

Features of local field in nematic and cholesteric liquid crystals with small optic anisotropy

E. M. Aver'yanov, P. V. Adomenas, V. A. Zhuikov, V. Ya. Zyryanov, and V. F. Shabanov

L. V. Kirenskiĭ Physics Institute, Siberian Division, USSR Academy of Sciences

(Submitted 18 May 1984)

Zh. Eksp. Teor. Fiz. **87**, 1686–1695 (November 1984)

Features of the local field of a light wave in a nematic liquid crystal with low optic anisotropy are investigated experimentally. Isotropization of the Lorentz tensors and of the local field with decreasing macroscopic-optic and molecular-electro-optic anisotropy was observed, an effect unexpected on the basis of the existing theories of liquid-crystal polarization. Local-field anisotropy in cholesteric liquid crystals is considered. A new approach, which permits a quantitative interpretation of the experimental results, is developed for the problem of the local field in liquid crystals having arbitrary optic anisotropy.

1. INTRODUCTION

The tensor \mathbf{f} of the local field of a light wave connects the amplitude E_i^L of the local field acting on the molecule with the amplitude E_j of the macroscopic field in the medium: $E_i^L = f_{ij}E_j$. In the system of the director of a uniaxial liquid crystal (LC), the tensor \mathbf{f} is uniaxial and its components

$$f_{\parallel,\perp} = 1 + L_{\parallel,\perp}(n_{\parallel,\perp}^2 - 1) \quad (1)$$

are expressed in terms of the components $L_{\parallel,\perp}$ of the Lorentz tensor and in terms of the principal refractive indices $n_{\parallel,\perp}$ of the LC. A method of experimentally determining $L_{\parallel,\perp}$ was proposed in Ref. 1, where the anisotropic properties and the dispersion of the tensor \mathbf{f} were investigated in the nematic and smectic *A* phases of LC with large optic anisotropy. From the applied and fundamental viewpoint, great interest attaches to a determination of the features of the local field in an LC with low optic anisotropy. Such crystals include, besides the well known cholesteric LC, also the recently discovered nematic LC with birefringence $\Delta n < 0$ (Refs. 2–4), which are promising for technical applications³ and for physicochemical research.⁴ At present there are no data whatever on the anisotropy Δf in cholesteric LC. At the same time such information is essential for the use of refractometric⁵ measurements of the molecular and structural parameters that are important for the development of the theory of this class of LC and for optimization of their technological characteristics.^{3,6,7}

Low-birefringence nematic LC are convenient objects for the verification of existing theoretical approaches to the calculation of the tensor L in anisotropic molecular media. According to contemporary premises, the tensor L is a structural characteristic of an LC and, by virtue of the principle of close packing of anisotropic molecules, is determined by the anisotropy of the radial distribution function of the molecules,⁸ by the anisotropy of the molecular shape,⁹ or by the anisotropy and orientational ordering of the molecules.^{1,10,11} No account is taken of the features of the polarizability distribution over the molecular volume, but it is precisely this characteristic that differentiates essentially between LC with high¹ and low^{2–4} optic anisotropy. The features of the

local field in these two classes of LC are the subject of recently started debates.^{12–15} A clear-cut answer can be obtained only by experimentally solving the problem; this is the subject of our paper.

The method used in Ref. 1 to determine $L_{\parallel,\perp}$ is generalized in Sec. 2 to include uniaxial LC with biaxial tensor S_{ii} of orientational ordering of the molecular axes relative to the director. In Sec. 3 we report an experimental investigation of the local-field anisotropy in a low-birefringence nematic LC and determine the anisotropy of the tensor \mathbf{f} in cholesteric LC. In Sec. 4 is established a connection between the anisotropy of the tensor \mathbf{f} and birefringence, orientational ordering of the molecules, and the anisotropic properties of the molecular polarizability. The experimental data are quantitatively interpreted.

2. MEASUREMENT OF LORENTZ TENSOR IN UNIAXIAL LC

Consider a uniaxial LC consisting of platelike molecules. The *z* and *y* axes of the molecular coordinate system lie in the plane of the plate and coincide respectively with its long and central axes. The orientational ordering of the molecular axes relative to the director, which coincides with the *Z* axis, is described by the diagonal matrix¹⁵

$$S_{ii} = \langle 3 \cos^2 \theta_{iz} - 1 \rangle / 2, \quad i = x, y, z, \quad (2)$$

with zero trace. If the rotation of the molecules about their longitudinal axes is blocked, the parameter $G = S_{yy} - S_{xx}$ differs from zero and describes the biaxial nature of the molecular tensor S_{ii} . Introducing the Euler angles $\theta \equiv \theta_{zz}$ and ψ , which describe the orientation of the long molecular axis relative to the director and the molecule rotation about the long axis, we obtain from (2)

$$G = \langle 3 \sin^2 \theta \cos 2\psi \rangle / 2.$$

We choose an intramolecular isolated nondegenerate transition in the electronic or vibrational spectrum of the intrinsic (impurity) absorption of an LC whose polarization in the molecular coordinate frame is fixed by a polar angle β and by an azimuthal angle φ . The oscillator strength A of the chosen transition can vary in the mesophase and in the phase

transitions as a result of direct (complex formation, onset of hydrogen bonds, etc.) or indirect (e.g., change of conformation) manifestations of intermolecular interaction. The molecular order in LC is determined by the anisotropy of the short-range Van der Waals and steric interactions. In isotropic liquid (I)-nematic (N)-smectic A (SmA) transitions, the short range molecular order, and accordingly the short-range perturbation of the oscillator strengths of the intramolecular transitions, changes little. If an intramolecular transition is chosen which is not sensitive to the above specific interactions and to change of conformation, it can be assumed that its oscillator strength is the same in the isotropic and ordered phases, i.e., $A_n = A_i = A$. The deviation of the measured optical densities of the sample in the mesophases ($D_{\parallel, \perp}$) and in an isotropic liquid (D_i) from the corresponding components $A_{\parallel, \perp, i}$ is then determined only by the long-range effect of the local field of the light wave¹⁶

$$\begin{aligned} K \frac{n_{\parallel}}{\rho f_{\parallel}^2} D_{\parallel} &= A_{\parallel} = \frac{1}{3} A \left(1 + 2SS_{\beta} - \frac{2GG_{\beta\varphi}}{3} \right), \\ K \frac{n_{\perp}}{\rho f_{\perp}^2} D_{\perp} &= A_{\perp} = \frac{1}{3} A \left(1 - SS_{\beta} + \frac{GG_{\beta\varphi}}{3} \right), \\ K \frac{n_i}{\rho_i f_i^2} D_i &= A_i = \frac{1}{3} A, \end{aligned} \quad (3)$$

where $K = \text{const}$, $n_{\parallel, \perp, i}$ and $f_{\parallel, \perp, i}$ are the background values of the refractive indices and of the components of the tensor f within the investigated absorption band (in the case of impurity absorption these are the refractive indices of the matrix), while ρ and ρ_i are the densities of the nematic and isotropic phases,

$$S = S_{zz}, \quad S_{\beta} = (3 \cos^2 \beta - 1)/2, \quad G_{\beta\varphi} = (3 \sin^2 \beta \cos 2\varphi)/2.$$

If the molecules have a planar orientation in the cell, one can determine experimentally the dichroic ratios

$$N_1 = D_{\parallel}/D_{\perp}, \quad N_2 = D_{\perp}/D_i, \quad N_3 = D_{\parallel}/D_i,$$

which can be used to calculate the parameter

$$\Sigma = SS_{\beta} - GG_{\beta\varphi}/3 \quad (4)$$

that depends on the orientational order of the molecules and on the intramolecular properties. It follows from (3) that

$$\begin{aligned} \Sigma_1 &= (N_1 g_1 - 1)/(N_1 g_1 + 2), \\ \Sigma_2 &= 1 - N_2 g_2, \quad \Sigma_3 = (N_3 g_3 - 1)/2, \end{aligned} \quad (5)$$

where the correction factors are given by

$$g_1 = \frac{n_{\parallel}}{n_{\perp}} \left(\frac{f_{\perp}}{f_{\parallel}} \right)^2, \quad g_2 = \frac{\rho_i n_{\perp}}{\rho n_i} \left(\frac{f_i}{f_{\perp}} \right)^2, \quad g_3 = \frac{\rho_i n_{\parallel}}{\rho n_i} \left(\frac{f_i}{f_{\parallel}} \right)^2. \quad (6)$$

It can be seen from (5) that the components $L_{\parallel, \perp}$ are easiest to determine in experiment at $S = G \equiv 0$, corresponding to the

case of spherically symmetric molecules. Then $\Sigma_k = 0$ and $g_k = 1/N_k$ ($k = 1, 2, 3$). This possibility was first realized in Ref. 17 for the dichroism N_1 of the absorption of a spherically symmetric probe molecule in an LC matrix. The condition $\Sigma = 0$ can in principle be satisfied also for molecules that have no spheric symmetry, but can be realized only at a strictly fixed orientation of the dipole moment of the transition in the molecular system ($S_{\beta} = G_{\beta\varphi} = 0$) or in an isolated temperature region of the mesophase, where the contributions of the two terms in (4) cancel out.

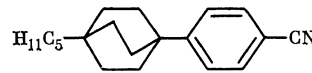
Joint use of measurements of N_{1-3} provides a universal method for determining in experiment the components $L_{\parallel, \perp}$. The physical basis of the method is the fact that the correction to the parameter Σ for the local field depends on the type of dichroic ratio N_k used in the calculation.¹ Real values of $L_{\parallel, \perp}$ should satisfy the system of two equations

$$\Sigma_1 = \Sigma_2 = \Sigma_3, \quad L_{\parallel} + 2L_{\perp} = 1. \quad (7)$$

Using (5) and (6) we can show that the three equations $\Sigma_k = \Sigma_j$ are equivalent. From a comparison of (5), (6), and (7) it can be seen that in the most general case considered here the determination of $L_{\parallel, \perp}$ does not require information on the orientation of the dipole moment of the investigated transition relative to the molecular axes.

3. FEATURES OF LOCAL FIELD IN A NEMATIC LC WITH LOW OPTIC ANISOTROPY

The experiments were performed on the LC 1-(4'-cyanophenyl)-4-pentyl-bicyclo (2,2,2) octane (5BCO); C 60.5° N 101° 1):



We indicate here the temperatures (in °C) of the crystal-nematic-isotropic liquid phase transitions. 5BCO is a typical LC with low optical anisotropy,^{2,12,14} and is isomorphic in shape to the previously investigated 4-pentyl-4'-cyanobiphenyl (5CB), but has a different electronic structure a different polarizability anisotropy. The isolated characteristic IR-absorption band of the C≡N bond valence oscillation ($\lambda_{\text{max}} = 4.5 \mu\text{m}$) is useful for experiment determination of $L_{\parallel, \perp}$. This oscillation has $\beta = 0$, $S_{\beta} = 1$, $G_{\beta\varphi} = 0$, and $\Sigma = S$. Reproducible planar molecule orientation in planar fluoroite (IR spectroscopy) and wedge-shaped glass (refractometry) sandwich cells was achieved as a result of the previously described¹ special finish of the inner surfaces of the cells. Homeotropic orientation of molecules in fluorite cells was obtained by adding a small amount of lecithin to the LC. The sample temperature was stabilized and monitored to within ± 0.1 °C.

The refractive indices $n_{\parallel, \perp, i}$ in the nematic and isotropic phases of 5BCO were measured at four light wavelengths by a wedge procedure¹⁸ accurate to $2 \cdot 10^{-3}$. Control measurements of $n_{\perp, i}$ at $\lambda = 0.589 \mu\text{m}$ were made with a refractometer accurate to $3 \cdot 10^{-4}$. The measurement results are shown in Fig. 1. Compared with 5CB, the investigated LC

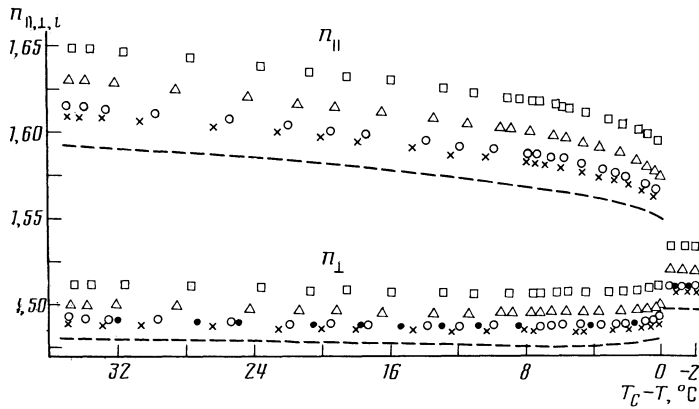


FIG. 1. Temperature dependences of the refractive indices $n_{||, \perp, i}$ of the LC 5BCO at $\lambda = 0.42$ (\square), 0.49 (\triangle), 0.589 (\circ) and $735 \mu\text{m}$ (\times). The points correspond to the values of $n_{||, i}$ ($0.589 \mu\text{m}$) measured with a refractometer, while the dashed lines are the calculated plots of $n_{||, i}^b$ (ΔT) at $\lambda = 4.5 \mu\text{m}$. T_c is the N - I phase-transition temperature.

has noticeably less birefringence and dispersion of the refractive indices $n_{||, \perp, i}$. The background $n_{||, \perp, i}^b$ within the investigated absorption band was calculated in analogy with Ref. 1 from the measured values of $n_{||, \perp, i}$ at $\lambda = 0.49$ – $0.735 \mu\text{m}$. For lack of dilatometric data on 5BCO we determined ρ_i/ρ from the known empirical relation

$$(\bar{n}^2 - 1)/\rho(\bar{n}^2 + 2) = (n_i^2 - 1)/\rho_i(n_i^2 + 2),$$

which holds with high accuracy for the nematic and isotropic phases,¹⁰ $\bar{n}^2 = (n_{||}^2 + 2n_{\perp}^2)/3$.

Owing to its low birefringence, light passing through a 5BCO sample is noticeably less scattered by transverse fluctuations of the director than in the previously studied strongly refracting LC (Ref. 1). The depolarizing effect of this scattering on the IR absorption spectrum is correspondingly weakened. The dichroic ratios $N_{2,3}$ were measured for planar-orientation samples $15 \mu\text{m}$ thick. The experimental values of N_{2e} and N_{3e} were corrected for the imperfection of the polarizer (efficiency 98%) to the true values by the relations

$$N_2 = N_{2e}(1 - \Delta_2), \quad N_3 = N_{3e}(1 + \Delta_3),$$

$$\Delta_2 = \frac{N_1}{D_{||}} \lg \left[\frac{1 + \varepsilon}{1 + \varepsilon \exp\{-2.303 D_{||}(1 - 1/N_1)\}} \right]$$

$$\Delta_3 = \frac{1}{D_{||}} \lg \left[\frac{1 + \varepsilon \exp\{2.303 D_{||}(1 - 1/N_1)\}}{1 + \varepsilon} \right],$$

where $\varepsilon = 0.02$, and replacement of $D_{||}$ and N_1 by $D_{||e}$ and N_{1e} introduces a second-order error. The instrumentation, the spectrum photography procedure, and the reduction of the measurement results are analogous to those previously described.¹ A check has shown that the measured N_2 of planar- and homeotropic-orientation samples of equal thickness agree within the limits of experimental error. The temperature dependences of $N_{2,3}$ obtained by averaging over a run of several measurements of freshly prepared samples are shown in Fig. 2.

The experimental values of L_1 and S , which satisfy Eqs. (7), are shown in Fig. 3. The parameters L_1 for 5BCO are noticeably lower than for 5CB,¹ although both have the

same geometric anisotropy. This result is unexpected from the viewpoint of modern theories of LC polarization,⁸⁻¹¹ in which the tensor \mathbf{L} is a purely structural characteristic of the LC. It is difficult to assume that the spatial distributions of the shape-isomorphic molecules differ noticeably in these LC. X-ray measurement data¹⁹ offer evidence that 5CB and 5BCO have the same type of short-range translational correlations of the molecules in the mesophase. The absolute values of the order parameter in the mesophases of 5BCO and 5CB, at equal values of ΔT , also differ insignificantly. The experimental data listed in the table for several LC investigated by us, however, show a regular decrease of the Lorentz-tensor anisotropy with decreasing optical anisotropy of the LC.

The experimental values of L_1 differ little from the critical values¹⁰:

$$L_{1cr} = \frac{1}{3} + \frac{n_{||}^2 - n_{\perp}^2}{9[n^2 - 1 + (n_{||}^2 - n_{\perp}^2)/3]}, \quad (8)$$

which agree with the condition that the tensor \mathbf{f} be isotropic. The anisotropy $\Delta f = f_{||} - f_{\perp}$ is small in the entire range $\lambda = 0.42$ – $4.5 \mu\text{m}$ and is practically independent of ΔT . It can be seen from the table that Δf decreases rapidly with decreasing birefringence of the LC. These experimental data corroborate the assumed low anisotropy of the tensor \mathbf{f} in nematic LC with small birefringence,^{4,12} and make things clear in the debates¹²⁻¹⁵ by pointing out the limitations of the contemporary theories of LC polarization and the need for developing them further.

Comparison of the results of Refs. 1 and 20 with ours shows that the ellipsoidal Lorentz cavity model^{1,10,11} can be used to calculate the components $L_{||, \perp}$ in liquid crystals with strongly polarizable molecules and with large birefringence. In LC with low optical anisotropy, the shape of the cavity corresponding to $S = 1$ has a lower anisotropy than the shape of the molecular ellipsoid. From the microscopic point of view this means that calculation of the tensor \mathbf{L} in LC must take into account not only the spatial translational⁸ correlations of the molecules, but also the orientational ones, as well as of the features of the polarizability distribution over the molecular volume, as is done in the theory of the

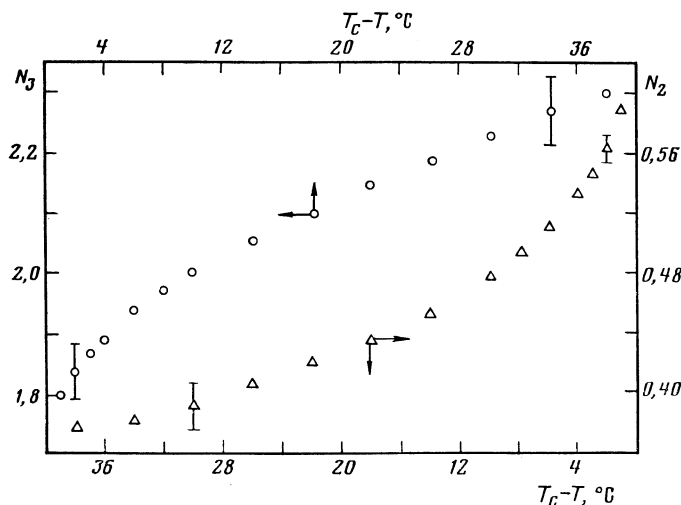


FIG. 2. Temperature dependences of the dichroic ratios $N_{2,3}$ of the $C\equiv N$ oscillation band in the nematic phase of 5BCO.

polarization of molecular crystals with strongly anisotropic molecules.^{21,22} Comparison of the theoretical values of L and f with the measured ones can single out the most important intermolecular correlations in LC.

The question of the anisotropy Δf_{ch} of the tensor f_{ch} in a cholesteric LC can be answered by comparing the optical properties of a nematic (cholesteric) with the optical properties of the cholesteric (nematic) obtained from it by adding an optically active impurity (untwisting of the cholesteric spiral in a magnetic field, producing a racemic mixture of optically active components). Experiments of this type show^{6,23-25} that regardless of the value of the birefringence, the equality $n_{||ch} = n_{\perp n}$ holds with high accuracy for the extraordinary refractive index $n_{||ch}$ of the planar texture of a cholesteric LC and the ordinary refractive index $n_{\perp n}$ of a quasineumatic layer or of the corresponding nematic analog. Therefore^{5,10}

$$\gamma_{\perp}(\bar{f}_{ch} + 2\Delta f_{ch}/3) = \gamma_{\perp}(\bar{f}_n - \Delta f_n/3),$$

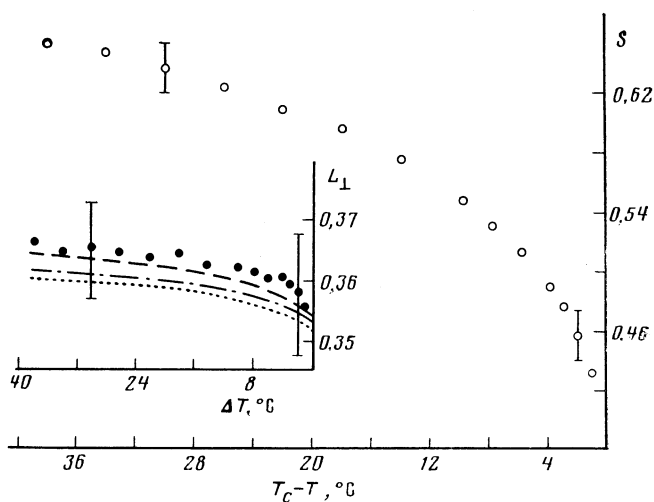


FIG. 3. Temperature dependences of the order parameter S and of the components L_1 of the Lorentz tensor (inset) in the nematic phase of the LC 5BCO. Dashed, dash-dot, and dotted lines—temperature dependences of the parameter L_{1c} calculated from Eq. (8) at $\lambda = 0.42, 0.589,$ and $4.5 \mu\text{m}$, respectively.

where γ_{\perp} is the component, perpendicular to the director of the nematic LC (to the director of the quasineumatic layer), of the molecular-polarizability tensor averaged over the orientations. Since $\bar{f}_{ch} = \bar{f}_n$, we have

$$\Delta f_{ch} = -\Delta f_n/2.$$

The relative contribution of the anisotropy of the local field to the birefringence of a cholesteric LC agrees in magnitude and sign with the analogous contribution for the nematic analog or for a quasineumatic layer. Since the birefringence of cholesteric derivatives is low, the anisotropy of the local field in them is also low. This assumption was set forth in Ref. 26 and used in Ref. 5 in a refractometric investigation of cholesteric ester.

4. LOCAL-FIELD ANISOTROPY AND MOLECULAR-OPTICAL ANISOTROPY OF A LIQUID CRYSTAL

The results of the preceding section and analysis of the tabulated data demonstrate the strong dependence of the anisotropy of the tensor f on the macroscopic optical anisotropy of LC and of the anisotropic properties of the molecular polarizability. Indeed, breaking of the π -electron conjugation chain of the fragments of the molecular core of the COO bridge group in cyanophenyl ester of hexyloxybenzoic acid (CPEHOBA) and replacement of the benzene ring by the bicyclo-octane one in 5BCO lead to a negligible change of the average value $\bar{\gamma}$ of the molecular polarizability, but to a noticeable decrease of the anisotropy $\Delta\gamma$ of the polarizability and of the ratio $\Delta\gamma/\bar{\gamma}$. This circumstance is not taken into account at all in contemporary theories of LC polarization but, as will be shown below, is decisive for the interpretation of the effect observed here, the isotropization of the tensor f with decrease of Δn .

Let us find the ratio $\Delta\gamma/\bar{\gamma}$ for 5BCO at $\lambda = 0.589 \mu\text{m}$. Inasmuch as for this substance the anisotropy Δf can be neglected in the entire range ΔT , the following relation holds¹⁰:

$$S\Delta\gamma/\bar{\gamma} = (n_{||}^2 - n_{\perp}^2)/(n^2 - 1). \quad (9)$$

The temperature dependence of the right-hand side of (9) is

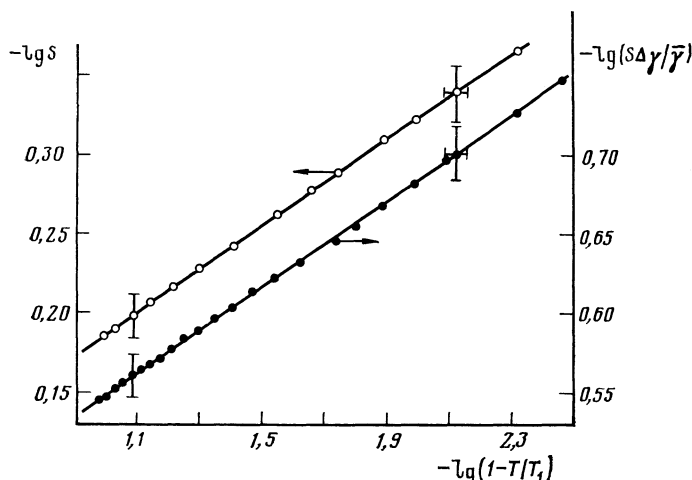


FIG. 4. Temperature dependences of the absolute values of S and of $S\Delta\gamma/\bar{\gamma}$ [Eq. (9)] in the nematic phase of the LC 5BCO in a log-log scale.

shown in Fig. 4 in log-log scale. It is well approximated by the formula

$$S\Delta\gamma/\bar{\gamma} = (S\Delta\gamma/\bar{\gamma})_0(1-T/T_1)^\beta \quad (10)$$

with parameters $\beta = 0.135$ and $T_1 - T_c = 0.8^\circ\text{C}$. Extrapolation of the plot to $T = 0$ yields $(S\Delta\gamma/\bar{\gamma})_0 = 0.385$. It can be seen from Fig. 4 that the temperature dependence of the absolute values of S is well approximated by Eq. (10) with the same values of β , $T_1 - T_c$, and $S_0 = 0.886$. This means that the ratio $\Delta\gamma/\bar{\gamma} = 0.435$ does not change with the temperature of the mesophase. The obtained value of $\Delta\gamma/\bar{\gamma}$ agrees well with the results of an independent experiment²⁷ on the Kerr effect in an isotropic solution. — 0.43, thus confirming our measurements of the parameters L_\perp and S . For the isotropic phase of 5CB in the same region of the spectrum, the experimental values $\bar{\gamma} = 33 \text{ \AA}^3$ (refractometry¹⁸) and $\Delta\gamma = 27 \text{ \AA}^3$ (optic Kerr effect²⁸) yield $\Delta\gamma/\bar{\gamma} = 0.818$. We note that the ratio of the values of $\Delta\gamma/\bar{\gamma}$ for 5CB and 5BCO (equal to 1.88) is close to the ratio of the values of Δn (equal to 1.81) and that the isotropization of the tensor \mathbf{f} is the result of simultaneous isotropization of the macroscopic optical and molecular properties of the LC.

Our experimental results can be explained by starting from the general relation¹⁰

$$n_{\parallel,\perp}^2 - 1 = 4\pi\mathcal{N}^2\gamma_{\parallel,\perp}f_{\parallel,\perp}, \quad (11)$$

which is based on two assumptions: equality of the tensor \mathbf{f} for all the LC molecules, and uniaxiality in the director system. Here \mathcal{N} is the number of molecules per unit volume,

and

$$\gamma_{\parallel} = \bar{\gamma} + \frac{1}{3}S\Delta\gamma + \frac{1}{3}G\Delta\gamma', \quad \gamma_{\perp} = \bar{\gamma} - \frac{1}{3}S\Delta\gamma - \frac{1}{3}G\Delta\gamma', \quad (12)$$

where

$$\bar{\gamma} = (\gamma_{xx} + \gamma_{yy} + \gamma_{zz})/3, \quad \Delta\gamma = \gamma_{zz} - (\gamma_{xx} + \gamma_{yy})/2, \quad \Delta\gamma' = \gamma_{yy} - \gamma_{xx}.$$

Substitution of (12) in (11) yields

$$\frac{f_{\perp}}{f_{\parallel}} = \frac{n_{\perp}^2 - 1}{n_{\parallel}^2 - 1} \frac{1 + 2S\Delta\gamma/3\bar{\gamma} + G\Delta\gamma'/3\bar{\gamma}}{1 - S\Delta\gamma/3\bar{\gamma} - G\Delta\gamma'/6\bar{\gamma}}. \quad (13)$$

We note that in the derivation of (1) we used no specific form of the tensor \mathbf{f} , such as (1). For ordinary mesogenic rod-shaped molecules we have $G \ll S$ (Ref. 15), $\Delta\gamma' < \Delta\gamma$ (Ref. 29), and the corresponding terms in (13) can be neglected. To verify (13) we find the ratio f_{\perp}/f_{\parallel} for 5CB at $T_c - T = 10^\circ\text{C}$ and $\lambda = 0.589 \mu\text{m}$, using the parameters $n_{\parallel,\perp}$ of Ref. 18, the value of given above, and $S = 0.595$ (Ref. 1) (the mean value of the results of the magnetic and radiospectroscopic measurements). The resultant estimate $f_{\perp}/f_{\parallel} = 1.09$ agrees well with the experimental 1.11 (Ref. 1).

It follows from (13) that the anisotropy of the tensor \mathbf{f} is determined by the optic anisotropy of the polarizability and by the orientational order of the molecules. For strongly polarizable molecules with large ratio $\Delta\gamma/\bar{\gamma}$, the last two factors predominate and $f_{\perp}/f_{\parallel} > 1$ (Ref. 1). Simultaneous lowering of $\Delta\gamma/\bar{\gamma}$ and of Δn by changing the electron structure of the molecules should lead to rapid isotropization of \mathbf{f} , as is indeed observed in experiment. The correlated lowering of the parameters $\Delta\gamma/\bar{\gamma}$ and Δn with elongation of the flexible

TABLE I. Anisotropy of the optical properties and of the local-field tensor in nematic LC at $\lambda = 0.589 \mu\text{m}$ and $T_c - T = 10^\circ\text{C}$.

LC	Δn	L_\perp	$(f_{\parallel} - f_{\perp})/\bar{f}$	Reference
5CB	0.185	0.40	-0.110	[1]
80CB	0.166	0.39	-0.084	[1]
CPEHOBA	0.150	0.38	-0.043	[20]
5BCO	0.102	0.36	-0.013	Present work

alkyl chains, which is typical of homologous series of LC,^{15,30} should be accompanied by a lowering of the anisotropy of the local field. For LC with small (Refs. 2 and 4) the anisotropy Δf can become positive in the region $f_{\perp}/f_{\parallel} \approx 1$. Comparison of (1) and (13) points to a lowering of the anisotropy of the Lorentz tensor with decrease of $\Delta\gamma/\bar{\gamma}$ and explains the tendency of the variation of L_{\perp} in the 5CB–5BCO series (see Table I). The dispersion of the tensor f depends on the singularities of the dispersion of the refractive indices and of the polarizability components, and its general analysis within the framework of expression (13) is difficult. This question can be solved experimentally by using LC absorption bands located in different spectral regions.

The authors thank L. M. Blinov for support and the participants of the Moscow Seminar on Liquid Crystals for a helpful discussion.

- ¹E. M. Aver'yanov, V. A. Zhuikov, V. Ya. Zyryanov, and V. F. Shabanov, *Zh. Eksp. Teor. Fiz.* **86**, 2111 (1984) [*Sov. Phys. JETP* **59**, 1227 (1984)].
- ²L. Pohl, R. Eidenschink, J. Krause, and G. Weber, *Phys. Lett.* **A60**, 421 (1977); **A65**, 169 (1978).
- ³L. M. Blinov, *Elektro-i magnitooptika zhidkikh kristallov* (Electro- and Magneto-Optics of Liquid Crystals), Nauka, 1978, pp. 243, 333.
- ⁴V. G. Rumyantsev and L. M. Blinov, *Opt. Spektrosk.* **47**, 324 (1979) [*Opt. Spectrosc.* **47**, 183 (1979)].
- ⁵E. M. Aver'yanov and V. F. Shabanov, *Kristallografiya* **24**, 184, 992 (1979) [*Sov. Phys. Crystallography* **24**, 107, 567 (1979)].
- ⁶V. A. Belyakov and A. S. Sonin, *Optika kholestericheskikh zhidkikh kristallov* (Optics of Cholesteric Liquid Crystals), Nauka, 1982.
- ⁷G. S. Chilaya and L. N. Lisetskii, *Usp. Fiz. Nauk* **134**, 185 (1981) [*Sov. Phys. Usp.* **24**, 447 (1981)].
- ⁸P. Palffy-Muhoray and D. A. Balzarini, *Can. J. Phys.* **59**, 375 (1981).

- ⁹W. H. de Jeu and P. Bordewijk, *J. Chem. Phys.* **68**, 109 (1978).
- ¹⁰E. M. Aver'yanov and V. F. Shabanov, *Kristallografiya* **23**, 320, 1232 (1978) [*Sov. Phys. Crystallography* **23**, 177, 696 (1978)].
- ¹¹U. Segre, *Mol. Cryst. Liq. Cryst.* **90**, 239 (1983).
- ¹²R. Seeliger, H. Haspeko, and F. Noack, *Mol. Cryst.* **49**, 1039 (1983).
- ¹³L. G. P. Dalmolen and W. H. de Jeu, *J. Chem. Phys.* **73**, 7353 (1983).
- ¹⁴L. G. P. Dalmolen, E. Egberst, and W. H. de Jeu, *J. de Phys.* **45**, 129 (1984).
- ¹⁵W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon & Breach, 1980. Russ transl. Mir, 1982, pp. 20, 43, 52, 61.
- ¹⁶E. M. Aver'yanov, *Fiz. Tverd. Tela* (Leningrad) **22**, 1867 (1980) [*Sov. Phys. Solid State* **22**, 1088 (1980)].
- ¹⁷L. M. Blinov, V. A. Kizel', V. G. Rumyantsev, and V. V. Titov, *Kristallografiya* **20**, 1245 (1975) [*Sov. Phys. Crystallography* **20**, 750 (1975)].
- ¹⁸E. M. Aver'yanov, V. Ya. Zyryanov, V. A. Zhuikov, and Yu. I. Ruolene, *Zh. Strukt. Khim.* **24**, 101 (1983).
- ¹⁹M. J. Bradshaw, E. P. Raynes, J. Fedak, and A. J. Leadbetter, *J. de Phys.* **45**, 157 (1984).
- ²⁰E. M. Aver'yanov, V. A. Zhuikov, V. Ya. Zyryanov, and V. F. Shabanov, *Kristallografiya* **29** (1984) [*Sov. Phys. Crystallography*, **29** (1984)] (in press).
- ²¹V. F. Shabanov, V. G. Posoprigora, A. N. Botvich, and V. P. Ermakov, *Kristallografiya* **26**, 677 (1981) [*Sov. Phys. Crystallography* **26**, 383 (1981)].
- ²²D. A. Dunmur and R. W. Munn, *Chem. Phys.* **76**, 249 (1983).
- ²³G. Pelzl, *Z. Chem.* **17**, 264 (1977).
- ²⁴S. N. Aronishidze, M. N. Kushnirenko, T. S. Pilashvili, G. S. Chilaya, and Z. M. Elashvili, *Soobshch. AN Gr. SSR* **89**, 333 (1978).
- ²⁵N. -M. Chao, K. C. Chu, and Y. R. Shen, *Mol. Cryst. Liq. Cryst.* **81**, 103 (1982).
- ²⁶Yu. V. Denisov, V. A. Kizel', and E. P. Sukhenko, *Zh. Eksp. Teor. Fiz.* **71**, 679 (1976) [*Sov. Phys. JETP* **44**, 357 (1976)].
- ²⁷D. A. Dunmur and A. E. Tomes, *Mol. Cryst. Liq. Cryst.* **97**, 241 (1983).
- ²⁸H. J. Coles and B. R. Jennings, *Mol. Phys.* **36**, 1661 (1978).
- ²⁹M. F. Vuks, N. B. Rozhdestvenskaya, and K. Eidner, *Opt. Spektrosk.* **45**, 914 (1978) [*Opt. Spectrosc.* **45**, 768 (1978)].
- ³⁰E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.* **36**, 193 (1976).

Translated by J. G. Adashko