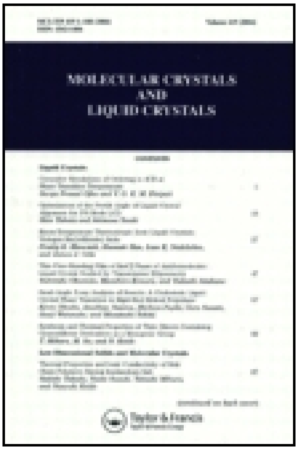


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Experimental Solution of the Local Field Problem in Uniaxial Liquid Crystals†

E. M. Averyanov [a] , V. A. Zhuikov [a] , V. YA. Zyryanov [a] & V. F. Shabanov [a]

[a] USSR Academy of Sciences, L. V. Kirensky Institute of Physics, Siberian Branch, 660036, Krasnoyarsk, USSR

To cite this article: E. M. Averyanov , V. A. Zhuikov , V. YA. Zyryanov & V. F. Shabanov (1986): Experimental Solution of the Local Field Problem in Uniaxial Liquid Crystals† , Molecular Crystals and Liquid Crystals, 133:1-2, 135-149

To link to this article: http://dx.doi.org/10.1080/00268948608079567

Mol. Cryst. Liq. Cryst., 1986, Vol. 133, pp. 135–149
0026-8941/86/1332-0135/$20.00/0

Printed in the United States of America

Experimental Solution of the Local Field Problem in Uniaxial Liquid Crystals†

E. M. AVERYANOV, V. A. ZHUIKOV, V. YA. ZYRYANOV, and V. F. SHABANOV

L. V. Kirensky Institute of Physics, USSR Academy of Sciences, Siberian Branch, 660036 Krasnoyarsk, USSR

(*Received July 3, 1984*)

A method of experimental determination of the Lorentz-factor tensor in uniaxial liquid crystals is suggested. The specific features of the local field tensor of the light wave in a nematic liquid crystal with low optical anisotropy have been investigated experimentally. Anisotropy of the local field and Lorentz-factor tensors has been found to decrease with the decreasing optical and molecular-optical anisotropies. These results appear to contradict the existing polarization theories of liquid crystals. The local field problem in cholesteric liquid crystals has been considered. A new approach to the local field problem in uniaxial liquid crystals with arbitrary optical anisotropy is developed and the experimental results are explained.

I. INTRODUCTION

The local field tensor f of the light wave connects the amplitude E_i^l of the local field experienced by a molecule with the amplitude E_j of the macroscopic field: $E_i^l = f_{ij}E_j$. In the director coordinate system of an uniaxial liquid crystal the tensor f is uniaxial and its components are written as

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

where $L_{\parallel,\perp}$ and $n_{\parallel,\perp}$ are the principal components of the Lorentz-

---

†Presented at the Tenth International Liquid Crystal Conference, York, July 15–21, 1984.

factor tensor and the refractive indices, respectively. The subscripts $\parallel$ and $\perp$ refer to the directions parallel and perpendicular to the director, respectively. In a previous paper[1] a method of experimental determination of the $L_{\parallel,\perp}$ components was suggested and the anisotropic properties and the dispersion of f in nematic and smectic A phases of liquid crystals with high optical anisotropy were studied. The investigation of the specific features of the local field in a liquid crystal with low optical anisotropy is of both applied and fundamental interest. Except for the well known cholesterics, this class of liquid crystals includes the recently discovered nematics with low birefringence (i.e. $\Delta n = (n_\parallel - n_\perp) < 0.1$ (See Refs. 2–4)), which are of great interest for technical applications[3] and physical-chemical investigations.[4] No data on the anisotropy $\Delta f = f_\parallel - f_\perp$ in a cholesteric liquid crystal are available at present. However, such information is required for the refractometric method[5] of determination of the molecular and structural parameters, which are important for the development of a theory for this class of liquid crystals and to improve their technological parameters.[3,6,7]

Nematic liquid crystals with low birefringence are the convenient objects for experimental examination of the existing theoretical approaches to the calculation of the L-tensor in anisotropic molecular media. In accordance with modern theories, the L-tensor is the structural characteristic of a liquid crystal only and depends on the following factors: (i) anisotropy in the radial distribution function,[8] (ii) anisotropy of the molecular dimensions,[9] (iii) anisotropy of the molecular shape and (iv) the orientational order parameter.[1,10,11] Moreover, the anisotropic properties of the molecular polarizability tensor γ are disregarded, yet it is this parameter which is very different for liquid crystals of high and low birefringence. The local field effects in the two classes of liquid crystals considered has been the subject of much recent discussion.[12–15] This paper presents an experimental and theoretical treatment of the above problems.

The plan of the paper is as follows: In **II**, we extend the method of determination of the L-tensor[1] to the case of uniaxial liquid crystals with a biaxial molecular tensor S_{ii} of the orientational ordering. Then, in **III**, the local field anisotropy in a nematic liquid crystal of low optical anisotropy is studied experimentally and the question of the local field anisotropy in a cholesteric liquid crystal is discussed theoretically. Finally, in **IV**, the dependence of the anisotropy Δf on the birefringence, the order parameter S and the anisotropic properties of the molecular polarizability tensor is established and an interpretation of the experimental results is given.

II. EXPERIMENTAL METHOD OF DETERMINATION OF THE LORENTZ-FACTOR TENSOR IN UNIAXIAL LIQUID CRYSTALS

Consider a uniaxial liquid crystal consisting of plank-like molecules. The axes z and y of the molecular coordinate frame lie in the plane of plank and coincide with the longer and shorter molecular axes, respectively. The orientational ordering of the molecular axes with respect to the director $r \| Z$ is described by a traceless matrix[15]

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

where θ_{iZ} is the angle between the i-axis of the molecules and the director, while the brackets denote averaging over the orientation of all molecules. If the rotation of the molecules around their longer axes is broken the parameter $G = S_{yy} - S_{xx} \neq 0$ describes the biaxiality of the molecular tensor S_{ii}. Using Euler-angles $\theta \equiv \theta_{zZ}$ and ψ to specify the orientation of the longer molecular axis with respect to the director and the longitudinal molecular rotation, respectively, we may obtain from Eq. (2) $G = \langle 3\sin^2\theta\cos 2\psi\rangle/2$.

Let us consider the intramolecular isolated nondegenerate transition in the electronic or vibrational spectra of the liquid crystal or a dissolved impurity absorption. The orientation of the transition moment in the molecular frame is fixed by the polar angle β and azimuthal angle ϕ. The oscillator strength A of the chosen transition may change in the mesophase and at the phase transitions as a result of the direct (molecular complexing, origin of the hydrogen bond etc.) or indirect (conformational changing) manifestation of the intermolecular interactions. In liquid crystals the molecular ordering is caused by anisotropy of the short-range dispersion and steric interactions. At the phase transitions isotropic liquid-nematic (I-N) and nematic-smectic A (N-SmA) the short-range molecular order and, consequently, the short-range perturbation of the intramolecular oscillator strengths change little. Therefore, the choice of the intramolecular transition is insensitive to the above specific interactions and conformational changes and its oscillator strength may be assumed constant in the isotropic and ordered phases, i.e. $A_N = A_I \equiv A$. Then the relation between the experimentally measured optical densities $D_{\|,\perp,i}$ of the sample and the corresponding components $A_{\|,\perp,i}$ are given by the formulas below[16]

$$K\frac{n_\|}{\rho f_\|^2}D_\| = A_\| = A(1 + 2SS_\beta - 2GG_{\beta\phi}/3)/3,$$

$$K\frac{n_\perp}{\rho f_\perp^2}D_\perp = A_\perp = A\,(1 - SS_\beta + GG_{\beta\phi}/3)/3, \tag{3}$$

$$K\frac{n_i}{\rho_i f_i^2}D_i = A_i = A/3,$$

where K is a constant, $n_{\|,\perp,i}$ and $f_{\|,\perp,i}$ are the background refractive indices and the local field tensor components within the chosen absorption band, ρ and ρ_i are the densities of meso- and isotropic phases,

$$S \equiv S_{zz},\ S_\beta = (3\cos^2\beta - 1)/2,\ G_{\beta\phi} = (3\sin^2\beta\cos2\phi)/2.$$

Under planar orientation of molecules in the cell the following dichroic ratios can be measured

$$N_1 = D_\|/D_\perp, \qquad N_2 = D_\perp/D_i, \qquad N_3 = D_\|/D_i.$$

These ratios can be used for the calculation of the parameter

$$\Sigma = SS_\beta - GG_{\beta\phi}/3, \tag{4}$$

which depends on the orientational ordering and the molecular properties. From Eq. (3) we get

$$\Sigma_1 = \frac{N_1g_1-1}{N_1g_1+2}, \qquad \Sigma_2 = 1 - N_2g_2, \qquad \Sigma_3 = (N_3g_3-1)/2, \tag{5}$$

where

$$g_1 = \frac{n_\|}{n_\perp}(f_\perp/f_\|)^2, \qquad g_2 = \frac{\rho_i n_\perp}{\rho n_i}(f_i/f_\perp)^2, \qquad g_3 = \frac{\rho_i n_\|}{\rho n_i}(f_i/f_\|)^2. \tag{6}$$

Eq. (5) shows that for the simplest case when $S = G \equiv 0$ the components $L_{\|,\perp}$ can easily be determined experimentally. Then $\Sigma_k = 0$ and $g_k = 1/N_k$ $(k=1,2,3)$. This possibility was first realized in Ref. 17 for the absorption dichroism N_1 of the spherical impurity molecules in a liquid crystalline matrix. In principle, the condition $\Sigma = 0$ may be satisfied for molecules without spherical symmetry when $S_\beta = G_{\beta\phi} = 0$ or in the limited temperature range where $SS_\beta = GG_{\beta\phi}/3$.

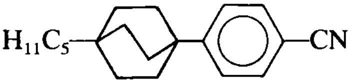
A combined employment of the ratios N_{1-3} gives a universal method for the experimental determination of the components $L_{\|,\perp}$. The physical background of the method lies in the fact, that the local field correction to the parameter Σ depends on the type of the dichroic ratio N_k used for the calculation.[1] The true values of $L_{\parallel,\perp}$ must satisfy the two equations

$$\Sigma_1 = \Sigma_2 = \Sigma_3 \quad \text{and} \quad L_\parallel + 2L_\perp = 1. \tag{7}$$

Combining Eqs. (5) and (6) shows, that the above equations for Σ_k are mutually equivalent. From Eqs. (5), (6) and (7) it follows that for the most general case considered here for the determination of $L_{\parallel,\perp}$ information on the band polarization studied with respect to molecular frame is not necessary.

III. SPECIFIC FEATURE OF THE LOCAL FIELD IN THE NEMATIC LIQUID CRYSTAL WITH LOW OPTICAL ANISOTROPY

For the experimental investigation we used the 1-(4′-cyanophenyl)-4-n-pentyl-bicyclo(2.2.2)octane (5BCO)



with a nematic range 60.5–101.0°C. This compound is typical of liquid crystals with a low optical anisotropy.[2,12,14] It has the same molecular dimensions as 4-n-pentyl-4′-cyanobiphenyl (5CB) studied earlier,[1] but differs in the electronic properties and the polarizability anisotropy. An isolated band of the IR absorption given by the cyano-stretch vibration (at $\lambda_{max} = 4.5$ μm) is well suited for the experimental determination of $L_{\parallel,\perp}$. For this vibration $\beta = 0$, $S_\beta = 1$, $G_{\beta\Phi} = 0$ and $\Sigma = S$. A reproducible planar alignment in plane-parallel CaF_2 (IR spectroscopy) and wedge-like glass cells (refractometry) was achieved by a special preparation of the inner surfaces of the cell-sandwich as described in an earlier paper.[1] Qualitatively, the orientation was monitored with a polarization microscope in parallel and converging light beams. The temperature stabilization was of the order of ±0.1°C.

The refractive indices for 5BCO in the nematic ($n_{\parallel,\perp}$) and isotropic (n_i) phases were measured at four light wavelengths λ as a function of temperature using the wedge method[18] with an accuracy of 2×10^{-3}. Moreover, the refractive indices $n_{\perp,i}$ were measured to an accuracy of 3×10^{-4} at $\lambda = 0.589$ μm with an Abbé refractometer.

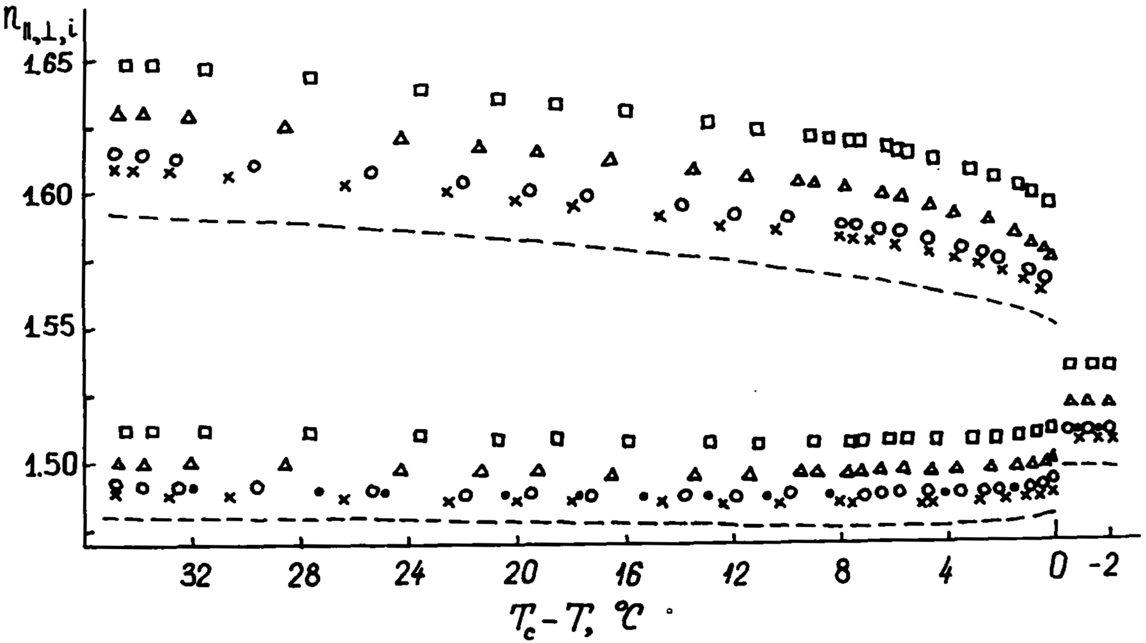


FIGURE 1 Refractive indices $n_{\parallel,\perp,i}$ of 5BCO obtained by the wedge method as a function of temperature at $\lambda = 0.42$ (□), 0.49 (△), 0.589 (○) and 0.735 μm (X). Dots (·) are the values $n_{\perp,i}$ (0.589 μm) measured with a refractometer. The dashed lines are the background values $n_{\parallel,\perp,i}$ at $\lambda = 4.5$ μm (see text). T_c is the isotropic-nematic transition temperature.

The refractive indices $n_{\|,\perp,i}$ as a function of reduced temperature are shown in Figure 1. The calculation of the background refractive indices $n_{\|,\perp,i}$ for the investigated band were carried out by the same procedure as in Ref. 1 using the measured values $n_{\|,\perp,i}$ in the region $\lambda = 0.49$ to 0.735 μm. Since the dilatometric data for 5BCO are absent the ratio ρ/ρ_i was found using a well known empirical relation

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

which is fulfilled to a high accuracy for the nematic and isotropic phases,[10] $\bar{n}^2 = (n_\|^2 + 2n_\perp^2)/3$. Due to low birefringence for 5BCO, the scattering of the light transmitted through the sample on the transversal director fluctuations is sufficiently less in comparison with the liquid crystals studied earlier.[1] Consequently, the depolarising influence of this scattering on the IR absorption spectrum is also reduce. The dichroic ratios $N_{2,3}$ were measured in the uniformly aligned planar samples with the thickness of 15 μm. Because of imperfections in the polariser (i.e. the efficiency is only 98%) the measured ratios N_{2m} and N_{3m} were corrected to the true values using the following formulas

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

where

$$\Delta_2 = \frac{N_1}{D_\|} \lg \left[\frac{1 + \epsilon}{1 + \epsilon \exp\{-2{,}303D_\|(1 - 1/N_1)\}}\right],$$

$$\Delta_3 = \frac{1}{D_\|} \lg \left[\frac{1 + \epsilon \exp\{2{,}303D_\|(1 - 1/N_1)\}}{1 + \epsilon}\right],$$

$\epsilon = 0.02$ and the substitution of $D_\|$, N_1 by $D_{\|m}$, N_{1m} gives the errors of the second order. Our measuring technique has been reported earlier[1] and will not be described here. The temperature dependences of $N_{2,3}$, obtained by averaging over a number of separate measurements are shown in Figure 2.

The experimental values $L_\perp$ and S satisfying Eqs. (7) are presented in Figure 3. The components $L_\perp$ for 5BCO are sufficiently lower than the ones found for 5CB,[1] although the geometrical anisotropy of these molecules is the same. This result is unexpected within the currently accepted theoretical predictions,[8-11] where the L-tensor is only a

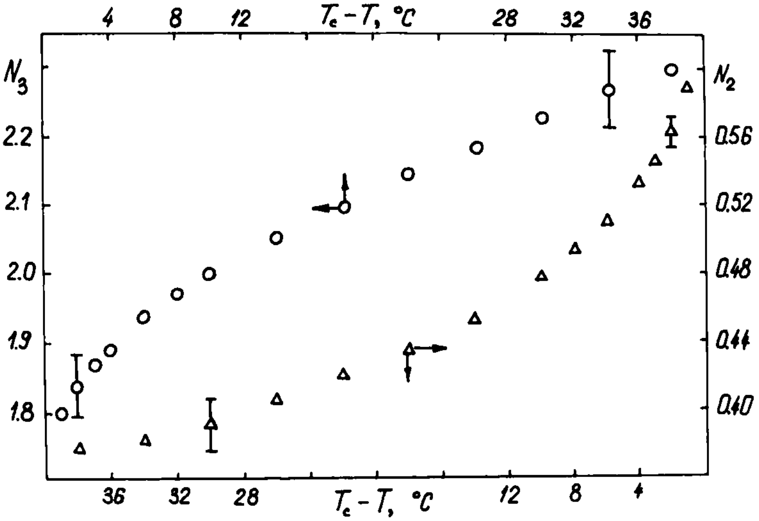


FIGURE 2 Dichroic ratios $N_{2,3}$ of cyano-stretch vibration band of 5BCO versus temperature.

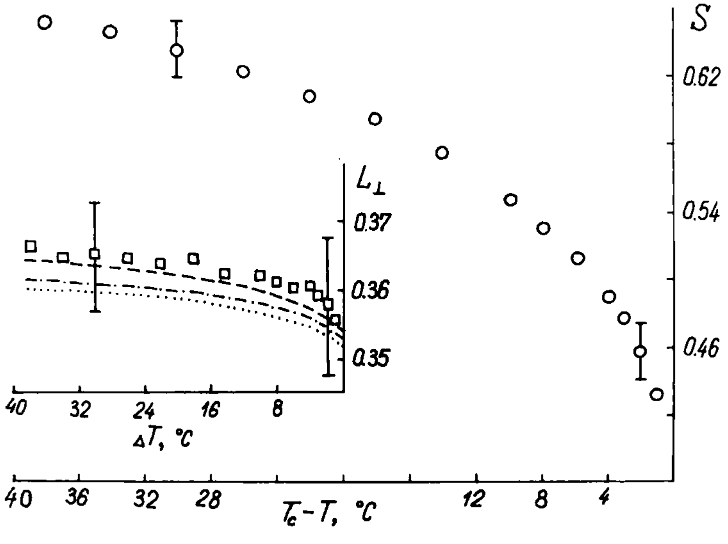


FIGURE 3 Variation of the order parameter S and the Lorentz-factor component $L_\perp$ with temperature for 5BCO. Dashed, dashed-dotted and dotted lines are the values $L_{\perp c}$ calculated from Eq. (8) at λ = 0.42, 0.589 and 4.5 μm, respectively.

structural characteristic of the liquid crystal. The spatial distributions of molecules can hardly be expected to differ sufficiently for the liquid crystals 5CB and 5BCO. According to x-ray structure analysis[19] short-range translational molecular correlations for 5BCO are approximately the same as the ones found for 5CB. The absolute values of the order parameter S for these compounds at the same reduced temperature ΔT do not differ much. However, the experimental data presented in Table I, for a number of liquid crystals studied, show a normal decrease of the Lorentz-factor when the optical anisotropy of the liquid crystals decreases. Figure 3 shows, that the experimental values of $L_\perp$ are almost indistinguishable from the critical values of $L_{\perp c}$, having the form[10]

$$L_{\perp c} = \frac{1}{3} + \frac{n_\parallel^2 - n_\perp^2}{g[\bar{n}^2 - 1 + (n_\parallel^2 - n_\perp^2)/3]} \tag{8}$$

and corresponding to the condition $\Delta f = 0$. The anisotropy Δf is small over the whole range $\lambda = 0.42$ to 4.5 μm and does not depend on ΔT. From the Table one can see rapid drop of Δf with decreasing Δn. These experimental data strongly support the supposition about the small anisotropy Δf in nematics with low birefringence[4,12] and prove the insufficiency of the existing polarisation theories of liquid crystals.

Comparison of the present data with our earlier results[1,20] shows that the ellipsoidal Lorentz cavity model[1,10,11] is quite good for calculations of $L_{\parallel,\perp}$ in liquid crystals with strongly polarisable molecules and high birefringence. In liquid crystals of low birefringence the cavity shape corresponding to $S = 1$ has a lower anisotropy compared with a molecular ellipsoidal shape. From the microscopic point of view this means that in order to calculate the L-tensor it is

TABLE I

Optical and internal field parameters for a number of nematic liquid crystals at $T_c - T = 10°C$ and $\lambda = 0.589$ μm

Compound	$n_\parallel - n_\perp$	$L_\perp$	$(f_\parallel - f_\perp)/\bar{f}$	Ref.
5CB	0.185	0.40	−0.110	1
8OCB[a]	0.166	0.39	−0.084	1
CPE6OBA	0.150	0.38	−0.043	20
5BCO	0.102	0.36	−0.013	this work

[a] 4-n-octyloxy-4′-cyanobiphenyl

important to take into account the spatial translational correlations[8] as well as the orientational molecular correlations and the specific feature of the polarizability distribution over the molecular volume. This can be achieved by treating each molecule not as a single point, but as a set of points or submolecules.[21,22] The comparison of the theoretical values of L, f with those measured experimentally will reveal more important types of the molecular correlations in liquid crystals.

The problem of the anisotropy Δf_{ch} of the local field tensor f_{ch} in cholesteric liquid crystals can be solved by comparing the refractive indices of the helical planar structure of the cholesteric liquid crystal with the local refractive indices in the quasinematic layer. According to the experimental data[6,23–25], independent of the birefringence value, the relation

$$n_{e_{ch}} = n_{o_N} \tag{9}$$

is fulfilled with a high accuracy, where $n_{e_{ch}}$ is the extraordinary refractive index of the cholesteric liquid crystal and n_{o_N} is the local ordinary refractive index in the quasi-nematic layer. We can now use the theory developed in Refs. 5, 10 to rewrite Eq. (9) in the form

$$\gamma_{\perp ch}(\bar{f}_{ch} + 2\Delta f_{ch}/3) = \gamma_{\perp N}(\bar{f}_N - \Delta f_N/3), \tag{10}$$

where $\bar{f} = (f_{\parallel} + 2f_{\perp})/3$, $\gamma_{\perp}$ is the molecular polarizability component transverse to the director. Subscripts *ch* and *N* belong to the helical cholesteric structure and quasi-nematic layer, respectively. Taking into account that $\gamma_{\perp ch} = \gamma_{\perp N}$ and $\bar{f}_{ch} = \bar{f}_N$ we obtain from Eq. (10) the relation

$$\Delta f_{ch} = -\Delta f_N/2. \tag{11}$$

The relative contribution of the local field anisotropy to the birefringence of the cholesteric liquid crystal has the same value as for the nematic liquid crystal or for the quasi-nematic layer. Because of the low optical anisotropy of the cholesteryl esters the local field anisotropy is also small for this class of liquid crystals, as follows from Eq. (11) and the experimental data presented above. This supposition had been made earlier in Ref. 26 and then was used in the refractometrical investigation of the cholesteryl esters.[5]

IV. LOCAL FIELD AND MOLECULAR-OPTICAL ANISOTROPY OF LIQUID CRYSTALS

From the experimental data presented above it is seen that the anisotropy Δf is strongly dependent on the macroscopic optical anisotropy of liquid crystals as well as on the anisotropic properties of the molecular polarizability. In fact, breaking of the π-conjugation of the molecular core of the 4-cyanophenyl ester of 4'-n-hexyloxybenzoic acid (CPE60BA) by a COO central group and replacing a benzene ring by the BCO ring in 5CB result in a relatively small variation of the average molecular polarizability $\bar{\gamma}$, but in a significant decrease of the polarizability anisotropy $\Delta\gamma$ and therefore in the ratio $\Delta\gamma/\bar{\gamma}$. This fact is absolutely neglected in the existing theories of the polarization of liquid crystals but as will be shown below it is extremely important for the explanation of the Δn dependence of Δf.

Let us find the ratio $\Delta\gamma/\bar{\gamma}$ for 5BCO at $\lambda = 0.589$ μm. Because of low anisotropy Δf for this compound over the whole range ΔT the following relation is valid[10]

$$S\Delta\gamma/\bar{\gamma} = (n_{\|}^2 - n_{\perp}^2)/(\bar{n}^2 - 1). \qquad (12)$$

The temperature dependence of the right hand part of Eq. (12) is shown in Figure 4 using a double logarithmic scale. It is well approximated by the formula

$$S\Delta\gamma/\bar{\gamma} = (S\Delta\gamma/\bar{\gamma})_0(1 - T/T_1),^{\beta} \qquad (13)$$

where $\beta = 0.135$ and $T_1 - T_c = 0.8$°C. Extrapolating to T = 0 we obtain $(S\Delta\gamma/\bar{\gamma})_0 = 0.385$. As can be seen from Figure 4 the temperature dependence of the absolute values S is also well approximated by Eq. (13) with the same parameters β, $T_1 - T_c$ and $S_0 = 0.886$. This means that the ratio $\Delta\gamma/\bar{\gamma} = 0.435$ does not depend on the temperature in the mesophase. This value of $\Delta\gamma/\bar{\gamma}$ is in a very good agreement with the independent experimental result on the Kerr-effect in a diluted isotropic solution -0.43 (Ref. 27). This confirms our measurement of the $L_{\perp}$ and S parameters. For the isotropic phase of 5CB in the same spectral range the experimental values $\bar{\gamma} = 33\text{Å}^3$ (refractometry[18]) and $\Delta\gamma = 27\text{Å}^3$ (optical Kerr-effect[28]) give $\Delta\gamma/\bar{\gamma} = 0.818$. It should be emphasized that the values of $\Delta\gamma/\bar{\gamma}$ for 5CB and 5BCO are in the same relation to each other (1.88) as well as the values of Δn (1.81). Then, the isotropization of the f-tensor is the

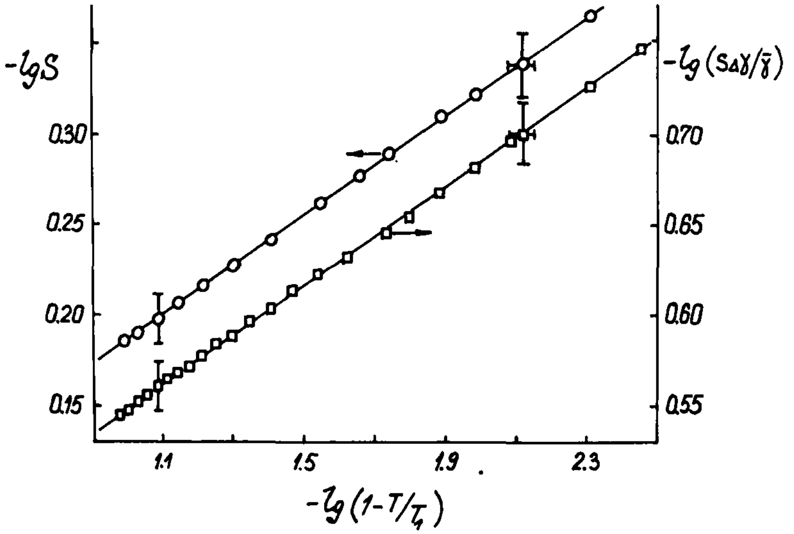


FIGURE 4 Log-Log plots of S and of $S\Delta\gamma/\bar{\gamma}$ (12) at $\lambda = 0.589$ μm versus the reduced temperature for 5BCO.

result of the simultaneous isotropization of macroscopic optical and molecular properties of a liquid crystal.

In order to explain these results we assume that the f-tensor is the same for all molecules of the liquid crystal and is uniaxial in the director frame. Then we can write[10]

$$n^2_{\parallel,\perp} - 1 = 4\pi \mathcal{N} \gamma_{\parallel,\perp} f_{\parallel,\perp}, \tag{14}$$

where $\mathcal{N}$ is the number of molecules per unit volume,

$$\begin{aligned} \gamma_\parallel &= \bar{\gamma} + \frac{2}{3} S\Delta\gamma + \frac{1}{3} G\Delta\gamma^1, \\ \gamma_\perp &= \bar{\gamma} - \frac{1}{3} S\Delta\gamma - \frac{1}{6} G\Delta\gamma^1, \end{aligned} \tag{15}$$

and

$$\begin{aligned} \bar{\gamma} &= (\gamma_{xx} + \gamma_{yy} + \gamma_{zz})/3, \\ \Delta\gamma &= \gamma_{zz} - (\gamma_{xx} + \gamma_{yy})/2, \\ \Delta\gamma^1 &= \gamma_{yy} - \gamma_{xx}. \end{aligned}$$

Using Eq. (15) we can rewrite Eq. (14) in the form

$$\frac{f_\perp}{f_\parallel} = \frac{n_\perp^2 - 1}{n_\parallel^2 - 1} \cdot \frac{1 + 2S\Delta\gamma/3\bar{\gamma} + G\Delta\gamma^1/3\bar{\gamma}}{1 - S\Delta\gamma/3\bar{\gamma} - G\Delta\gamma^1/6\bar{\gamma}}. \tag{16}$$

For the prolonged mesogenic molecules the inequalities $G << S$ (Ref. 15) and $\Delta\gamma^1 < \Delta\gamma$ (Ref. 29) are valid and for the numerical calculations the corresponding terms in Eq. (16) may be neglected. In order to verify Eq. (16), we find the ratio $f_\perp/f_\parallel$ for 5CB at $T_c - T = 10°C$ and $\lambda = 0.589$ μm using the refractive indices $n_{\parallel,\perp}$ from Ref. 18, the value $\Delta\gamma/\bar{\gamma}$ obtained above and use $S = 0.595$ – the average value from the magnetic and radiospectroscopic measurements.[1] The results of the calculation $f_\perp/f_\parallel = 1.09$ is in a good agreement with the experimental value of 1.11 (See Ref 1).

From Eq. (16) we can see that the anisotropy Δf is determined by the optical anisotropy of a liquid crystal as well as by the polarizability anisotropy and molecular orientational ordering. For strongly-polarizable molecules with a high ratio $\Delta\gamma/\bar{\gamma}$ the latter two factors are dominant and we have $f_\perp/f_\parallel > 1$ (Ref. 1). The simultaneous decrease of $\delta\gamma/\bar{\gamma}$ and Δn as a result of the electronic molecular structure change must lead to a rapid isotropization of f which is in accordance with the experimental data obtained. Typical for the homologous series, the decrease of $\Delta\gamma/\bar{\gamma}$ and Δn with the growing length of the flexible chains[15,30] should be accompanied by a decrease of the local field anisotropy. For liquid crystals with small values of $\Delta\gamma/\bar{\gamma}$ (Refs. 2,4) the change of the sign of the anisotropy of Δf from negative to positive is possible in the region $f_\perp/f_\parallel \simeq 1$. The comparison of Eq. (1) with Eq. (16) shows the Lorentz-tensor anisotropy to decrease with the decreasing values $\Delta\gamma/\bar{\gamma}$ and Δn and makes clear the observed tendency of the $L_\perp$ change shown in Table I.

V. CONCLUSION

The suggested method for the experimental determination of the Lorentz-factor tensor can be successfully used for studying uniaxial liquid crystals with molecules of different chemical classes. The experimental data presented above and obtained earlier[1] have shown a strong dependence of the local field tensor f and the Lorentz tensor L on the specific features of the molecular electronic structure. Equation (16) obtained herein may be useful for analysis of the local field anisotropy in liquid crystals of any optical anisotropy. This formula can also be used to calculate the ratio $f_\perp/f_\|$ provided the values of S and $\Delta\gamma/\bar{\gamma}$ are known from independent measurements. It should be pointed out that the correction factors for the experimental data on the absorption dichroism and Raman scattering depend on the ratio $f_\perp/f_\|$ only and not on the components $f_{\|,\perp}$ (See Ref 31). Application of the method discussed to a wide class of impure systems can be expected to answer the question of how the local field depends on the impurity molecular properties and on the liquid crystalline matrix properties. Investigation of the absorption bands in various spectral ranges will give the information on the dispersion of the local field tensor. Finally, the employment of the experimental values of L and f in optical experiments on refractometry, absorption IR and UV spectroscopy, Raman scattering and luminescence may provide new information on the effect of the intermolecular interactions on the orientational-statistical, conformational, electronic and electro-optical molecular properties in the mesophase.

Acknowledgments

The authors would like to express their appreciation to Dr. P. V. Adomenas for providing us with the compound used in this investigation. We are grateful to Prof. L. M. Blinov for support and helpful discussions.

References

1. E. M. Averyanov, V. A. Zhuikov, V. Ya. Zyryanov and V. F. Shabanov, *Zh. Eksp. Teor. Fiz.*, **86**, 2111 (1984).
2. L. Pohl, R. Eidenschink, J. Krause and G. Weber, *Phys. Lett.*, **A60**, 421 (1977); *ibid.*, **A65**, 169 (1978).
3. L. M. Blinov, "Electro- i magnitooptika zhidkikh kristallov" (*in Russian*, Nauka, Moskva, 1978), Chaps. 2, 6 and 8.
4. V. G. Rumyantsev and L. M. Blinov, *Optika i spektroskopiya.*, **47**, 324 (1979).
5. E. M. Averyanov and V. F. Shabanov, *Kristallographiya*, **24**, 184, 992 (1979).
6. V. A. Belyakov and A. S. Sonin, *"Optika kholestericheskikh zhidkikh kristallov"* (*in Russian*, Nauka, Moskva, 1982), Chaps 2 and 6.
7. G. S. Chilaya and L. N. Lisetskii, *Usp. fiz. Nauk.*, **134**, 185 (1981).
8. P. Palffy-Muhoray and D. A. Balzarini, *Can. J. Phys.*, **59**, 375 (1981).
9. W. H. de Jeu and P. Bordewijk, *J. Chem. Phys.*, **68**, 109 (1978).
10. E. M. Averyanov and V. F. Shabanov, *Kristallographiya.*, **23**, 320, 1232 (1978).
11. U. Segre, *Mol. Cryst. Liq. Cryst.*, **90**, 239 (1983).
12. R. Seeliger, H. Haspeko and F. Noack, *Mol. Phys.*, **49**, 1039 (1983).
13. L. G. P. Dalmolen and W. H. de Jeu, *J. Chem. Phys.*, **78**, 7353 (1983).
14. L. G. P. Dalmolen, E. Egberst and W. H. de Jeu, *J. Phys.* (*Paris*)., **45**, 129 (1984).
15. W. H. de Jeu, *"Physical properties of liquid crystalline materials,"* (Gordon and Breach, New York, London and Paris, 1980), chaps. 1, 3 and 4.
16. E. M. Averyanov, *Sov. Phys. Solid State.*, **22**, 1088 (1980).

17. L. M. Blinov, V. A. Kizel, V. G. Rumyantsev and V. V. Titov, *J. Phys.* (*Paris*), *Colloq. C1, Suppl. No3.*, **36**, C1-69 (1975).
18. E. M. Averyanov, V. Ya. Zyryanov, V. A. Zhuikov and Yu. I. Ruoliene, *Zh. Strukt. Khim.*, **24(No5)**, 101 (1983).
19. M. J. Bradshaw, E. P. Raynes, I. Fedak and A. J. Leadbetter, *J. Phys.* (*Paris*)., **45**, 157 (1984).
20. E. M. Averyanov, V. A. Zhuikov, V. Ya. Zyryanovv, L. I. Mineev and V. F. Shabanov, Kristallographiya., **30**, 764 (1985).
21. V. F. Shabanov, V. G. Podoprigora, A. N. Botvitch and V. P. Ermakov, *Kristallographiya.*, **26**, 677 (1981).
22. D. A. Dunmur and R. W. Munn, *Chem. Phys.*, **76**, 249 (1983).
23. G. Pelzl, *Z. Chem.*, **17**, 264 (1977).
24. S. N. Aronishidze, M. N. Kushnirenko, T. S. Piliashvili, G. S. Chilaya and Z. M. Elashvili, *Repts of Georg. Sov. Rep. Acad. Sci.*, **89**, 333 (1978).
25. N.-M. Chao, K. C. Chu and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **81**, 103 (1982).
26. Yu. V. Denisov, V. A. Kizel and E. P. Sukhenko, *Zh. Exp. Teor. Fiz.*, **71**, 679 (1976).
27. D. A. Dunmur and A. E. Tomes, *Mol. Cryst. Liq. Cryst.*, **97**, 241 (1983).
28. H. J. Coles and B. R. Jennings, *Mol. Phys.*, **36**, 1661 (1978).
29. M. F. Vuks, N. B. Rozhdestvenskaya and K. Eidner, *Optika i spectroskopiya.*, **45**, 914 (1978).
30. E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **36**, 193 (1976).
31. E. M. Averyanov, W. Waitkiavichus, A. Ya. Korets, R. Sirutkaitis, A. V. Sorokin and V. F. Shabanov, *Zh. Eksp. Teor. Fiz.*, **76**, 1791 (1979) and references therein from the same authors.