STATISTICAL, NONLINEAR, AND SOFT MATTER PHYSICS

Long-Range Orientational Order, Local-Field Anisotropy, and Mean Molecular Polarizability in Liquid Crystals

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Abstract—The problems on the relation of the mean effective molecular polarizability $\bar{\gamma}$ to the long-range orientational order of molecules (the optical anisotropy of the medium) in uniaxial and biaxial liquid crystals, the local anisotropy on mesoscopic scales, and the anisotropy of the Lorentz tensor L and the local-field tensor f are formulated and solved. It is demonstrated that the presence of the long-range orientational order of molecules in liquid crystals imposes limitations from below on the molecular polarizability $\bar{\gamma}$, which differs for uniaxial and biaxial liquid crystals. The relation between the local anisotropy and the molecular polarizability $\bar{\gamma}$ is investigated for calamitic and discotic uniaxial liquid crystals consisting of lath- and disk-shaped molecules. These liquid crystals with identical macroscopic symmetry differ in the local anisotropy and the relationships between the components $L_{\parallel} < L_{\perp}, f_{\parallel} < f_{\perp}$ (calamitic) and $L_{\parallel} > L_{\perp}, f_{\parallel} > f_{\perp}$ (discotic) for an electric field oriented parallel and perpendicular to the director. The limitations from below and above on the molecular polarizability $\bar{\gamma}$ due to the anisotropy of the tensors L and f are established for liquid crystals of both types. These limitations indicate that the molecular polarizability $\bar{\gamma}$ depends on the phase state and the temperature. The factors responsible for the nonphysical consequences of the local-field models based on the approximation $\bar{\gamma} = \text{const}$ are revealed. The theoretical inferences are confirmed by the experimental data for a number of calamitic nematic liquid crystals with different values of birefringence and the discotic liquid crystal Col_{ho}.

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1. INTRODUCTION

The self-organization of molecules into an anisotropic molecular ensemble (crystal, liquid crystal, Langmuir–Blodgett film, etc.) with long-range (uniaxial or biaxial) order of molecules and optical anisotropy of the medium is accompanied by a change in the effective molecular polarizability tensor γ due to intermolecular interactions of the short- and long-range orders. The effective molecular polarizability tensor γ is an indicator of changes in polarization, electronic structure, and molecular conformation in the medium, as well as in intermolecular interactions, which reflect structural transformations of the short- and long-range orders. It is reasonable to expect that there are limitations on the polarizability tensor γ due to the long-range orientational order of molecules and specific features of the local anisotropy of liquid crystals as a general model of anisotropic statistically ordered molecular media. To date, these problems have not been formulated and the paradigm of experimental and theoretical works on the molecular optics and physics of liquid crystals (like other anisotropic molecular media) has been represented by the equality [1]

$$\bar{\gamma}_i = \bar{\gamma} = \text{const} \qquad (1)$$

for the mean molecular polarizabilities in the isotropic ($\bar{\gamma}_i$) and liquid-crystal ($\bar{\gamma}$) phases. The use of relationship (1) in the refractometry of liquid crystals in the framework of different approaches [2–5] has revealed nonphysical consequences that follow from experimental data [5–7]; however, the factors responsible for these consequences remain unclear. Although a number of theoretical and experimental works indicate that relationship (1) is violated as a result of intermolecular interactions and the transformation of the conformation or the electronic structure of molecules in liquid crystals [6–8], the change in the paradigm "$\bar{\gamma} = \text{const}$" requires rigorous limitations on the quantity $\bar{\gamma}$ or the ratio $\bar{\gamma}/\bar{\gamma}_i$, which can be verified experimentally. In [9], we revealed that there is a strong nonlinear relation of the polarizability tensor $\bar{\gamma}$ to the anisotropy of the Lorentz tensor L and the local-field tensor f in uniaxial liquid crystals; we established rigorous limitations from below on the ratio $\bar{\gamma}/\bar{\gamma}_i$, which suggest that relationship (1) is inadequate. The dependence $\Delta f(\bar{\gamma})$ offers a clue to explaining and eliminating nonphysical consequences of relationship (1) and indicates the

direction in which new limitations on the ratio $\bar{\gamma}/\bar{\gamma}_i$ should be sought.

This work is devoted to the development and generalization of the approach proposed in [9] to the investigation of the relation of the molecular polarizability $\bar{\gamma}$ to the orientational ordering of molecules and the anisotropy of the tensors L and f in uniaxial and biaxial calamitic and discotic liquid crystals consisting of lath- and disk-shaped molecules. In liquid crystals, the molecular packing and the local anisotropy are determined by the steric repulsion of molecules and the molecular shape. The difference in the local anisotropy of uniaxial calamitic (nematics N, smectics SmA, SmB) and discotic (nematics N_D, discotics $Col_{h(o,d)}$) liquid crystals manifests itself in the relationships $L_\parallel < L_\perp, f_\parallel < f_\perp$ (calamitic) and $L_\parallel > L_\perp, f_\parallel > f_\perp$ (discotic) between the components of the tensors L and f for an electric field oriented parallel ($\parallel$) and perpendicular ($\perp$) to the director **n** [6, 7]. The known methods for experimentally determining the components L_j for liquid crystals of both types [6, 7, 10] make it possible to use the values of L_j as characteristics of the local anisotropy of these objects.

In Section 2, we establish the limitations from below on the ratio $\bar{\gamma}/\bar{\gamma}_i$ due to the occurrence of the long-range orientational order of molecules in uniaxial liquid crystals. In Section 3, we investigate the relation of the molecular polarizability tensor $\bar{\gamma}$ to the tensors L and f in uniaxial calamitic and discotic liquid crystals. We reveal the factors responsible for the nonphysical consequences of approximation (1) as it is used in the framework of different approaches [2–5], and we determine the conditions for eliminating these consequences and limitations (following from them) on the ratio $\bar{\gamma}/\bar{\gamma}_i$ from below and above. Section 4 involves the experimental verification of the results obtained for calamitic nematic liquid crystals with different values of birefringence and the discotic liquid crystal Col_{ho}. In Section 5, we summarize the main results and conclusions.

2. LONG-RANGE ORIENTATIONAL ORDER OF MOLECULES AND THE MOLECULAR POLARIZABILITY $\bar{\gamma}$

Let us consider an optically biaxial liquid crystal with point symmetry group D_{2h} (biaxial nematics N_b, smectics SmA_b), C_{2h} (smectic SmC), or D_2 (quasi-nematic layer of cholesterics) consisting of molecules with point symmetry group D_{2h}, C_{2D}, or D_2. The intrinsic coordinate system of matrices $S_{jk,\alpha\alpha}$ is chosen as the laboratory coordinate system ($j, k = X, Y, Z$), and the intrinsic coordinate system of matrices $S_{jj,\alpha\beta}$ is chosen

as the molecular coordinate system ($\alpha, \beta = x, y, z$), where the Saupe matrix has the form [11]

$$S_{jk,\alpha\beta} = \frac{1}{2}\langle 3\cos\theta_{j\alpha}\cos\theta_{k\beta} - \delta_{jk}\delta_{\alpha\beta}\rangle. \quad (2)$$

Here, $\theta_{j\alpha}$ is the angle between the j and α axes and the brackets $\langle\ldots\rangle$ indicate statistical averaging over molecular orientations in the liquid crystal. The permittivity tensor ε_{jk} of the liquid crystal in the optical transparency range is diagonal in the laboratory coordinate system and has components $\varepsilon_j = n_j^2$, where n_j are the principal refractive indices of the liquid crystal. The components of the tensors f_{jk} and L_{jk}, which are also diagonal in the same coordinate system, are related to each other and to the quantities ε_j by the expression [6, 7]

$$f_j = 1 + L_j(\varepsilon_j - 1). \quad (3)$$

The molecular polarizability components γ_j averaged over molecular orientations have the form [7]

$$\gamma_X = \bar{\gamma} - \frac{\Delta\gamma}{3}(S - R) - \frac{\Delta\gamma'}{6}(G - P),$$

$$\gamma_Y = \bar{\gamma} - \frac{\Delta\gamma}{3}(S + R) - \frac{\Delta\gamma'}{6}(G + P), \quad (4)$$

$$\gamma_Z = \bar{\gamma} + 2\Delta\gamma S + \frac{\Delta\gamma'G}{3}.$$

Here, we used the designations $\bar{\gamma} = (\gamma_{xx} + \gamma_{yy} + \gamma_{zz})/3$, $\Delta\gamma = \gamma_{zz} - (\gamma_{xx} + \gamma_{yy})/2$, and $\Delta\gamma' = \gamma_{xx} - \gamma_{yy}$ for the polarizability parameters and the parameters of the uniaxial (S, G) and biaxial (R, P) orientational order of molecules:

$$S = S_{ZZ,zz}, \quad G = S_{ZZ,xx} - S_{ZZ,yy},$$

$$R = S_{XX,zz} - S_{YY,zz}, \quad (5)$$

$$P = S_{XX,xx} - S_{YY,xx} - S_{XX,yy} + S_{YY,yy}.$$

For a liquid crystal with N molecules per unit volume, the components ε_j, f_j, and γ_j are related by the following expression:

$$\varepsilon_j - 1 = 4\pi N f_j\gamma_j. \quad (6)$$

Then, we use the known inequality for positive quantities x_j:

$$(x_1 + x_2 + x_3)(1/x_1 + 1/x_2 + 1/x_3) > 9, \quad (7)$$

which reduces to the equality for equal quantities x_j. With allowance made for relationships (3) and (6), setting $x_j = 4\pi N\gamma_j$ and $1/x_j = L_j + (\varepsilon_j - 1)^{-1}$, and taking into account that $\text{Tr}L = 1$, we obtain the limitation on the polarizability $\bar{\gamma}$ from below:

$$4\pi N\bar{\gamma}\sum_j(\varepsilon_j + 2)(\varepsilon_j - 1)^{-1} > 9. \quad (8)$$

In order to check relationship (1), we determine the limitation on the ratio $\bar{\gamma}/\bar{\gamma}_i$. Setting $x_j = \varepsilon_j - 1$ in formula (7), we have the inequality $\sum_j (\varepsilon_j - 1)^{-1} > 3(\bar{\varepsilon} - 1)^{-1}$. By adding unity to each side of this inequality, we find

$$\sum_j \frac{\varepsilon_j + 2}{\varepsilon_j - 1} > 3\frac{\bar{\varepsilon} + 2}{\bar{\varepsilon} - 1}. \tag{9}$$

With due regard for this relationship, we introduce the parameter $r_{1b} > 1$ for the biaxial liquid crystal by means of the expression

$$r_{1b} = \frac{1}{3}\sum_j \frac{\varepsilon_j + 2}{\varepsilon_j - 1}\frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2}. \tag{10}$$

In the isotropic phase, we have $\varepsilon_i - 1 = 4\pi N_i f_i \bar{\gamma}_i$ and $f_i = (\varepsilon_i + 2)/3$. With the use of the designations $r = C/C_i$,

$$C = \frac{\bar{\varepsilon} - 1}{\rho(\bar{\varepsilon} + 2)}, \quad C_i = \frac{\varepsilon_i - 1}{\rho_i(\varepsilon_i + 2)} \tag{11}$$

(where ρ and ρ_i are the densities of the liquid-crystal and the isotropic phases, respectively), formula (8) can be rearranged to the form

$$\bar{\gamma}/\bar{\gamma}_i > r/r_{1b}. \tag{12}$$

In [12, 13], the order parameters (5) for the smectic liquid crystal SmC was estimated from the refractive indices with the use of formulas (3) and (6) within the approximation $L_j = 1/3$ [1]. Within paradigm (1), this approximation corresponds to the conditions [1]

$$C_i = C_B \equiv \frac{1}{3\rho}\sum_j \frac{\varepsilon_j - 1}{\varepsilon_j + 2} = \text{const.} \tag{13}$$

The temperature dependence $C_B(T)$ noted in [13] does not correspond to the constancy of the quantity C_B. In order to check the equality $C_i = C_B$ and, in view of its use for determining the extraordinary refractive index for uniaxial nematic liquid crystals [14], we establish the limitations on the quantities C_B and C_B/C_i. Setting $x_j = \varepsilon_j + 2$ in relationship (7), we obtain the inequality $\sum_j (\varepsilon_j + 2)^{-1} > 3(\bar{\varepsilon} + 2)^{-1}$. By multiplying each side of this inequality by (-1) and adding unity to them, we have

$$3\frac{\bar{\varepsilon} - 1}{\bar{\varepsilon} + 2} > \sum_j \frac{\varepsilon_j - 1}{\varepsilon_j + 2}, \quad C > C_B. \tag{14}$$

At the same time, setting $x_j = \rho(\varepsilon_j + 2)(\varepsilon_j - 1)^{-1}$ in relationship (7) with allowance made for formula (10), we find $C_B > C/r_{1b}$ or

$$r > C_B/C_i > r/r_{1b}. \tag{15}$$

Therefore, the equality $C_i = C_B$ is possible only for the liquid crystal with $r(T, \lambda) > 1$, at a particular tempera-

ture point of the mesophase, and at a specific light wavelength λ. Since the quantities r and r_{1b} for the liquid crystals are close to unity [3–7], limitations (15) explain the approximate equality $C_i \approx C_B$ [1, 15].

For the uniaxial liquid crystals (N, SmA, SmB) with $R = P = 0$ and two independent components of the tensors L_j, f_j, γ_j, and ε_j in the case of the light wave polarized parallel ($j = \parallel$) and perpendicular ($j = \perp$) to the director $\mathbf{n} \parallel Z$, the use of the quantities $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$ and $Q = (\varepsilon_\parallel - \varepsilon_\perp)/(\bar{\varepsilon} - 1)$ enables us to represent the parameter r_1 (expression (10)) in the form

$$r_1 = 1 + \frac{6Q^2}{(\bar{\varepsilon} + 2)(3 - Q)(3 + 2Q)}. \tag{16}$$

If the conditions $\varepsilon_Z = \varepsilon_\parallel$ and $(\varepsilon_X + \varepsilon_Y)/2 = \varepsilon_\perp$ are satisfied upon transition from the biaxial phase to the uniaxial phase, from relationship (10) in the approximation quadratic in $\Delta\varepsilon' = (\varepsilon_X - \varepsilon_Y)$, we obtain

$$r_{1b} = r_1 + \frac{(\Delta\varepsilon')^2(\bar{\varepsilon} - 1)}{2(\varepsilon_\perp - 1)^3(\bar{\varepsilon} + 2)}. \tag{17}$$

At identical densities of the above phases, this leads to the limitations of the first level:

$$\bar{\gamma}/\bar{\gamma}_i > r/r_1 > r/r_{1b}. \tag{18}$$

These limitations reflect the existence of the long-range uniaxial or biaxial orientational order of molecules (optical anisotropy of the liquid crystal) and do not depend explicitly on the anisotropy of the tensors L and f. This means the mutual complementarity of local-field effects determined by the properties of the tensors L and f [6, 7] and the effects associated with the change in the molecular polarizability in the anisotropic medium.

The anisotropic properties of the tensors L and f are determined by the long-range orientational order of molecules, the optical anisotropy of liquid crystals [6], and their local anisotropy [7]. In order to reveal the higher level limitations on the ratio $\bar{\gamma}/\bar{\gamma}_i$, it is necessary to analyze the dependences $L_j(\bar{\gamma})$ and $\Delta f(\bar{\gamma})$. It should be noted that the known methods for experimentally determining the components L_j for biaxial liquid crystals [7] have not been used to date. In this respect, we will restrict our consideration to the case of uniaxial liquid crystals.

3. ANISOTROPY OF THE TENSORS L AND f AND THE MOLECULAR POLARIZABILITY $\bar{\gamma}$

The approach used in our study consists in revealing and analyzing the nonphysical consequences of relationship (1) using refractometry as the simplest and most direct method for determining the molecular polarizability $\bar{\gamma}$. The conditions for the elimination of these consequences will permit us to obtain the sought limitations on the quantity $\bar{\gamma}$.

Relationship (1) underlies the known method for determining the components L_j in uniaxial liquid crystals from refractometric data [2]. With due regard for relationships (6) and $\mathrm{Tr}L = 1$, the equality $\bar{\gamma}_i = \bar{\gamma}$ is equivalent to the Saupe–Maier–Neugebauer equation [2] for calculating the component $L_\perp$; that is,

$$
\frac{3(\varepsilon_i - 1)}{\rho_i(\varepsilon_i + 2)} = \frac{1}{3\rho}
$$

$$
\times \left[\frac{\varepsilon_\parallel - 1}{1 + (1 - 2L_\perp)(\varepsilon_\parallel - 1)} + \frac{2(\varepsilon_\perp - 1)}{1 + L_\perp(\varepsilon_\perp - 1)} \right].
$$
(19)

For the calamitic nematic liquid crystals, the sign of the anisotropy $\Delta f^{\mathrm{SMN}} = (f_\parallel - f_\perp) > 0$ obtained using this method in the visible and IR spectral ranges contradicts the experimental data [6, 7], the components L_j^{SMN} for some objects do not correspond to the real anisotropy of the pair correlation function $g_2(\mathbf{R})$ of molecules in liquid crystals [7], and the temperature dependences $L_j^{\mathrm{SMN}}(T)$ for a number of liquid crystals exhibit a nonmonotonic nonphysical behavior [5]. The factors responsible for the anomalous solutions of Eq. (19), as a rule, have been attributed to inaccuracies in the measurement of the parameters $n_{i,j}$, ρ_i, and ρ [16]. With the aim of revealing the real factors responsible for these anomalies, we determine the dependences of the quantities Δf and $L_\perp$ on the parameter $A = \bar{\gamma}_i / \bar{\gamma}$ by the method that differs from that used in [9]. We consider calamitic and discotic uniaxial liquid crystals separately.

3.1. Calamitic Liquid Crystals (N, SmA, SmB)

We introduce the parameter $q = (\Delta\gamma S + \Delta\gamma' G/2)/(3\bar{\gamma})$. Here, $\Delta\gamma > 0$, the signs of the quantities $\Delta\gamma'$ and G coincide [7] and $q > 0$. From formulas (3) and (6), we have

$$
4\pi N\bar{\gamma}[L_j + (\varepsilon_j - 1)^{-1}]
$$

$$
= \frac{1}{1 + a_j q} \quad (a_\parallel = 2, \ a_\perp = -1).
$$
(20)

The term-by-term summation of these expressions leads to the equation for the parameter q:

$$
B \equiv \frac{4\pi N\bar{\gamma}}{3} \left[\frac{\varepsilon_\parallel + 2}{\varepsilon_\parallel - 1} + \frac{2(\varepsilon_\perp + 2)}{\varepsilon_\perp - 1} \right]
$$

$$
= \frac{1}{1 + 2q} + \frac{2}{1 - q}.
$$
(21)

Making allowance for relationship (16), the quantity B can be written in the form $B = 3r_1/Ar$. However, with due regard for the right-hand side of expression (21), we have

$$
B = 3\bar{\gamma}[(1/\gamma_\parallel + 2/\gamma_\perp)/3]
$$

and, at $\gamma_\parallel \neq \gamma_\perp$ ($q \neq 0$), relationship (7) results in the inequality $B > 3$. This corresponds to the requirement $r_1 > Ar$ and limitation (18). At $q > 0$, the solution to Eq. (21) has the form

$$
q = \frac{1}{4r_1}[r_1 - Ar + [(r_1 - Ar)(9r_1 - Ar)]^{1/2}]. \quad (22)
$$

For liquid crystals with $r > r_1$, approximation (1) ($A = 1$) violates limitation (18) and corresponds to complex values of the parameter q, which means that $\bar{\gamma}/\bar{\gamma}_i > 1$. From formulas (6) and (20), we can obtain the relationship

$$
q = \frac{Q(3 + Q)(\bar{\varepsilon} + 2)r_0 - \Delta f(3 - Q)(3 + 2Q)}{3(3 + Q)(\bar{\varepsilon} + 2)r_0 + \Delta f(3 - Q)(3 + 2Q)} \quad (23)
$$

with the parameter

$$
r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}. \quad (24)
$$

Substitution of relationship (23) into expression (21) leads to the equation for the quantity Δf:

$$
\Delta f^2 - \Delta f \frac{(3 + Q)(\bar{\varepsilon} + 2)}{6}[(b_1 b_2)^{1/2} - b]
$$

$$
+ br_0 \frac{(3 + Q)^2(\bar{\varepsilon} + 2)^2}{2(3 - Q)(3 + 2Q)} = 0. \quad (25)
$$

Here, we used the following designations:

$$
b = Ar - r_0, \quad b_1 = \frac{2r_0 Q^2}{(3 - Q)(3 + 2Q)},
$$

$$
b_2 = b_1 \left(\frac{6 + Q}{Q} \right)^2. \quad (26)
$$

The solution to Eq. (25), which corresponds to $q \geq 0$, has the form

$$
\Delta f = \frac{1}{12}(3 + Q)(\bar{\varepsilon} + 2)
$$

$$
\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}] \quad (27)
$$

and coincides with the result of substitution of relationship (23) into formula (22) with due regard for the expressions $r_1 - Ar = b_1 - b$ and $9r_1 - Ar = b_2 - b$.

It should be noted that, for the isotropic phase of liquid crystals, the relation $C_i \sim \bar{\gamma}_i$ is linear and the experimental fact $C_i = \mathrm{const}$ [3–7] corresponds to the constancy of the polarizability $\bar{\gamma}_i$. For liquid crystals, the dependence of the anisotropy Δf (relationship (27)) on b ($\bar{\gamma}$) is nonlinear and an insignificant change in the quantity b due to the change in the parameter A ($\bar{\gamma}$) and/or C leads to a considerable change in the anisotropy Δf; in this case, the signs of the quantities Δf and b coincide with each other. As a result of the smallness of the parameter $Q \ll 3$ and the closeness of the parame-

ters r_0 and r_1 to unity, the experimental fact of the closeness of the quantity r to unity [3–7] enhances the dependence $\Delta f(\bar\gamma)$. For the liquid crystals with $r > r_1$, approximation (1) violates limitation (18) and results in complex values of the anisotropy Δf (expression (27)).

The anisotropy Δf is conveniently represented in the form

$$\Delta f = (L_{\perp k} - L_\perp)(\bar\varepsilon - 1)(3 + Q),$$
$$L_{\perp k} = \frac{1}{3}\left(1 + \frac{Q}{3 + Q}\right). \tag{28}$$

With due regard for this expression, from formula (27), we find

$$L_\perp = L_{\perp k} - \frac{\bar\varepsilon + 2}{12(\bar\varepsilon - 1)} \tag{29}$$
$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}].$$

At $A = 1$, this relationship gives the solution to Eq. (19). For the liquid crystals with $r > r_1$, approximation (1) corresponds to complex values of the component $L_\perp^{SMN}$ defined by relationship (29). At $r_1 > r > r_0$, Eq. (19) has the solution $L_\perp^{SMN} < L_{\perp k}$. Since $L_{\perp k} > 1/3$, there are variants $1/3 < L_\perp^{SMN} < L_{\perp k}$ and $L_\perp^{SMN} < 1/3$. In the case of a nonmonotonic temperature variation in the difference $b = r - r_0$ between the function $r(T) = C(T)/C_i$ that is almost linear [17] and the downward convex function $r_0(T)$ (expression (24)), the dependence $L_\perp^{SMN}(T)$ can exhibit a minimum. This situation corresponds to the conditions used by Haller [5], who was the first to observe this minimum. Therefore, apart from the incorrectness of approximation (1), the presence of the nonphysical minimum in the dependence $L_\perp^{SMN}(T)$ suggests the necessity of including the dependence $C(T)$, which is also important in order to exactly describe the dependences $n_j(T)$ [17]. This extends the relation between the refractometry and dilatometry of liquid crystals, which up to now has been based on the approximation $C = \text{const}$ [18–21].

The limitations of the next levels on the ratio $\bar\gamma/\bar\gamma_i$ depend on the local anisotropy of liquid crystals and the components $L_\perp$. The local anisotropy of the liquid crystals is characterized by the anisotropy of the surface $F(\mathbf{R})$ satisfying the condition $g_2(\mathbf{R}) = \text{const}$ for the pair correlation function of molecules $g_2(\mathbf{R})$, which is averaged over the molecular orientations [7]. Here, $\mathbf{R}$ is the radius vector between the centers of masses of two molecules. In the uniaxial nematic liquid crystal (smectic liquid crystals A, B) on scales $R_m < R \ll R_M$ between the molecular (R_m) and macroscopic (R_M) scales, the surface $F(\mathbf{R})$ has the form of a spheroid (cylinder) elongated along the director $\mathbf{n}$ [7]. This corresponds to the requirement $L_\perp > 1/3$ for these liquid crystals.

It follows from formula (23) or (27) that, at $b = b_1$, the maximum possible positive anisotropy for calamitic liquid crystals,

$$\Delta f_c = \frac{Q(3 + Q)(\bar\varepsilon + 2)r_0}{(3 - Q)(3 + 2Q)}, \tag{30}$$

corresponds to the values $q = 0$ and $\Delta\varepsilon_c = 4\pi N\bar\gamma\Delta f_c > 0$. Substitution of relationship (30) into expression (28) gives the component

$$L_{\perp c} = \frac{1}{3}\left[1 - \frac{9Q}{(3 - Q)(3 + 2Q)(\bar\varepsilon - 1)}\right], \tag{31}$$

which contradicts the condition $L_\perp > 1/3$ and is nonphysical for calamitic liquid crystals. Making allowance for formula (29), the requirement $L_\perp > 1/3$ is equivalent to the relationship $r_2 > Ar$, where

$$r_2 = 1 + \frac{6Q^2(\bar\varepsilon - 1)}{(\bar\varepsilon + 2)[(3 - Q)(3 + 2Q)(\bar\varepsilon - 1) + 27]}. \tag{32}$$

This leads to the limitation of the second level:

$$\bar\gamma/\bar\gamma_i > r/r_2. \tag{33}$$

For nematic liquid crystals with an anomalously low birefringence $\Delta n = n_\parallel - n_\perp$ and an inversion of the sign of the anisotropy Δf [22], the experimental values of $L_\perp > 1/3$ and $\Delta f > 0$ in the visible and IR spectral ranges correspond to the limitations $r_2 > Ar > r_0$ or

$$r/r_0 > \bar\gamma/\bar\gamma_i > r/r_2. \tag{34}$$

For calamitic liquid crystals with high and moderate values of birefringence Δn in the visible and IR spectral ranges, the experimental values of $L_\perp$ satisfy the inequalities $L_\perp > L_{\perp k}$ and $\Delta f < 0$ [6, 7]. In turn, they correspond to values of $b < 0$ and the limitation of the third level:

$$\bar\gamma/\bar\gamma_i > r/r_0. \tag{35}$$

For conventional smectics A with a weak sinusoidal modulation of the density along the director $\mathbf{n}$ and the order parameters S that do not considerably exceed those in the nematic phase, the difference between the components $L_\perp(\text{Sm}A) > L_\perp(\text{N})$ is insignificant [6, 7, 23]. The maximum component $L_\perp = 1/2$ [7] corresponds to a locally quasi-two-dimensional smectic liquid crystal with $S \approx 1$ and the relationship $d_\parallel \gg d_\perp$ between the interlayer spacing $d_\parallel$ and the intermolecular distance $d_\perp$ in the layer. For real smectic and nematic liquid crystals, the conditions $L_\perp < 1/2$ and $\Delta f < 0$ correspond to the limitations $r_0 > Ar > r_3$ or

$$r/r_3 > \bar\gamma/\bar\gamma_i > r/r_0. \tag{36}$$

With due regard for expression (29), the quantity r_3 is defined by the relationship

$$r_3 = 1$$
$$- \frac{(\bar{\varepsilon} - 1)[(3 - Q)(3 + 2Q)(\bar{\varepsilon} - 1) + 6Q(6 - Q)]}{(\bar{\varepsilon} + 2)[(3 - Q)(3 + 2Q)(\bar{\varepsilon} - 1) + 54]}. \quad (37)$$

The inequalities $r_1 > r_2 > 1 > r_0 > r_3$ determine the hierarchy of the limitations

$$r/r_3 > \bar{\gamma}/\bar{\gamma}_i > r/r_0 > r/r_2 > r/r_1, \quad (38)$$

which depend only on the refractive indices and the densities of the liquid-crystal and isotropic phases.

3.2. Horn Procedure [4]

This known procedure for determining the parameter q is based on a combination of Eq. (21) with the incorrect expression [3, 24, 25]

$$4\pi N\bar{\gamma} = \frac{3(\bar{\varepsilon} - 1)}{\bar{\varepsilon} + 2}. \quad (39)$$

The above expression is inconsistent with formula (20), which is initial for Eq. (21). Expression (39) corresponds to the equality $\bar{\gamma}/\bar{\gamma}_i = r$ ($Ar = 1$), which is valid for values of $b^H = (1 - r_0) > 0$, $\Delta f^H > 0$, and $L_{\perp k} > L_\perp^{(H)} > 1/3$ and limitations (34) irrespective of the nature of molecules, the birefringence Δn, and the spectral range. This contradicts the experimental data [6, 7]. Since the condition $Ar = 1$ is equivalent to the simultaneous fulfillment of conditions (1) and $r = 1$, the component $L_\perp^{(H)}$ corresponding to the Horn procedure coincides with the solution $L_\perp^{SMN}$ of Eq. (19) at $r = 1$. Function (23) can be represented in the form

$$q = q_0(1 + \sigma), \quad (40)$$

where $q_0 = q(\Delta f = 0) = Q/3$, σ is the correction for the anisotropy Δf, and the sign of σ is opposite to the sign of the anisotropy Δf. Substitution of formula (40) into relationship (22) results in the expression

$$\sigma = \frac{3}{4Qr_1}[r_1 - Ar + [(r_1 - Ar)(9r_1 - Ar)]^{1/2}] - 1. \quad (41)$$

Substitution of $Ar = 1$ and r_1 given by formula (16) into expression (41) leads to the relationship

$$\sigma^H = \frac{9\{\sqrt{3}Q + [4(\bar{\varepsilon} + 2)(3 - Q)(3 + 2Q) + 27Q^2]^{1/2}\}}{2\sqrt{3}[(\bar{\varepsilon} + 2)(3 - Q)(3 + 2Q) + 6Q^2]} - 1. \quad (42)$$

In view of the smallness of the parameter $Q \ll 3$, the dependence $\sigma^H(Q) < 0$ is very weak, so that an increase in the parameter Q with a decrease in the temperature of the liquid crystal results in an increase in the magnitude $|\sigma^H|$ and a decrease in the ratio q^H/q_0. The change in the quantity σ^H upon variation in the parameter Q with temperature in the mesophase is equal to a few percent. This explains the constancy of the ratio $q^H/q_0 = (1 + \sigma^H)$ in the range of the nematic and smectic A liquid-crystal phases [4]. At $Q \longrightarrow 0$, owing to the transformation of the chemical and electronic structures of molecules, the quantities σ^H and q^H/q_0 tend to their limiting values,

$$\sigma_{lim}^H = \left(\frac{3}{\bar{\varepsilon} + 2}\right)^{1/2} - 1,$$
$$\left(\frac{q^H}{q_0}\right)_{lim} = \left(\frac{3}{\bar{\varepsilon} + 2}\right)^{1/2}. \quad (43)$$

Therefore, the specific features and consequences of the Horn procedure, which are usually attributed to Eq. (21) [4, 16, 26], are consequences of a combination of the correct equation with the incorrect relationship (39) introduced in order to approach condition (1) to the greatest possible extent [24, 25].

3.3. Discotic Liquid Crystals (N_D, $Col_{h(o,d)}$)

In the planar molecules of these liquid crystals, the z axis is perpendicular to the plane of the molecular core and parallel to the symmetry axis C_n ($n \geq 3$) of the core. The molecular tensor γ is uniaxial with the anisotropy $\Delta\gamma < 0$. For these liquid crystals with permittivities $\varepsilon_\parallel < \varepsilon_\perp$, we use the following designations: $\Delta\gamma_d = -\Delta\gamma$, $q_d = S(\Delta\gamma_d)/(3\bar{\gamma})$, and $Q_d = (\varepsilon_\perp - \varepsilon_\parallel)/(\bar{\varepsilon} - 1)$. The replacement of the parameter q by $-q_d$ in Eq. (21) leads to the solution

$$q_d = \frac{1}{4r_{1d}}[[(r_{1d} - Ar)(9r_{1d} - Ar)]^{1/2} - r_{1d} + Ar]. \quad (44)$$

The changeover from the parameters r_m ($m = 0, 1, 2$) for the calamitic liquid crystals to the parameters r_{md} for the discotic liquid crystals is performed using the replacement of the parameter Q by $-Q_d$. The values of $q_d > 0$ correspond to the condition $r_{1d} > Ar$ or

$$\bar{\gamma}/\bar{\gamma}_i > r/r_{1d}. \quad (45)$$

The relationship $q_d(\Delta f)$ is represented in the form

$$q_d = \frac{Q_d(3 - Q_d)(\bar{\varepsilon} + 2)r_{0d} + \Delta f(3 + Q_d)(3 - 2Q_d)}{3(3 - Q_d)(\bar{\varepsilon} + 2)r_{0d} + \Delta f(3 + Q_d)(3 - 2Q_d)}. \quad (46)$$

Substitution of relationship (46) into expression (44) gives the formula

$$\Delta f = -\frac{1}{12}(3 - Q_d)(\bar{\varepsilon} + 2)$$
$$\times [(d_1 d_2)^{1/2} + d - [(d_1 - d)(d_2 - d)]^{1/2}]. \quad (47)$$

Here, we used the designations

$$d = Ar - r_{0d}, \quad d_1 = \frac{2r_{0d}Q_d^2}{(3 + Q_d)(3 - 2Q_d)},$$
$$d_2 = d_1\left(\frac{6 - Q_d}{Q_d}\right)^2, \quad (48)$$

where $d_1 - d = r_{1d} - Ar$ and $d_2 - d = 9r_{1d} - Ar$. The quantities Δf and d have opposite signs. Instead of Eqs. (28), we have

$$\Delta f = (L_{\perp k} - L_{\perp})(\bar{\varepsilon} - 1)(3 - Q_d),$$
$$L_{\perp k} = \frac{1}{3}\left(1 - \frac{Q_d}{3 - Q_d}\right). \quad (49)$$

With allowance made for these equations, from expression (47), we obtain

$$L_{\perp} = L_{\perp k} + \frac{\bar{\varepsilon} + 2}{12(\bar{\varepsilon} - 1)}$$
$$\times [(d_1 d_2)^{1/2} + d - [(d_1 - d)(d_2 - d)]^{1/2}]. \quad (50)$$

For liquid crystals with $r > r_{1d}$, approximation (1) corresponds to complex values of $L_{\perp}$ determined from formula (50). At $r_{1d} > r > r_{0d}$, Eq. (19) has the solution $L_{\perp}^{SMN} > L_{\perp k}$. Since $L_{\perp k} < 1/3$, we have variants $1/3 > L_{\perp}^{SMN} > L_{\perp k}$ and $L_{\perp}^{SMN} > 1/3$. In the case of a nonmonotonic temperature variation in the difference $d = r - r_{0d}$ between the functions $r(T)$ and $r_{0d}(T)$, the dependence $L_{\perp}^{SMN}(T)$ can exhibit a nonphysical maximum.

For nematic liquid crystals N_D (discotic liquid crystals $Col_{h(o,d)}$), the surface $F(\mathbf{R})$ has the form of a spheroid (cylinder) oblate along the director $\mathbf{n}$ [7]. This results in the requirement $L_{\perp} < 1/3$. It follows from formula (46) that the values of $q_d = 0$ and $\Delta\varepsilon_d = 4\pi N\bar{\gamma}\Delta f_d < 0$ correspond to the maximum possible negative anisotropy for discotic liquid crystals:

$$\Delta f_d = -\frac{Q_d(3 - Q_d)(\bar{\varepsilon} + 2)r_{0d}}{(3 + Q_d)(3 - 2Q_d)}. \quad (51)$$

Substitution of relationship (51) into expression (49) gives the component

$$L_{\perp d} = \frac{1}{3}\left[1 + \frac{9Q_d}{(3 + Q_d)(3 - 2Q_d)(\bar{\varepsilon} - 1)}\right], \quad (52)$$

which contradicts the condition $L_{\perp} < 1/3$ for the discotic liquid crystals and is nonphysical. The requirement $L_{\perp} < 1/3$ is equivalent to the relationship $r_{2d} > Ar$ or the limitation of the second level:

$$\bar{\gamma}/\bar{\gamma}_i > r/r_{2d}. \quad (53)$$

For nematic liquid crystals N_D with anomalously low values of $\Delta\gamma_d$ and $\Delta n_d = n_{\perp} - n_{\parallel}$ [7], the inversion of the sign of the anisotropy Δf is possible, when experimental values of $L_{\perp} < 1/3$ and $\Delta f < 0$ in the visible and IR spectral ranges correspond to the limitations $r_{2d} > Ar > r_{0d}$ or

$$r/r_{0d} > \bar{\gamma}/\bar{\gamma}_i > r/r_{2d}. \quad (54)$$

In the Horn approximation $Ar = 1$, these limitations and relationships $1/3 > L_{\perp}^{(H)} > L_{\perp k}$ should be satisfied regardless of the nature of molecules, the birefringence Δn, and the spectral range. This contradicts the experimental data [7, 10, 27].

For nematic liquid crystals N_D and discotic liquid crystals $Col_{h(o,d)}$ with high and moderate values of birefringence Δn_d in the visible and IR spectral ranges, experimental values of $L_{\perp}$ satisfy the inequalities $L_{\perp} < L_{\perp k}$ and $\Delta f > 0$ [7, 10]. They correspond to values of $d < 0$ and the limitation of the third level:

$$\bar{\gamma}/\bar{\gamma}_i > r/r_{0d}. \quad (55)$$

The structure of the discotic phases $Col_{h(o,d)}$ represents a two-dimensional hexagonal lattice that consists of molecular columns perpendicular to this lattice and parallel to the director $\mathbf{n}$, and the z molecular axes are oriented along the columns [28]. For these phases with an order parameter $S \approx 0.9$, the experimental components are $L_{\perp} \approx 0.17$ [7, 10, 27]. The limiting value of $L_{\perp} = 0$ corresponds to a locally quasi-one-dimensional discotic liquid crystal with $S \approx 1$ and the relationship $d_{\parallel} \ll d_{\perp}$ for the intermolecular distance $d_{\parallel}$ in the column and the distance $d_{\perp}$ between columns. The real phases $Col_{h(o,d)}$ and N_D with values of $L_{\perp} > 0$ and $\Delta f > 0$ correspond to the limitations $r_{0d} > Ar > r_{3d}$ or

$$r/r_{3d} > \bar{\gamma}/\bar{\gamma}_i > r/r_{0d}. \quad (56)$$

The quantity r_{3d} is defined by the expression

$$r_{3d} = 1 - \frac{2(\bar{\varepsilon} - 1)[(3 + Q_d)(3 - 2Q_d)(\bar{\varepsilon} - 1) + 6Q_d(3 - Q_d)]}{(\bar{\varepsilon} + 2)[2(3 + Q_d)(3 - 2Q_d)(\bar{\varepsilon} - 1) + 27]}. \quad (57)$$

The inequalities $r_{1d} > r_{2d} > 1 > r_{0d} > r_{3d}$ determine the hierarchy of the limitations similar to that described by relationship (38). Unlike qualitatively different dependences $\gamma_{zz}(S)$ and $\gamma_{xx}(S)$ for calamitic and discotic liquid

crystals [7, 27], the limitations on the quantity $\bar{\gamma}$ independent of the molecular orientation with respect to the director **n** differ only quantitatively for these types of liquid crystals.

4. OBJECTS OF INVESTIGATIONS, RESULTS, AND DISCUSSIONS

The results obtained were verified using the following three calamitic nematic and columnar discotic liquid crystals:

(CHCA)

(5BCO)

(3O7T)

R: $-OC_7H_{15}$

(THE7) .
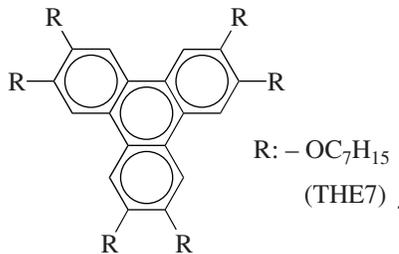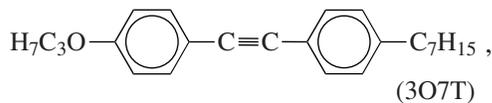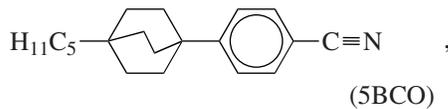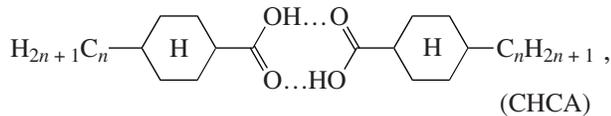
The CHCA nematic mixture of homologs (T_{NI} = 92°C [17, 22], where T_{NI} is the temperature of the nematic–isotropic liquid phase transition) has the lowest birefringence Δn and is the sole known object with the inversion of the sign of the anisotropy Δf [6, 7, 22]. The nematic liquid crystals 5BCO (101°C [17, 29]) and 3O7T (65°C [30, 31]) are characterized by moderate and high values of birefringence Δn. For the CHCA [22] and 5BCO [29] nematic liquid crystals, we have the experimental dependences $L_\perp(T)$ measured by independent spectral methods. The THE7 discotic liquid crystal with the temperature of the transition from the hexagonal ordered columnar phase Col_{ho} to the isotropic phase $T_{Col-I} = 92.5°C$ [10, 27, 32] is the only representative of discotic liquid crystals with the known values of the component $L_\perp(T)$ measured by several spectral methods [7, 10, 27]. In the cited works, the temperature dependences of the densities ρ_i and ρ and the refractive indices $n_{i,j}(\lambda)$ at different wavelengths are tabulated.

For the CHCA nematic liquid crystal, the values of ρ_i, ρ, and $n_{i,j}$ ($\lambda = 589$ nm) [17, 22] over the entire mesophase range $\Delta T = T_{NI} - T = 70°C$ lead to $r/r_1 > 1$ and complex solutions of Eq. (19), which means the violation of relationship (1) and the inequality $\bar{\gamma}/\bar{\gamma}_i > 1$

following from limitation (18). Only at $\Delta T = 72.5°C$, the inequality $r = 1.0028 < 1.0029 = r_1$ is satisfied and Eq. (19) has a real but nonphysical solution $L_\perp^{SMN} = 0.3032 < 1/3$ for calamitic nematics. For the CHCA nematic liquid crystal, the experimental values $L_\perp > 1/3$ [22] obtained by the independent method from the dichroism of the electronic absorption band of the impurity probe molecule ($\lambda_{max} = 336$ nm) at $\lambda = 589$ nm result in ratios $(\bar{\gamma}/\bar{\gamma}_i)_{exp} = \Gamma/(3C_i)$ (where Γ is the right-hand side of formula (19)) that satisfy relationship (34) expected for the given liquid crystal with the inversion of the sign of the anisotropy Δf. In the nematic phase range, the ratio $(\bar{\gamma}/\bar{\gamma}_i)_{exp}$ varies from 1.004 to 1.006, which indicates a high sensitivity of the anisotropy Δf to the molecular polarizability $\bar{\gamma}$. In the case of the CHCA nematic liquid crystal, the values of σ^H (expression (42)) vary from -0.144 ($\Delta T = 1°C$) to -0.154 ($\Delta T = 72.5°C$) and almost coincide with the limiting values of $\sigma_{lim}^H = -0.143$ and $\sigma_{lim}^H = -0.152$ (relationship (43)) at the same values of ΔT, which should be expected for the liquid crystal under consideration with the lowest values of Δn and Q.

For the 5BCO nematic liquid crystal, the values of ρ_i, ρ [17], and $n_{i,j}$ ($\lambda = 589$ nm) [17, 29] lead to the inequality $1 > r > r_0$. Equation (19) has solutions $1/3 < L_\perp^{SMN} < L_{\perp k}$ and $\Delta f^{SMN} > 0$ with a nonmonotonic decrease in the quantity $L_\perp^{SMN}(T)$ with an increase in the temperature T and a minimum at $\Delta T \approx 4°C$, which is associated with the nonmonotonic variation in the difference between the linear function $r(T)$ [17] and the downward convex function $r_0(T)$. However, the independent experimental values of $L_\perp$ [29] obtained from the dichroism of the IR absorption band assigned to the C≡N molecular vibrations ($\lambda_{max} = 4.5$ μm) decrease monotonically with an increase in the temperature T, obey the inequality $L_\perp > L_{\perp k}$, and correspond to a weak anisotropy $\Delta f < 0$ in the IR and visible ranges. The use of these values of $L_\perp$ at $\lambda = 589$ nm results in the ratio $(\bar{\gamma}/\bar{\gamma}_i)_{exp}$ that satisfies limitation (35) and varies from 1.002 to 1.004 in the mesophase range $\Delta T = 40°C$. For the 5BCO nematic liquid crystal, the values of σ^H vary from -0.168 ($\Delta T = 0.5°C$) to -0.175 ($\Delta T = 38°C$) and are very close to the limiting values of $\sigma_{lim}^H = -0.165$ and $\sigma_{lim}^H = -0.170$ at the same values of ΔT.

The dependences $L_\perp^{SMN}(\Delta T)$ following from expression (29) at $A = 1$ for the 3O7T nematic liquid crystal are plotted in Fig. 1. Their strong dependence on the wavelength is inconsistent with the meaning of the quantities L_j as structural characteristics of liquid crystals [2] and the experimental data [6, 7]. At $\Delta T = 0$ ($\lambda = 546$ nm) and $\Delta T = 0$ and 2°C ($\lambda = 436$ nm), the complex
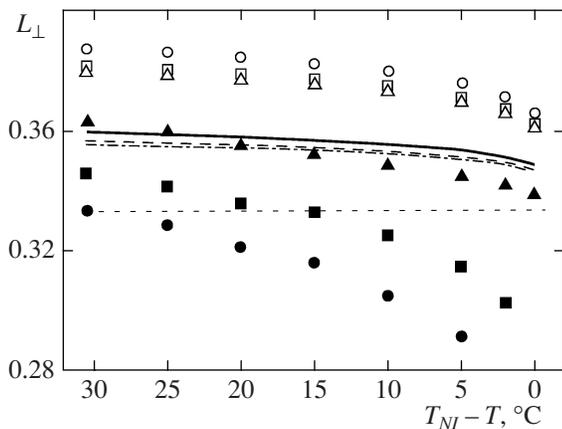
Fig. 1. Temperature dependences of the quantities $L_\perp^{SMN}$ (closed symbols) and $L_{\perp k}$ (open symbols) calculated from relationship (29) at $A = 1$ and $A = r_0/r$ ($b = 0$) for the nematic phase of the 3O7T liquid crystal at $\lambda = (\bullet, \circ)$ 436, ($\blacksquare, \square$) 546, and ($\blacktriangle, \triangle$) 644 nm. Solid, dashed, and dot-dashed lines indicate the temperature dependences of the parameter $L_\perp^{(H)}$ calculated from relationship (29) at $Ar = 1$ for $\lambda = 436$, 546, and 644 nm, respectively. The dotted line represents the value of $L_\perp = 1/3$.

Fig. 2. Temperature dependences of the quantities ($\bullet$) $L_\perp^{SMN}$, ($\circ$) $L_{\perp k}$, and ($\square$) $L_\perp^{(H)}$ for the discotic phase of the THE7 liquid crystal according to the calculations from expression (50) at $A = 1$, $A = r_{0d}/r$ ($d = 0$), and $Ar = 1$, respectively.

values of $L_\perp^{SMN}$ (absent in Fig. 1) correspond to experimental values of $r/r_1 > 1$ and the ratio $\bar\gamma/\bar\gamma_i > 1$ (relationship (18)). At the points $\Delta T = 30°C$ ($\lambda = 436$ nm) and $\Delta T = 15°C$ ($\lambda = 546$ nm) with $L_\perp^{SMN}(\Delta T, \lambda) = 1/3$, expression (13) is valid, which confirms the consequences of limitations (15). At $\lambda = 436$ nm (546 nm), the values of $L_\perp^{SMN} < 1/3$ over the entire nematic phase range ($\Delta T < 15°C$) contradict limitation (33). These nonphysical consequences of approximation (1) are eliminated taking into account an increase in the quantity $1/A = \bar\gamma/\bar\gamma_i > 1$ in formula (29) with an increase in ΔT. It can be seen from Fig. 1 that an increase in the ratio $\bar\gamma/\bar\gamma_i$ to r/r_0 leads to values of $L_\perp = L_{\perp k}$ with a weak dependence on the wavelength λ. In this case, at $\lambda = 436$ nm (644 nm), an increase in the quantity ΔT from 0 to 30°C results in a monotonic increase in the ratio r/r_0 from 1.030 to 1.040 (from 1.007 to 1.011). In actual fact, for the 3O7T nematic liquid crystal as a homolog of the class of tolanes with a high birefringence Δn and the anisotropy $\Delta f < 0$ [6, 7], the ratio r/r_0 is the lower limit of the ratio $\bar\gamma/\bar\gamma_i$ in relationship (18) and the variation in the ratio $\bar\gamma/\bar\gamma_i$ is stronger.

The dependences $L_\perp^{(H)}(\Delta T) < L_{\perp k}$, which correspond to the Horn procedure and follow from expression (29) at $Ar = 1$, depend only weakly on the wavelength λ. For $\lambda = 644$ nm, the equality $L_\perp^{(H)} \approx L_\perp^{SMN}$ expected for the given liquid crystal is observed at the points $\Delta T = 15$

and 20°C with $r \approx 1$. At $r > 1$, the inequality $L_\perp^{(H)} > L_\perp^{SMN}$ is satisfied over the entire mesophase range ($\Delta T < 15°C$) at $\lambda = 436$ and 546 (644) nm. At $\lambda = 589$ nm, the values of σ_H vary from –0.184 ($\Delta T = 0$) to –0.188 ($\Delta T = 30°C$) and are very close to the limiting values of $\sigma_{lim}^H = -0.180$ and $\sigma_{lim}^H = -0.183$ at the same values of ΔT. Therefore, at $\lambda = 589$ nm, the values of σ_H (relationship (42)) for each of the three nematic liquid crystals CHCA, 5BCO, and 3O7T with a considerably different birefringence Δn almost coincide with the limiting value σ_{lim}^H over the entire mesophase range. This confirms the consequences of formula (42).

For the THE7 discotic liquid crystal, the values of ρ_i, ρ, and $n_{i,j}$ ($\lambda = 589$ nm) [32] result in a constant value of $C_i = 0.2818$ in the range ΔT from –1 to –5°C in the isotropic phase. In the discotic phase, the inequality $r < r_{0d}$ is satisfied and approximation (1) obeys limitation (55). The values of $L_\perp^{SMN} < L_{\perp k}$ following from formula (19) or (50) at $A = 1$ are presented in Fig. 2. The temperature dependences of these parameters exhibit a behavior opposite to that for the calamitic liquid crystals (Fig. 1). The sign of the anisotropy $\Delta f^{SMN} > 0$ corresponds to the experimental data [7, 10, 27]; however, the values of $L_\perp^{SMN}$ are significantly overestimated and the function $L_\perp^{SMN}(\Delta T)$ is nonmonotonic. Both these consequences of relationship (19) suggest the limitation of approximation (1). Unlike the calamitic nematic liquid crystals, the dependence $r_{0d}(T)$ for the THE7 discotic liquid crystal with an insignificant variation in the birefringence $\Delta n(T)$ and the order parameter $S(T)$ is very weak and almost linear, whereas the function $r(T)$

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