Anisotropy of the local field in uniaxial liquid crystals

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A new method is proposed and implemented experimentally for measuring the components of the Lorentz tensor in uniaxial liquid crystals. This method is not restricted to special objects of study or to a special spectral range. The anisotropy of the local field of a light wave has been studied in the nematic and smectic *A* phases of three liquid crystals of the cyanobiphenyl class. The experimental data are compared with the predictions of theoretical models in the literature.

1. INTRODUCTION

The methods of molecular optics play a special role in research on molecular and structural conversions in liquid crystals. Experiments by refractometry,[1] UV and IR absorption spectroscopy,[2,3] luminescence,[4,5] spontaneous Raman scattering,[6] active Raman scattering,[7] and generation of the second optical harmonic[8,9] yield information on several properties: the second moment $\overline{P}_2 \equiv S$ and the fourth moment $\overline{P}_4$ of the orientational molecular distribution function, the linear and nonlinear molecular susceptibilities, their dependence on the particular features of the intermolecular interaction in the mesophase, the conformation, dynamics, and mutual correlations of the molecules, and their changes upon phase transitions. These characteristics are important both for deriving a theory of the liquid-crystal state and for optimizing the characteristics of a variety of devices which make use of liquid crystals.

A quantitative interpretation of the results of optical experiments requires information on the anisotropy $\Delta f = f_{\|} - f_{\perp}$ of the local-field tensor of the light wave, which relates the amplitude (E^l) of the local field polarizing the molecule to the amplitude (E) of the macroscopic field in the liquid crystal: $E_i^l = f_{ii} E_i$. In the system of the director of uniaxial nematic and smectic *A* and *B* liquid crystals, the uniaxial tensor f has the components

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

where $n_{\|,\perp}$ are the principal refractive indices of the liquid crystal, and $L_{\|,\perp}$ are the components of the tensor Lorentz factor in the directions parallel and perpendicular to the director (SpL = 1). Local-field effects increase in importance for many-photon and nonlinear processes,[4–9] in which the dispersion of the tensor f in various spectral regions due to the dispersion of the refractive indices becomes important with increasing absolute values of the local-field corrections. For this reason, the expression

$$f = (\bar{n}^2 + 2)/3, \qquad (2)$$

which is frequently used and which has a narrow spectral range of applicability in the UV region,[2,10] can lead to an important distortion of the temperature dependence found for orientation-statistical and molecular characteristics of liquid crystals in the visible and IR regions.[1,6]

The problem of a microscopic calculation of the tensor f in a liquid crystal has not yet been solved, since it requires simultaneous consideration of the translational and orientational correlations of anisotropic molecules,[11,12] higher-order multipoles in the molecular polarization,[13] and the nonlocal nature of the molecular polarizability.[14,15] We thus see in the literature, along with isotropic approximation (2), the use of semiempirical methods for calculating the parameters $L_{\|,\perp}$ (Refs. 16 and 17); these methods lead to different signs for the anisotropy of the tensor f in the visible and IR regions: $\Delta f > 0$ (Ref. 16) and $\Delta f < 0$ (Refs. 1–6, 10, and 17). The assumptions underlying the method of Ref. 17 were recently confirmed theoretically,[11,15,18] but it has not been possible to compare theoretical and experimental values of $L_{\|,\perp}$, because the corresponding measurements have not been carried out.

Blinov *et al.*[2] have proposed a method for experimentally determining the components $L_{\|,\perp}$ in a liquid-crystal matrix from the dichroism of the UV absorption of a spherically symmetric impurity molecule. The values found for $L_{\|,\perp}$ at one temperature point in a nematic liquid crystal have yielded $\Delta f = 0$. The spectral interval of the measurements and the dispersion of the values of $n_{\|,\perp}$ correspond to the condition for the applicability of Eq. (2) (Ref. 10). This method was recently used[19] to determine $L_{\|,\perp}$ in a liquid-crystal matrix from the dichroism of the IR absorption of impurity molecules of tetrahedral symmetry. Since there are many factors which could give rise to an induced dichroism in these systems,[3,20,21] an unambiguous interpretation of "probe" experiments is not always possible, and the problem of measuring the anisotropy of the local field in a liquid crystal remains unresolved.

In the present paper we propose a method for experimentally determing the components $L_{\|,\perp}$ in pure and impure uniaxial liquid crystals. This method is not restricted to special objects or to a special spectral range. Section 2 of this paper sets forth the theory of the method. Section 3 describes the objects studied and the experimental procedure. In Section 4 we report the results of the measurements of $L_{\|,\perp}$ in the nematic and smectic phases of three liquid crystals. We discuss the results and compare them with the results calculated from various theoretical models.

2. METHOD FOR DETERMINING THE ANISOTROPY OF THE LOCAL FIELD IN UNIAXIAL LIQUID CRYSTALS

We selected for study an isolated band, of the intrinsic or impurity absorption of the liquid crystal in the IR, visual, or UV part of the spectrum. This band is insensitive to possible changes in the conformation of the molecules in the liquid-crystal phase. We use the results of two independent measurements of the dichroism, $N_p = D_\parallel / D_\perp$ and $N_h = D_\perp / D_i$, in cells with molecules in the planar and homeotropic orientations, respectively; here $D_{\parallel,\perp,i}$ are the integrated optical densities of the sample in the absorption band under study for light polarized parallel and perpendicular to the director and in the isotropic liquid. For these experimental configurations the values of the order parameter S of the long axes of the molecules are given by[2,3]

$$S_p S_\beta = \frac{N_p g_p - 1}{N_p g_p + 2}, \quad S_h S_\beta = 1 - g_h N_h. \tag{3}$$

Here $S_\beta = (3\cos^2\beta - 1)/2$, β is the angle between the direction of the dipole moment of the electronic or vibrational transition and the long axis of the molecule, and the correction factors are

$$g_p = \frac{n_\parallel}{n_\perp}\left(\frac{f_\perp}{f_\parallel}\right)^2, \quad g_h = \frac{\rho_i n_\perp}{\rho n_i}\left(\frac{f_i}{f_\perp}\right)^2, \tag{4}$$

where ρ and ρ_i are the densities of the liquid crystal and of the isotropic liquid. For the intrinsic absorption bands of a liquid crystal the refractive indices $n_{\parallel,\perp,i}$ in (1) and (4) are background indices within the band of interest, while for an impurity absorption band they pertain to the liquid-crystal matrix.

It can be seen from (3) that the components $L_{\parallel,\perp}$ can be determined experimentally with $S_p = S_h = 0$ or $S_\beta = 0$; we then have $g_p = 1/N_p$. The first of these possiblilities was implemented experimentally in Ref. 2 for the dichroism N_p of the absorption of a spherically symmetric "probe" molecule in a liquid-crystal matrix. The second possibility is difficult to implement because the condition $\beta = 54.7°$ must be met quite accurately.

The joint use of expressions (3) gives us a universal method for experimentally determining the components $L_{\parallel,\perp}$. The idea underlying the method is that the local-field correction to the order parameter determined from the dichroism depends on the orientation of the molecules in the cell; planar or homeotropic.[1] For simplicity we set $S_\beta = 1$, and we expand the right sides of Eqs. (3) in the small parameter $\Delta f / f_{\parallel,\perp}$. Restricting the discussion to the linear approximation, we find

$$\begin{aligned} S_p &= S_{\mathrm{Ip}} - {}^2/_3(1 - S_{\mathrm{Ip}})(1 + 2S_{\mathrm{Ip}})\Delta f/f_\parallel, \\ S_r &= S_{\mathrm{Ih}} - {}^2/_3(1 - S_{\mathrm{Ih}})\Delta f/f_\perp, \end{aligned} \tag{5}$$

where the quantities $S_{\mathrm{Ip},h}$ correspond to calculations from Eqs. (3) and (4) in the isotropic approximation ($\Delta f = 0$). We see from (5) that for the typical values $S_{\mathrm{Ip},h} = 0.3$–0.7 the correction to S_I for the local-field anisotropy is 1.5–2.5 times greater in measurements with a planar orientation of the molecules in the cell than in measurements with a homeotropic orientation. Accordingly, if we actually have $\Delta f \neq 0$, then the use of isotropic approximation (2) to analyze the results of these two experiments will give us different values for S_I, as we in fact observe experimentally (as discussed below). Since the order parameter S is a characteristic of the intermolecular interactions and must not depend on the experimental geometry, the actual values of $L_{\parallel,\perp}$ must satisfy the two equations

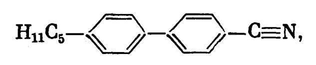
$$(N_p g_p - 1)/(N_p g_p + 2) = 1 - g_h N_h, \quad \mathrm{Sp}\, L = 1. \tag{6}$$

If the values of $N_{p,h}$, ρ, ρ_i, and $n_{\parallel,\perp,\mathrm{i}}$ are known, the solution of the first of Eqs. (6) can be sought conveniently by varying one of the parameters $L_{\parallel,\perp}$ until the left and right sides of the equation agree within the specified error. This procedure can be checked by comparing the values found for $S_p = S_h$ with the results of independent measurements which do not require consideration of local-field effects.

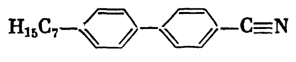
This method has the advantage that intrinsic or impurity absorption bands of the liquid crystals in various parts of the spectrum can be used. One can measure the parameters $L_{\parallel,\perp}$ for separate fragments of the molecules and use the associated normal vibrations and the corresponding characteristic absorption bands. The determination of $L_{\parallel,\perp}$ does not require information on the angle β for the moments of the corresponding transitions.

3. TEST OBJECTS AND EXPERIMENTAL PROCEDURE

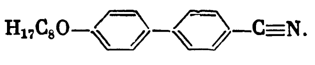
Experiments were carried out on three liquid crystals: 4-*n*-pentyl-4′-cyanobiphenyl (5CB; C 22.5° N 35.0° I),



4-*n*-heptyl-4′-cyanobiphenyl (7CB; C 29.1° N 41.4° I),



and 4-*n*-octyloxy-4′-cyanobiphenyl (80CB; C 53.0° Sm *A* 65.8° N 78.8 I),



In parentheses here we have given the Celsius temperatures of the phase transitions from the crystal (C) to the smectic *A* phase (Sm *A*) to the nematic phase (N) and to the isotropic liquid (I). Several factors made these particular compounds convenient for study. They are typical liquid crystals with a large positive dielectric anisotropy and are widely used in a variety of electrooptic devices and in physical and chemical research.[22] The IR spectrum of these liquid crystals has an isolated characteristic absorption band with $\lambda_{\max} = 4.5\,\mu\mathrm{m}$ which is convenient for interpretation of the experimental results. This band belongs to a normal valence vibration of the C≡N bond oriented along the long molecular axis ($S_\beta = 1$). The orientational order of the cyanobiphenyls has been studied in detail previously by methods which do not require corrections for the local field: the NMR method (5CB; Ref. 23) and measurements of the diamagnetic anisotropy (5CB and 7CB; Ref. 24). It is thus possible to test the values found for $L_{\parallel,\perp}$ by checking to see whether the values of $S_p = S_h$ agree with independent measurements. Finally, a study of 80CB yields information on the changes in the local-field anisotropy at the N-Sm *A* phase transition.

A reproducible planar orientation of the molecules in flat fluorite sandwich cells (for the IR spectroscopy) and wedge-shaped glass sandwich cells (for the refractometry) was achieved by treating the inner surfaces of the cells by the following procedure: directional polishing with diamond paste; cleaning; deposition of a film of polyvinyl alcohol from an aqueous solution; rubbing with paper along the direction of the original polishing. This procedure yields a planar orientation of the nematic and smectic A phases; repeated Sm $A \rightleftarrows$N transitions do not effect the quality of the orientation of the sample in either phase. The customary procedure for obtaining a planar orientation of the smectic A phase is to cool the nematic phase slowly in a magnetic field parallel to the director.[25] Homeotropically oriented layers of liquid crystals for measurements of the dichroism N_h were prepared by the method described in Ref. 3. The quality of the orientation of the samples was monitored by using a polarizing microscope to make sure that there were no disclinations. The error in the setting and regulation of the temperature of the samples during the experiments was ± 0.1°C.

The refractive indices $n_{\parallel,\perp,i}$ in the mesophase and in the isotropic-liquid phase of the samples were measured on a refractometer and also by the wedge method of Ref. 1 at four light wavelengths, within an error of $2\cdot10^{-3}$. The results for the 5CB and 7CB crystals are reported in Ref. 1, while those for 8OCB are shown in Fig. 1 of the present paper. The values of $n_{\parallel,\perp,i}$ in the literature for 8OCB refer only to the nematic phase[26]; and they agree with the results shown in Fig. 1 for $\lambda = 0.589\,\mu$m. The lines closest to the C≡N vibration band (of half-width ≈ 10 cm^{-1}) in the IR spectrum of the cyanobiphenyls are 300–600 cm^{-1}) away, so that the background values $n^b_{\parallel,\perp,i}$ for this band are determined primarily by electron resonances. Analysis of the experiment shows that the dispersion of the refractive indices in the mesophase and in the isotropic liquid of these samples in the region $\lambda = 0.735$–$0.49\,\mu$m can be approximated well by the simple dispersion relation

$$n_{\parallel,\perp,i}=1+\lambda^2 A_{\parallel,\perp,i}/(\lambda^2-B_{\parallel,\perp,i}). \tag{7}$$

The parameters A and B depend on the reduced temperature $\Delta T = T_c - T$, the polarization, and the approximation interval (λ_j, λ_k). To calculate $n^b_{\parallel,\perp,i}$ at $\lambda = 4.5\,\mu$m we use the values found for the parameters A and $B_{\parallel,\perp,i}$ from the experimental values of $n_{\parallel,\perp,i}$ at each fixed temperature ΔT, taking an average of the three pairs of values (λ_j, λ_k) from the set $\lambda = 0.49, 0.589, 0.735\,\mu$m. The deviation of the values calculated for $n_{\parallel,\perp,i}$ from (7) from the experimental values for 8OCB in this spectral range does not exceed $5\cdot10^{-3}$ (in the case of $n_\parallel$) or $2\cdot10^{-3}$ $(n_\perp)$ at $\Delta T = 20$ °C or $2\cdot10^{-3}$ $(n_{\parallel,\perp})$ at $\Delta T = 1$°C. In other words, the discrepancies correspond to the errors in the measurements of $n_{\parallel,\perp,i}$ The extension of approximation (7) to shorter wavelengths degrades the agreement between theory and experiment, because damping is ignored in the denominator of the second term on the right side of (7).

We measured the dichroic ratios N_p and N_h of liquid-crystal samples with planar and homeotropic orientations and of identical thickness ($10\,\mu$m). At this thickness, boundary effects are negligible and do not influence the bulk orientational-statistical properties of the liquid crystals.[6] The intense, isolated IR absorption band of the valence vibration in the liquid-crystal and isotropic phases was recorded in a parallel light beam on a Specord 75IR spectrophotometer with a K201 null-method chart recorder for logarithmic recording with an integrator. The rate (v) at which the spectrum was scanned, the slit width (σ), and the time constant (t) of the measuring instrument were chosen to minimize the shape distortion of the IR absorption line: $tv/\sigma \approx 0.21$ (Ref. 27).

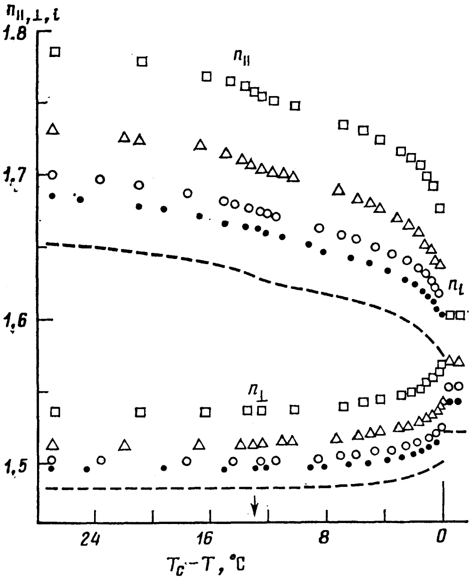


FIG. 1. Temperature dependence of the refractive indices $n_{\parallel,\perp,i}$ of the liquid crysal 8OCB at several wavelengths. □—$\lambda = 0.42$; △—0.49; ○—0.589; ●—0.735 μm. The dashed lines show values of $n^b_{\parallel,\perp,i}$ calculated from (7) for $\lambda = 4.5\,\mu$m; T_c is the temperature of the nematic-isotropic phase transition; and the arrow is the temperature of the transition from the nematic phase to the smectic A phase.

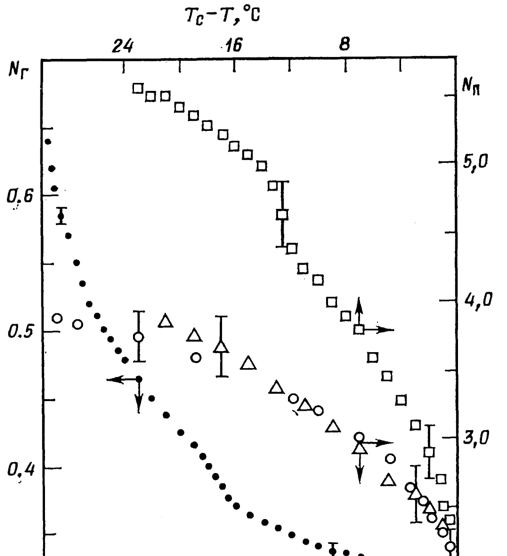


FIG. 2. Temperature dependence of the dichroic ratios N_p (△, ○, □) and N_h (●) for several liquid crystals. △—5CB; ○—7CB; □, ●—8OCB.

The measured integrated optical densities $D_{\parallel,\perp,i}$ in the mesophase and the isotropic liquid were corrected by the method of Ref. 28 for the finite slit width of the measuring instrument. To separate the components $D_{\parallel,\perp}$ for the samples in the planar orientation we used a polarizer with an efficiency of 98.5% between the sample and the entrance slit of the spectrometer. To avoid the depolarizing effect of the measuring instrument, we oriented the axis of the sample at 45° from the slit of the measuring instrument. The measured dichroic ratio was corrected by the method of Ref. 29 to allow for the imperfections of the polarizer. In cells holding molecules in the homeotropic orientation the light propagated along the optical axis, and we were able to measure the absorption spectrum polarized normal to the director without using a polarizer. This experimental geometry also minimizes the depolarizing effect of multiple scattering of light at fluctuations of the director; this scattering is significant in the polarization measurements of samples in the planar orientation. Figure 2 shows the temperature dependence of the dichroic ratios $N_{p,h}$ averaged over five measurements taken with newly prepared samples for each crystal studied. All the corrections listed above have been made. The temperature dependence of N_h for 5CB and 7CB is given in Ref. 3. The values of ρ and ρ_i required for the calculations from Eqs. (3)–(6) were taken from Refs. 30 and 31.

4. EXPERIMENTAL RESULTS AND DISCUSSION

The "experimental" values of S have some uncertainty because of the particular model chosen to calculate the components of the tensor L, as can be seen from (3) and (4). A convenient zeroth approximation is the isotropic approximation $\Delta f = 0$, which corresponds to the following critical value for the anisotropy $\tau = 1/3 - L_\perp$ of the tensor L (Ref. 10):

$$\tau_{\text{cr}} = -\frac{n_\parallel^2 - n_\perp^2}{9[\bar{n}^2 - 1 + (n_\parallel^2 - n_\perp^2)/3]}, \tag{8}$$

where $\bar{n}^2 = (n_\parallel^2 + 2n_\perp^2)/3$. The exact expression for the components $f_\parallel = f_\perp = \bar{f}$ in this case is

$$\bar{f} = \frac{\bar{n}^2 + 2}{3} - \frac{2(n_\parallel^2 - n_\perp^2)^2}{27[\bar{n}^2 - 1 + (n_\parallel^2 - n_\perp^2)/3]} \tag{8'}$$

and differs from the customary expression (2). The critical parameter τ_{cr} depends on the wavelength of the light and on the reduced temperature ΔT. The sign, values, and dispersion of the anisotropy Δf at a fixed ΔT depends on the relation between $\tau_{\text{cr}}(\lambda,\Delta T)$ and the actual anisotropy $\tau(\Delta T)$ and on the dispersion of the parameter τ_{cr}. Two cases are possible here.[10]

1. If the condition $|\tau_{\text{cr}}(\lambda,\Delta T)| > |\tau(\Delta T)|$ holds in the visible spectrum, where optical experiments are ordinarily carried out, we have $\Delta f(\lambda,\Delta T) > 0$. If $|\tau_{\text{cr}}(\lambda,\Delta T)|$ increases (decreases) as λ is varied, the anisotropy Δf increases (decreases). For molecules with a highly polarizable structure including π-conjugate fragments, an increase in $|\tau_{\text{cr}}(\lambda,\Delta T)|$ is observed as λ is reduced and as we approach the band (λ_0) of the long-wavelength electron transition, which is usually polarized along the long molecular axis. For molecules with a weakly polarizable structure, e.g., one which contains cyclohexane rings, the value of $|\tau_{\text{cr}}(\lambda,\Delta T)|$ may remain constant or decrease with decreasing λ because of the weak dispersion of the birefringence. In the long-wavelength part of the spectrum, the anisotropy of Δf decreases, but because of the weak dispersion of $n_{\parallel,\perp}$ the spectral point λ_{cr} at which we have $\tau_{\text{cr}}(\lambda_{\text{cr}},\Delta T) = \tau(\Delta T)$ and $\Delta f = 0$ may be unattainable experimentally.

2. If the condition $|\tau_{\text{cr}}(\lambda,\Delta T)| < |\tau(\Delta \tau)|$ holds in the visible region, then $\Delta f < 0$. Now the anisotropy $|\Delta f|$ decreases (increases) with increasing (decreasing) $|\tau_{\text{cr}}(\lambda,\Delta T)|$ as λ is changed. For highly polarizable molecules such as those studied in the present experiments, the quantity $|\Delta f|$ decreases in the limit $\lambda \to \lambda_0$ and may vanish at an experimentally accessible point λ_{cr}, since the dispersion of the refractive indices $n_{\parallel,\perp}$ and of the parameter $|\tau_{\text{cr}}(\lambda,\Delta T)|$ is large near λ_0. This effect was observed experimentally in Ref. 2. We should expect an increase in the anisotropy $|\Delta f|$ at long wavelengths, and it was for this reason that we selected the IR region for an experimental test of the method proposed here.

Let us examine the experimental data on 5CB in Fig. 3. A calculation of the order parameter from Eqs. (3), (4), and (8′) in the isotropic approximation leads to very disparate values $S_{\text{Ip}} < S_{\text{Ih}}$. We see from (5) that this situation corresponds to $\Delta f < 0$ for the real anisotropy of the tensor f in this crystal, and we are dealing with the second of the two cases which we just discussed. The critical parameter $L_{\perp\text{cr}}$ increases as λ decreases from 4.5 to 0.42 μm (Fig. 3b), and the anisotropy $|\Delta f|$ decreases correspondingly. The values of $L_\perp$ corresponding to the solution of Eqs. (6) and to the real an-

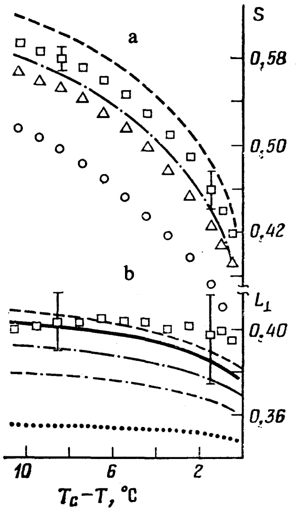


FIG. 3. a: Temperature dependence found for the orientational-order parameter S in the nematic liquid crystal 5CB by various methods. ○, △—Values of S_{Ip} and S_{Ih}, respectively, calculated from the IR dichroism (N_p and N_h) from Eqs. (3) in the isotropic approximation ($\Delta f = 0$); □—values of $S_p = S_h$ reflecting the local-field anisotropy with components $L_{\parallel,\perp}$ which satisfys Eqs. (6). The dashed and dot-dashed lines are interpolations of the results of magnetic[24] and NMR[23] measurements. b: Temperature dependence of experimental (□) and theoretical values of $L_\perp$ in the nematic liquid crystal 5CB. Solid line—Calculations of $L_\perp$ from Eqs. (10)–(12); dashed line—calculation of $L_\perp$ from Eqs. (10) and (13); dot-dashed and dot-dash-dashed lines—calculation of $L_{\perp\text{cr}}$ from Eq. (8) for $\lambda = 0.42$ and 4.5 μm, respectively; dotted line—calculation from Eq. (14).

isotropy of the local field in this crystal exceed the critical parameters $L_{\perp\mathrm{cr}}$ for all values of ΔT, and the anisotropy satisfies $\Delta f < 0$ in the interval 4.5–0.42 μm (Fig. 3b). At shorter wavelengths, the tensor f is approximately isotropic, within the experimental errors. The value of λ_{cr} is thus attainable in principle for 5CB and lies at $\lambda < 0.42$ μm.

The values found for $S_p = S_h$ with allowance for the local-field anisotropy agree within the experimental errors with independent data obtained by an NMR method[23] and by magnetic measurements,[24] lending support to the values found for the parameters $L_{\parallel,\perp}$ here. According to (5), the values of $S_p = S_h$ diverge from S_{Ih} to a far lesser extent than they diverge from S_{Ip}, even in the IR region, where the anisotropy of $|\Delta f|$ is at its maximum. In the visible and UV parts of the spectrum, with molecules in the homeotropic orientation, rather accurate values $S_{\mathrm{Ih}} \approx S_h$ can be found from the dichroism of N_h even in the isotropic approximation.

The experimental results on 7CB shown in Fig. 4 are evidence that the local field is more anisotropic in this crystal than in 5CB. Even at $\lambda = 0.42$ μm the values of $L_{\perp\mathrm{cr}}$ are significantly smaller than the experimental values; we have $\Delta f < 0$; and the spectral point (λ_{cr}) corresponding to the isotropy of the tensor f may be unattainable experimentally because of the optical absorption in this region. The order parameter $S_p = S_h$ found from the IR dichroism with allowance for the local-field anisotropy agrees completely with the results of magnetic measurements[24] over the entire range of ΔT. Since the magnitude and form of the local-field corrections are different for the independent optical and spectral measurements,[5–10] we could adopt as a further test of the validity of this new method the agreement between the values of S given by the different optical methods when the values found experimentally for the parameters $L_{\parallel,\perp}$ are used.

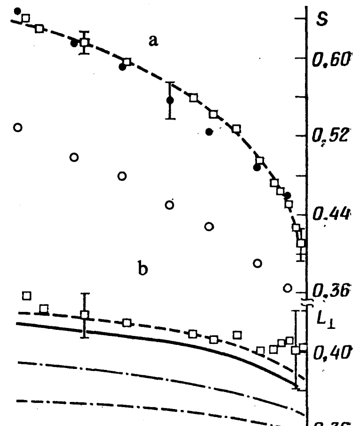


FIG. 4. a: Temperature dependence of the order parameter S in the nematic liquid crystal 7CB found by various methods. □—From the dichroism of the IR absorption with allowance for the local field anisotropy; ○—from the Raman effect without allowance for the local-field anisotropy[32]; ●—the same, but with allowance for the local-field anisotropy in accordance with Eq. (9); dashed line—interpolation of the results of magnetic measurements.[24] b: Temperature dependence of the experimental and theoretical values of $L_\perp$ in the nematic liquid crystal 7CB. The notation is the same as in Fig. 3b.

The order parameter S for 7CB was determined in Ref. 32 from data on the Raman scattering by the valence vibration of the C≡N bond in the approximation of an isotropic local field. From Fig. 4a we see that the values found for S_I in this manner are substantially lower than those found in the present study. We can show that this difference is erased by incorporating the anisotropy of the local field. The C≡N and C≡C valence vibrations have a highly anisotropic uniaxial Raman-effect tensor with transverse and longitudinal components forming a ratio[6] $r = \gamma_\perp'/\gamma_\parallel' = 0.05$–$0.07$. In analyzing the effect of the anisotropy Δf on the values found for S by means of the Raman effect we can set $r = 0$, since a variation of r over the interval 0–0.1 has essentially no effect on the value of S (Ref. 33). In the linear approximation in Δf, and for the scattering geometry used in Ref. 32, the general expressions of Ref. 6 give us

$$S = S_I - 2\,\frac{3(1-S_I)\rho_1 + 4(1+2S_I)\rho_2}{3\rho_1 + 12\rho_1\rho_2 + 8\rho_2}\,\frac{\Delta f}{f}, \tag{9}$$

where $\rho_{1,2}$ are the degrees of polarization of the Raman lines of a liquid crystal in the planar orientation (R_2/C_n and R_1/C_n in the notation of Ref. 32). Using the parameters S_I and $\rho_{1,2}$ (Ref. 32) and of the experimental values of $L_{\parallel,\perp}$ shown in Fig. 4b to calculate S from (9), we find that the results found by the three independent methods agree within the experimental errors (Fig. 4a).

In 8OCB the values of $L_{\perp\mathrm{cr}}$ for $\lambda = 0.42$ μm agree approximately with the experimental values, especially in the smectic A phase. In the region $\lambda \lesssim 0.42$ μm the tensor f in 8OCB is thus essentially isotropic. The temperature dependence of $L_\perp$ is essentially the same as that of $L_{\perp\mathrm{cr}}$ in this crystal. We see from Fig. 5a that, as in 7CB, the discrepancy between the values of $S_p = S_h$, on the one hand, and the parameters S_I measured by the Raman method,[32] on the other, can be eliminated by making a local-field correction from (9) and the experimental values of $L_{\parallel,\perp}$ (Fig. 5b).

The transition from the nematic phase to the smectic A

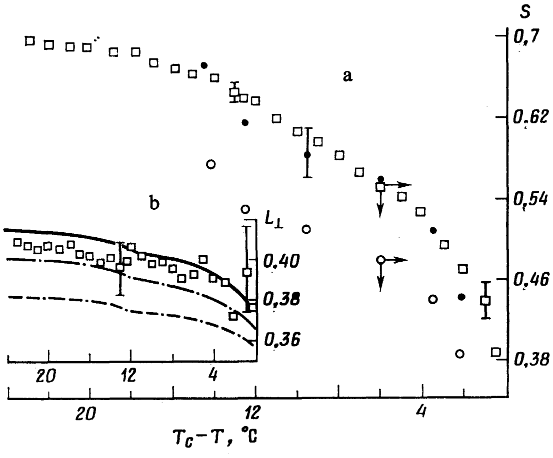


FIG. 5. Temperature dependence of the order parameter S (a) and of the component $L_\perp$; (b) of the Lorentz tensor in the mesophase of 8OCB. The notation is the same as in Figs. 4a and 4b.

phase is seen clearly on the temperature dependence $N_p(\Delta T)$ (Fig. 2), but the parameters $L_{\parallel,\perp}$ of the local field and the order parameter $S_p = S_h$ (Figs. 5a and 5b) are insensitive to this transition, within the experimental errors. This result agrees with the known fact that the transition from the nematic phase to the smectic A phase in this crystal is approximately continuous.[31] The increase in the translational order in the smectic A phase of 80CB does not influence the local-field factors, possibly implying both a small amplitude of the density wave of the smectic layers[31] and a predominant role of orientational order and of the short-range molecular surroundings in forming the local field.

The two latter possibilities have been used in models[10,17] for determining the magnitude and temperature dependence of the components $L_{\parallel,\perp}$ in uniaxial liquid crystals. It is assumed that in the liquid-crystal phase, on the average over all possible orientations, the molecule is in a spheroidal effective Lorentzian cavity whose shape is determined by the orientational-statistics properties of the mesophase. In a completely ordered sample ($S = 1$) the shape of the cavity would correspond to a molecular spheroid whose semiaxes $a < c$ can be calculated from a molecular model. The corresponding component $L_{\perp\max}$ is determined by the ratio $m = c/a$:

$$L_{\perp\max}=\frac{m}{2(m^2-1)}\left[m-\frac{1}{2(m^2-1)^{1/2}}\ln\frac{m+(m^2-1)^{1/2}}{m-(m^2-1)^{1/2}}\right]. \tag{10}$$

If $S \neq 1$, the long axis of the spheroidal cavity in the liquid crystal is along the director, the cavity is less anisotropic in shape than is the molecule, and the temperature dependence of τ can be approximated by

$$\tau=\tau_{\max}\Delta n/\Delta n_{\max}. \tag{11}$$

The birefringence $\Delta n_{\max}$ of a completely ordered sample is determined from the temperature dependence of Δn, which can be approximated well for known nematic liquid crystals by

$$\Delta n=\Delta n_{\max}(1-T/T_1)^{\beta}, \tag{12}$$

where T_1 and β are adjustable parameters. The parameters $\tau(\Delta T)$ found from Eqs. (11) and (12) are essentially independent of the wavelength (λ) at which Δn is measured. The use of this approach to determine the parameters $L_{\parallel,\perp}$ has made it possible to incorporate the anisotropy of the local field in experiments carried out to determine S from refractometry,[1,10,17] luminescence,[5] the Raman effect,[6] and absorption UV and IR spectroscopy.[6,34,35] The results found from optical experiments agree with each other and with the results of independent measurements which do not require a local-field correction.

Figures 3b–5b show the behavior $L_\perp(\Delta T)$ found by this method. The molecular parameters a and c required for calculations from (10) were taken from Refs. 31 and 36. The particular values used correspond to pairings of molecules with overlapping antiparallel aromatic structures. It can be seen from these figures that the calculated parameters agree with the experimental values within the errors. The discrepancies in the results near T_c might be due to both the neglect of short-range molecular correlations and the depolarization of the spectrum in cells with molecules in the planar orientation (this depolarization is caused when the light passing through the sample is scattered by thermal fluctuations of the director). The latter effect leads to an effective decrease in the measured dichroism N_p and to an overestimate of $L_\perp$ by (6). The model-based values of $L_\perp$ correspond to the case $\Delta f < 0$ in the region $\lambda = 0.42$–$4.5\ \mu$m.

A theoretical framework has recently been developed in the molecular-statistics theory[11] and a phenomenological theory[18] for the assumptions underlying this model-based approach to the calculations of $L_{\parallel,\perp}$. The following refinement of approximation (11) has been derived:

$$\tau=\tau_{\max}S. \tag{13}$$

Since the proportionality $\Delta n \propto S$ holds quite accurately,[17] the difference between the results calculated for τ from (11) and (13) is determined by the difference between the relative and absolute values of S in the mesophase—a difference which is usually a few percent.[35,37] It can be seen from Figs. 3b and 4b that the discrepancy between the values calculated for $L_\perp$ from Eqs. (11) and (13) is smaller than the error in the experimental determination of $L_\perp$.

We turn now to an analysis of the Sauper-Maier-Neugebauer model,[16] which is frequently used to determine the components $L_{\parallel,\perp}$. This model is based on the assumption that the average polarizability $\overline{\gamma}$ of the molecules is independent of their structural order and independent of the state of aggregation of the medium. The component $L_\perp$ is the solution of the equation

$$\frac{\rho_i}{3\rho}\left[\frac{n_\parallel^2-1}{1+(1-2L_\perp)(n_\parallel^2-1)}+\frac{2(n_\perp^2-1)}{1+L_\perp(n_\perp^2-1)}\right]=\frac{n_i^2-1}{n_i^2+2}. \tag{14}$$

Figures 3b and 4b show calculations of $L_\perp(\Delta T)$ for 5CB and 7CB from the Sauper-Maier-Neugebauer model. The values of $L_{\parallel,\perp}$ depend only slightly on the wavelength of the light at which the refractive indices $n_{\parallel,\perp,i}$ used in (14) are measured. For both crystals we find $L_\perp < L_{\perp\mathrm{cr}}$, which corresponds to the condition $\Delta f > 0$; the anistropy of the tensor f increases with decreasing λ. It can be seen from (5) and (9) that the Sauper-Maier-Neugebauer model predicts negative corrections to the values of S_I found from the dichroism of the absorption and from the Raman effect and also from refractometry.[10,17] The discrepancy between the values of S_{Ip} and S_{Ih} according to this model is even greater than in the isotropic approximation. The *a priori* assumption that $\overline{\gamma}$ is constant in the Sauper-Maier-Neugebauer model is thus equivalent to specifying an absolute value and a temperature dependence of the components $L_{\parallel,\perp}$ which contradict experiment. An analogous cause-and-effect relationship between the form of the local-field tensor and the dependence of $\overline{\gamma}$ on the density was established in Ref. 38 for isotropic liquids.

We will conclude by pointing out several problems which can be solved by the method proposed here. The value $L_\perp = 0.4$ measured[2] by optical probing of large spherical impurity molecules in a nematic liquid crystal far from T_c agrees with the results of the present study. For small impurity molecules of tetrahedral symmetry, on the other hand, this method has yielded[19] $L_\perp < L_{\perp\mathrm{cr}}$ in the IR region, in contradiction of the results of the present study. Since the method proposed here for determining $L_{\parallel,\perp}$ is not restricted to objects of a special type, its application to a large number of impurity systems will make it possible to experimentally resolve the fundamental question of how the local-field anisotropy at an impurity depends on the properties of the impurity molecule and of the anisotropic host.[13,39] Furthermore, it will be interesting to determine the degree of anisotropy of the local field for the end fragments of flexible alkyl chains, which are far less ordered than aromatic molecules. Finally, uniaxial liquid crystals with a slight optical anisotropy and a high orientational order, which play the important role of anisotropic hosts in research in physical chemistry, are of considerable interest in this connection.[40]

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