquid crystal. The last two quantities clearly depend implicitly on the order parameters of the liquid crystal and of the impurity (on the degree of incorporation of the impurity). It is usual to assume that, in any case for a liquid crystal impurity in a liquid crystal matrix, $S_{\text{mat}} \approx S_{\text{imp}}$. We can roughly assume that δ_0 and ΔD^{lin} are proportional to S_{imp}.

The results reported in Ref. 14 and our frequently repeated measurements have shown that this effect occurs in all the blue phases. We can assume that Eq. (3) is valid in the case of single-domain samples of the blue phases I and II. We found that this effect occurs both in the blue phase III and in the isotropic phase. This was done by introducing achiral linearly dichroic molecules as an impurity in all the substances mentioned above and observing a circular dichroism as a result of this procedure (we can call this the structural dissipative dichroism). A calculation carried out using Eq.

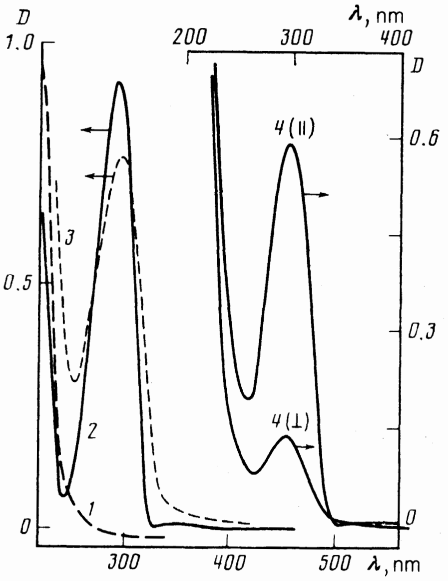

FIG. 6. Absorption in a solution of hexane: 1) CN; 2) CB; 3) CN + 1% CB, in the molten state, $L = 10\,\mu$; the absorption by CB in linearly polarized light in a nematic matrix LC-805 is also shown.

TABLE II. Dissipative circular dichroism ΔD ($\lambda_{\max} = 300$ nm) of different phases.

	Cholesteric phase $T_c - T \approx 15\,^\circ\mathrm{C}$	Cholesteric phase, blue phases I and II $T \approx T_c$	Blue phase III $T \approx T_c$	Isotropic phase $T \approx T_c$	Isotropic phase $T - T_c \approx 30^\circ$
ΔD	$5\cdot 10^{-2}$	$1\cdot 10^{-2}$	$5\cdot 10^{-4}$	$1\cdot 10^{-4}$	$2\cdot 10^{-5}$

(3) shows that the impurity absorption band should be located on the short-wavelength side of λ_c; the effect is very small on the long-wavelength side.

The selection of the impurity is governed moreover by the following considerations: the impurity molecules should be incorporated readily into the liquid crystal matrix, the impurity should have a convenient (isolated and not too broad) absorption band with a strong linear dichroism; the total absorption should be relatively weak, in accordance with the above comments on the dichrograph. After numerous experiments we concentrated mainly on a nematic liquid crystal in the form of 4-hexyloxy-4'-cyanobiphenyl (CB). Its absorption spectrum is shown in Fig. 6. Since this substance is mesogenic, it is readily incorporated in liquid crystal structures.

Measurements of the linear dichroism of CB in a well-oriented nematic matrix (LC-805) demonstrated that its absorption oscillator ($\lambda_m \approx 300$ nm) was oriented parallel to the long axis of the molecules. The CB concentration was selected to be ~1% so as to ensure that the impurity did not distort the structure of the matrix. The thickness of the samples and the impurity concentration were also affected by the following considerations. As is known, at a given impurity concentration the structural dichroism of the matrix and impurity increases linearly[1)] on increase in the thickness of the layer L, i.e., $\Delta D_{\text{imp}}/\Delta D_{\text{mat}} = \text{const}$. However, this increases also the total optical density; as pointed out above, if $D \approx 1$, then measurements become impossible. Therefore, for each thickness we have to select such a concentration $c \propto 1/L$ for which we have $d \approx 1$, i.e., we should have $\Delta D_{\text{imp}} \propto cL$. Then $\Delta D_{\text{mat}} \propto 1$ and their ratio becomes $\Delta D_{\text{imp}}/\Delta D_{\text{mat}} \propto L^{-1}$. This means that ΔD_{imp} becomes more difficult to measure in the case of greater thicknesses. Therefore, in the investigation of the impurity the layer thickness was selected to be small.

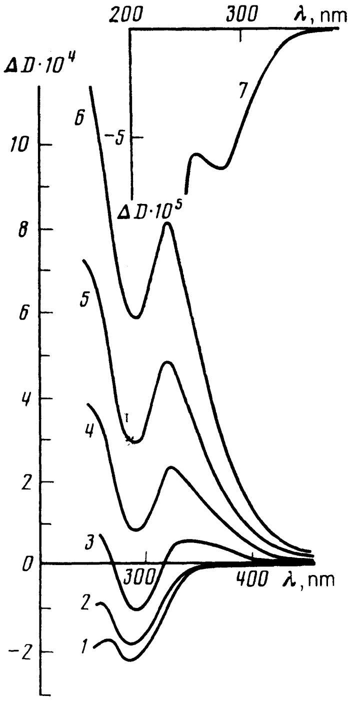

FIG. 7. Circular dichroism spectra of CN with 1% CB, $L = 10\,\mu$, at the following temperatures: 1) 91.94 °C; 2) 89.55 °C; 3) 89.36 °C; 4) 89.33 °C; 5) 89.32 °C; 6) 89.30 °C; 7) 122.06 °C ($c = 4\times 10^{-2}$ mol/liter, $L = 100\,\mu$ for curve 7).

The results of our measurements on CB are presented in Figs. 5 and 7 and in Table II. It is clear from Fig. 7 that a circular dichroism band of the impurity appears against the background of the behavior considered in the preceding section. In the case of nonanoate the cholesteric helix is left-handed, so that its structural circular dichroism is positive, whereas the circular dichroism in the absorption band of the impurity is negative, in accordance with the nature of the helix,[15] and appears against the background of the spectrum of the matrix as a dip.

Since the superposition of the circular dichroism band of the impurity deforms the spectrum of the matrix, and the circular dichroism of the isotropic phase is an order of magnitude less, the transition from the blue phase III to the isotropic phase becomes less clear. A very important observation was that the circular dichroism band of the impurity remained fully detectable even after complete disappearance of the structural circular dichroism of the matrix against the background of the "tail" of the molecular circular dichroism band of the matrix also when the excess temperature was up to 30 °C.

The circular dichroism of the CB band in the isotropic phase was evidence of the existence of local structural chiral entities and its magnitude could be used as a measure of the contribution of fluctuations to the permittivity tensor. Therefore, the fluctuation effects which created a correction to the permittivity tensor appeared in a very wide temperature range. It was difficult to estimate the relative contributions of the conical and planar helices. Similar effects were observed by us for several other nonmesogenic substances when they were introduced as an impurity, i.e., the effects were not specific to CB. The mesogenic nature was clearly important to ensure a satisfactory incorporation.

The temperature dependence of the negative structural dissipative circular dichroism of the impurity is given in Fig. 5 (since the band in question was detected against the slope of the curve of the matrix, the measurements were not very accurate). A comparison of the temperature dependences of the circular dichroism of the impurity and of the structural circular dichroism of the matrix far from the absorption band of the matrix ($\lambda \approx 360$ nm) is made in the inset in Fig. 5. We can see that after complete disappearance of the positive structural circular dichroism of the matrix, when only the tail of the band of the negative molecular dissipative dichroism remained (Figs. 3 and 6), the circular dichroism of the impurity was finite and then decreased slowly on increase in temperature. Throughout the investigated temperature range we were unable to find a single definite temperature dependence. This was due to the fact that the magnitude of the effect depended clearly on the conical and planar helix modes. Far from the transition the contribution of the conical helix mode characterized by the temperature dependence $(T - T_c^*)^{-1/2}$ predominated. However, on approach to the transition (to within ~ 1 °C) we observed the influence of an increasing contribution of the planar mode discovered by us and dependent strongly on $(T - T^*)^{-1}$.

It is worth noting that even when the temperature exceeded the melting point by up to 30 °C the circular dichroism did not disappear in the impurity absorption band. Two explanations of this effect could be advanced. Firstly, it is known that optically active solvents and matrices consisting of chiral molecules induce an optical activity in the molecules of the dissolved achiral substance and, consequently, give rise to a circular dichroism.[16] This effect occurs also at high temperatures. Secondly, it may be that some local fluctuations of the structure similar to those described above are retained even at these temperatures.

We checked the first hypothesis by measuring the dichroism of our cyanobiphenyl impurity in a heated melt of menthol (menthol melts at about 42 °C, i.e., the measurements were carried out close to the temperature interval of interest to us). As is known, menthol exerts an inducing action, its molecules are globular, and they form supramolecular structures, i.e., we can expect only a molecular inducing effect. In fact, the absorption band of cyanobiphenyl exhibited some induced dichroism: $\Delta D \sim 10^{-5}$. This however was considerably less than the dichroism of a liquid crystal, although the molecular activity of liquid crystals (and, consequently, the inducing action) was considerably less than in menthol. Therefore, the inducing effect by a solvent does occur but this effect is insufficient to account for the results obtained.

The second hypothesis is supported to some extent by the observations reported in Ref. 17 where an x-ray structure investigation revealed that strong overheating produced clusters estimated to consist of 100–150 molecules. These clusters could be relatively stable or they could appear as a result of fluctuations. In both cases they could make their own small contribution. In Ref. 18 such effects were discovered by overheating up to ≈ 40 °C by the ESR method. Finally, it was shown in Ref. 19 that changes in the short-range order in liquid crystals as a result of transitions were considerably less than those as a result of changes in the long-range order, i.e., in principle, there could be some traces of the local structure.

We could thus assume that the isotropic phase of the substances forming liquid crystals did not act as "conventional" liquids even well above the melting point and the proposed methods could be used to study the effects in this range of temperatures.

The magnitude of the circular dichroism in the absorption band of the impurity is approximately proportional, as pointed out already [see Eq. (3)], to the order parameter (and in the case of the isotropic phase to the fluctuations of this parameter) so that it would be interesting to carry out a rough approximate comparison of the magnitude of the circular dichroism of different phases. In the case of single-domain structures of the cholesteric phase and of the blue phases I and II this could be done on the basis of Eq. (3). In view of the polydomain structure of the blue phase III, this phase can be analyzed on the basis of, for example, the results of Ref. 20. Table II gives comparative estimates of the orders of magnitude of the circular dichroism of various phases.

CONCLUSIONS

Melting of chiral liquid crystals may involve the passage through the stage of various blue phases (a total of three) or a direct transition to the isotropic phase, depending on the pitch of the helix. The cholesteric phase and the first two blue phases have definite supramolecular structures and in the presence of orienting factors and for a specific thermal history we can expect formation of ordered macroscopic entities. The third blue phase is independent of the boundary conditions and of the thermal history and it is always of polydomain nature, but its local structure clearly retains some features in common with the other two blue phases. The third blue phase exhibits reversible behavior when it is melted and then cooled. Structural fluctuations (with a chiral structure) are observed in the isotropic phase. These fluctuations clearly consist of two components or modes which are different in respect of their temperature dependences and properties: one predominates near the melting point and the other is retained and manifested even at temperatures well above the melting point. The nature of the fluctuation spectrum of the circular dichroism of the isotropic phase is practically independent of which phase precedes it and it is also independent of the boundary conditions and of the thermal history. The observed fluctuations have a certain chiral structure and create a circular dichroism in the absorption bands of the achiral impurity. The appearance of the circular dichroism due to a helical distribution of the impurity molecules shows that the spatial dimensions of the regions where such ordered distribution takes place are fairly large.

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[1)] In the case of considerable thicknesses of the matrix the reflection of one of the components is total, but in the range of thicknesses used in our experiments the dependence was linear.

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