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Mean Polarizability of Molecules and Anisotropy of the Lorentz Tensor upon a Nematic–Smectic A Phase Transition: Their Behavior in a Homologous Series

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Abstract—Experimental values of the mean polarizability of molecules, $\overline{\gamma}$, and components of the Lorentz tensor, L_j, in the nematic and smectic A phases are obtained for a homologous series of *n*-alkyl-*p*-(4-ethoxybenzylideneamino)-α-methylcinnamates. Dependences of the $\overline{\gamma}$ and L_j values on the mesophase temperature, the orientational order parameter S of molecules, and the number n in the homologous series are revealed. The quadratic dependence of $\overline{\gamma}(S)$ in the nematic and smectic phases is established that is invariant with respect to the nematic–smectic A transition. Polarizability densities of the molecular core and the alkyl chain are found from the monotone decreasing dependence $\overline{\gamma}(n)/v$ (where v is volume per one molecule) in the smectic phase. The presence (or absence) of the odd–even alternation of $L_j(n)$ in the nematic (smectic) phase is shown. A monotone decrease in the Lorentz tensor anisotropy L with an increase in n is revealed in the smectic phase, and limiting values $L_j(n \to \infty)$ are determined.

Keywords: molecular polarizability, anisotropy, phase transition, nematic, smectic, homologues.

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INTRODUCTION

Liquid crystals (LCs) that possess a broad range of statistically ordered phases at temperatures corresponding to technical requirements and physicochemical (biological) conditions suitable for the functioning of living systems are convenient for modeling artificial anisotropic and natural self-organized molecular media. For their comprehension and utilization in various applications from molecular electronics to biology and medicine, we need to know the character and level of the influence of a long-range orientational and short-range or quasi-long-range positional order of molecules on their physical-chemical properties that determine the response of the molecules to electromagnetic forces, and affect the intermolecular interactions and biological activity of the molecules. A synthetic characteristic of such molecular properties is the polarizability tensor, γ [1], the alteration of which in an anisotropic medium reflects a change in the intermolecular interactions, and in the polarization, electronic structure, and conformation of the molecules during their self-organization [2].

Objective investigation of the γ alterations in uniaxial molecular media by refractometric analysis has recently become available, due to the development of a new method for experimental determination of the local field parameters for such media without a priori assumptions about unobservable molecular parameters (dimensions, shape, electronic structure, and polarizability) [3]. In order to determine the γ_j components of the γ tensor averaged over the orientations of molecules in the system of refraction ellipsoid axes, we must consider the difference between the local field of the optical wave that polarizes a molecule, $\mathbf{E}^{\mathrm{loc}}(\omega)$, and the macroscopic field of the optical wave in a medium, $\mathbf{E}(\omega)$ [2]. Amplitudes of these fields are determined by the expression $E_j^{\mathrm{loc}} = f_j E_j$. The components of the local field tensor, $f_j = 1 + L_j(\varepsilon_j - 1)$, which is diagonal in this coordinate system, are associated with the components L_j and ε_j of the diagonal Lorentz tensor ($\mathrm{Sp}L = 1$) and dielectric permeability.

Using the experimental dependences of the refractive index, $n_j(\lambda)$, on the optical wavelength, λ, in the visible region allows us to obtain the components $L_j(T)$ and the mean value of $\overline{\gamma}(T, \lambda)$ as has been done and confirmed for a broad range of uniaxial molecular media of various nature [3]. This method was used to investigate changes in the $\overline{\gamma}(T)$ in nematic LCs of various chemical classes [4].

The aim of this work is to investigate dependences $L_j(T)$ and $\overline{\gamma}(T)$ in the nematic and smectic A phases for one homologous series of LC and find the dependence of the L_j and $\overline{\gamma}$ values on the phase state of LC, the orientational order of the molecules, and the homologue number.

DETERMINING THE L_j COMPONENTS AND THEIR PROPERTIES

Let us note the basics of determining the L_j components, as described in detail in [3, 4]. In an uniaxial LC with N uniaxial molecules per unit volume the γ tensor with longitudinal (γ_l) and transversal (γ_t) components is characterized by the parameters $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$ and $\Delta\gamma = \gamma_l - \gamma_t$. In the coordinate system of director **n**, which lies parallel to the optical axis of the LC in the visible transparency range, we have $\varepsilon_j = n_j^2$, where n_j is the refractive index of the LC for the optical waves polarized along ($j = \|$) and normally ($j = \perp$) to **n**. Let us introduce the parameters $\bar{\varepsilon} = (\varepsilon_\| + 2\varepsilon_\perp)/3$, $Q = (\varepsilon_\| - \varepsilon_\perp)/(\bar{\varepsilon} - 1)$,

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_0,$$
$$b_1 = \frac{2r_0Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1[(6 + Q)/Q]^2. \tag{1}$$

Due to condition SpL =1, it is sufficient to determine $L_\perp$. The presence of the long-range orientational order of molecules in LC is reflected in the relation

$$L_\perp = L_{\perp k} - \frac{(\bar{\varepsilon} + 2)}{12(\bar{\varepsilon} - 1)}[(b_1b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}], \tag{2}$$

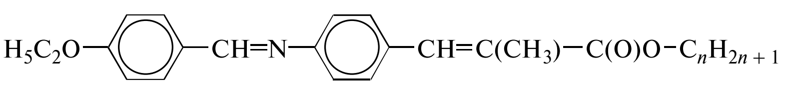
where $L_{\perp k} = (3 + 2Q)/[3(3 + Q)]$. The component $L_\perp(T)$ in the left part of Eq. (2) depends only on the temperature of the LC. All of the parameters in the right part of (2) are functions of T and λ, while the $b(\lambda, T)$ function depends on the unknown $\bar{\gamma}(\lambda, T)$ function. With the known $n_j(\lambda, T)$ values for a discrete set of the values λ_i ($i = 1 - p$) that lies in the visible transparency range of LC, the $b(\lambda, T)$ function in the $\lambda_1 - \lambda_p$ interval is approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \ldots + a_m(T)\lambda^m. \tag{3}$$

At each value of T, the total number $m + 2 = p$ of the unknown variables ($L_\perp^{(m)}$, $a_0 - a_m$) is determined from the system of p equations of type (2), each of which corresponds to one of the λ_i values ($i = 1 - p$). The modulus m of polynomial (3) and the maximum approximation for $L_\perp^{(m)}$ are determined by the p number of the λ_i values.

A higher approximation in (3) requires higher accuracy of the values $n_j(\lambda, T)$; otherwise the system of equations for the unknowns ($L_\perp^{(m)}$, $a_0 - a_m$) may have no physical solutions or may lead to an irregular dependence of $L_\perp^{(m)}(T)$. At a sufficient accuracy of the $n_j(\lambda, T)$ values over a wide range of variation in λ, the $L_\perp^{(m)}$ values coincide with the $\langle L_\perp^{(m-1)} \rangle$ values averaged over the $L_\perp^{(m-1)}$ values corresponding to $p - 1$ combinations of the λ_i values from the $\lambda_1 - \lambda_p$ set [3, 4].

We studied the homologues of a series of n-alkyl-p-(4-ethoxybenzylideneamino)-α-methylcinnamates with the structural formula [5] given below:



(LC1.n)

The LC1.1 homologue exhibits a nematic phase, and the homologues with n = 2–10 (11, 12) show nematic and smectic A phases (an SmA phase only). With an increase in n, the temperature interval of the nematic phase is reduced from 40° for LC1.1 to 2.7° (to a fraction of a degree) for LC1.9 (LC1.10) [5]. The presence of the nematic–smectic A transition (N–SmA) for homologues LC1.n allows us to investigate in detail the influence of the smectic molecular order on the $L_\perp$ value at temperature T_{NA} of the N–SmA transition and the $L_\perp(n)$ variation in a homologous series for both of the N and SmA phases.

Refraction indices $n_j(\lambda, T)$ for LC1.n at values $\lambda_1 = 0.5461$, $\lambda_2 = 0.5893$, and $\lambda_3 = 0.6438$ μm were measured on a refractometer and tabulated [5]. Due to the narrow interval of the nematic phase, the $n_j(\lambda_i)$ values for LC1.9 (LC1.10) are inaccurate or missing [5]. All of the homologues LC1.n in the smectic phase have their minimum on the temperature dependence $n_\perp(T)$ [5], while the depth of this minimum and its position with respect to T_{NA} depend on λ_i for a particular homologue LC1.n [6]. This raises the requirements for accuracy of the $n_j(\lambda_i, T)$ values when determining the ($L_\perp^{(m)}$, $a_0 - a_m$), $b(\lambda_i, T)$, and $\bar{\gamma}(\lambda_i, T)$ values in the vicinity of T_{NA} where single domain samples for both of the phases are difficult to obtain, especially in the nematic and smectic phases. Due to the narrow λ_1–λ_3 interval, the obtained $L_\perp^{(1)}(\Delta T)$ dependences for homologues LC1.n are less regular than dependences $\langle L_\perp^{(0)}(\Delta T)\rangle$, which are averaged over the $L_\perp^{(0)}(\Delta T)$ values for three pairs of values λ_i from the λ_{1-3} set. The $\langle L_\perp(\Delta T)\rangle$ values shown in Fig. 1, along with the indicated standard deviations of the $L_\perp^{(0)}(\Delta T)$ values with respect to $\langle L_\perp^{(0)}(\Delta T)\rangle$, are used as the $L_\perp(\Delta T)$ values for

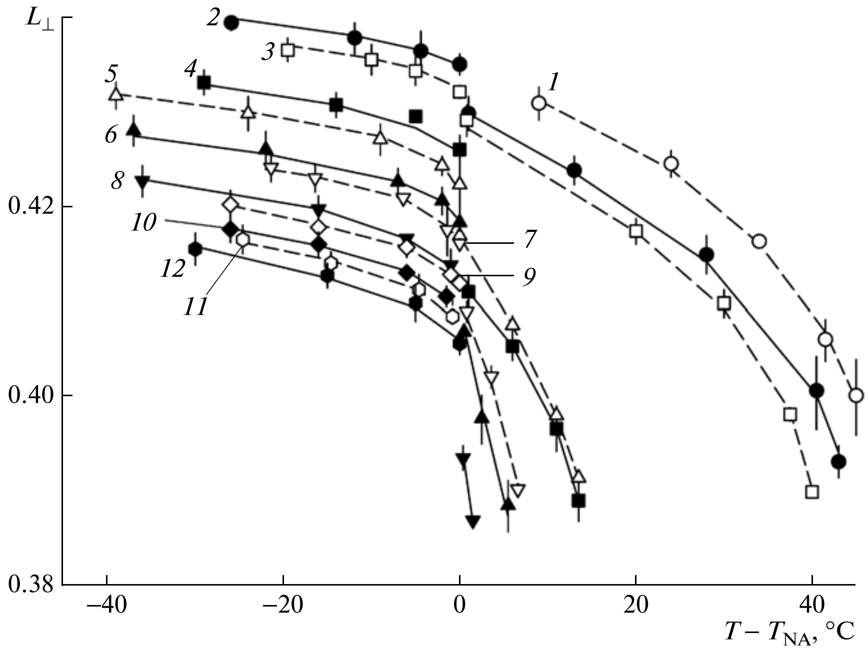


Fig. 1. Temperature behavior of components $L_\perp = \langle L_\perp^{(0)} \rangle$ in the nematic and smectic A phases of the LC1.*n* homologues; numbers correspond to the *n* values. Solid (dashed) lines are the dependences (4) for even (odd) values of *n* at $\lambda = 0.5893$ μm.

homologues LC1.*n*. Values of $T - T_{NI} + 45°$ for the homologue LC1.1 are projected on the abscissa axis, and the rightmost point corresponds to the temperature $T = T_{NI}$ of the nematic–isotropic liquid transition (N–I).

Let us discuss the dependence of $L_\perp$ on $\Delta T = T - T_{NA}$ and the phase state of the LC. When ΔT decreases, the rapid growth of $L_\perp(\Delta T)$ in the nematic phase becomes jump $\delta L_\perp(T_{NA})$ upon the N–SmA first order transition and subsequent weak growth in the smectic phase. For each homologue LC1.*n* at a fixed λ value, the $L_\perp(\Delta T)$ and $L_{\perp k}(\Delta T, \lambda)$ dependences are associated with the linear correlation

$$L_\perp(\Delta T) = A(\lambda)L_{\perp k}(\Delta T, \lambda) + B(\lambda). \qquad (4)$$

The $L_\perp(\Delta T)$ points for both phases are in line (4), which is invariant with respect to the N–SmA transition that is also typical of the transitions cholesteric–SmA [7, 8] and SmA–SmB [3] at low values of

Table 1. Coefficients of Eq. (4) and correlation coefficients *R* for homologues of the LC1.*n* series at $\lambda = 0.5893$ μm

n	$L_\perp = \langle L_\perp^{(0)} \rangle$				$L_\perp = L_\perp^{(H)}$			
	A	−*B*	(*A* − 1)/3	*R*	*A*	*B*	(1 − *A*)/3	*R*
1	1.5909	0.1942	0.1970	0.9979	0.5241	0.1567	0.1586	0.99994
2	1.4859	0.1526	0.1620	0.9991	0.5269	0.1557	0.1577	0.99984
3	1.5182	0.1647	0.1727	0.9993	0.5247	0.1566	0.1586	0.99983
4	1.5383	0.1722	0.1794	0.9934	0.5229	0.1573	0.1590	0.99982
5	1.5536	0.1775	0.1845	0.9995	0.5223	0.1575	0.1592	0.99987
6	1.4949	0.1547	0.1650	0.9975	0.5181	0.1591	0.1606	0.99986
7	1.5138	0.1614	0.1713	0.9987	0.5176	0.1593	0.1608	0.99988
8	1.6764	0.2235	0.2255	0.9998	0.5163	0.1598	0.1612	0.99996
9	1.5695	0.1822	0.1898	0.9982	0.5295	0.1548	0.1568	0.99942
10	1.5750	0.1841	0.1917	0.9981	0.5199	0.1585	0.1600	0.99999
11	1.5729	0.1832	0.1910	0.9946	0.5190	0.1588	0.1603	0.99999
12	1.6900	0.2273	0.2300	0.9911	0.5157	0.1600	0.1614	0.99999

$\delta L_\perp(T_{NA})$. The coefficients of Eq. (4) given in Table 1 depend on the length of the alkyl chain, but lines (4) for all the homologues LC1.*n* are close. The coefficients of (4) are correlated with a high level of accuracy by the expression $B = (1 - A)/3$, indicating fulfilment of the expression

$$A(\Delta T) = (L_\perp - 1/3)/(L_{\perp k} - 1/3) \approx \text{const}, \quad (5)$$

expected for a nematic phase at the fixed λ in the visible and IR ranges [2]. The relationship

$$Q = \frac{S\Delta\gamma}{\bar{\gamma}(1+\sigma)}, \quad (6)$$

where $S = \langle 3\cos^2\theta - 1\rangle/2$ is the orientational order parameter of molecules, θ is the angle between the long molecular axis **l** and the director **n**, and the angle brackets ⟨...⟩ denote averaging over a molecular ensemble, is considered to describe the $L_\perp(\Delta T)$ and $\delta L_\perp(T_{NA})$ variations for an individual homologue [3]. Correction σ for an anisotropy $\Delta f = f_\parallel - f_\perp$ is given by the formula [3]

$$\sigma = -\frac{\Delta f(9 - Q^2)(3 + 2Q)}{Q[3(3+Q)(\bar{\varepsilon}+2)r_0 + \Delta f(3-Q)(3+2Q)]}. \quad (7)$$

Substitution of the expression

$$\Delta f = Q(\bar{\varepsilon} - 1)(1 - A)/3 \quad (8)$$

and consideration of inequality $A > 1$ show that the signs of σ and Δ*f* are opposite each other, and the $\sigma(\Delta T)$ variation for homologues LC1.*n* is weakly expressed in both mesophases due to the inequality $Q \ll 3$. In the case of LC1.2 at $\Delta T = -25.9°$ and 43°, the σ values are thus equal to 0.278 ± 0.005 and 0.288 ± 0.020, respectively (λ = 0.5893 μm). The relation $Q \propto S$ is fulfilled in the approximation linear with respect to *S* in formula (6). On the other hand, the proportion $(L_{\perp k} - 1/3) \propto Q$ is valid at $Q \ll 3$. Allowing for this, the growth of $L_\perp(\Delta T)$ for fixed homologue LC1.*n* with decreasing Δ*T* in the nematic phase is due to an increase in *S*. The invariance of dependence (4) with respect to the N–SmA transition means that changes $\delta L_\perp$ upon this transition and in the smectic phase are determined by the change in δ*S* as a result of the interaction between the nematic and smectic order parameters upon the one-dimensional translational ordering of molecules along director **n** of the smectic phase [9].

The behavior of *S*(*n*) for the homologues of one series in the nematic phase reveals odd–even alternation which is usually studied at $T = T_{NI}$ or at fixed difference $T_{NI} - T$ [10, 11]. It is interesting to compare the $L_\perp(n)$ dependences at the N–SmA transition point at the values $T = T_{NA}^{(+)}$ in the nematic phase and $T = T_{NA}^{(-)}$ in the smectic phase. The $L_\perp(n)$ dependences for homologues LC1.*n* are given in Fig. 2. The $L_\perp(n)$ function in the nematic phase for the homologues of the same parity decreases monotonically along with an increase in *n*. Strong odd–even alternation of $L_\perp(n)$ is superimposed on this trend, in which the $L_\perp(n)$ values for homologues with the odd *n* values are higher than the $L_\perp(n \pm 1)$ values for the adjacent even homologues. The longitudinal axis of the terminal C–CH$_3$ fragment upon the *trans*-conformation of the alkyl chain of the odd LC1.*n* homologues makes a smaller angle with the molecular longitudinal axis **l**, relative to the even homologues. The alternation of $L_\perp(n)$ in the nematic phase at $T = T_{NA}^{(+)}$ thus corresponds to alternation of *S*(*n*) [10, 11] and indicates sufficient rigidity in the alkyl chains of the LC1.*n* homologues in the nematic phase. Monotone (or stronger nonmonotone) growth of the value $\delta L_\perp(T_{NA}) = L_\perp(T_{NA}^{(-)}) - L_\perp(T_{NA}^{(+)})$ is observed upon the N–SmA transition for the odd (even) LC1.*n* homologues with an increase in *n*. This is consistent with the known growth of δ*S*(*n*) upon the N–SmA transition with the elongation of the molecules' terminal alkyl chains [9, 11, 12].

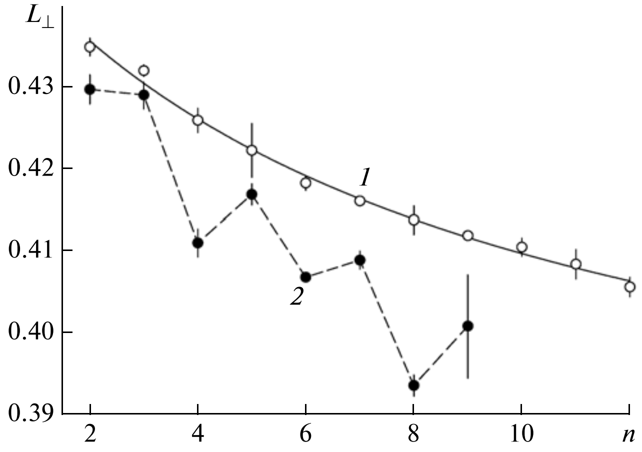


Fig. 2. Dependences of $L_\perp$ on number *n* of LC1.*n* homologues in the smectic A phase at temperature $T_{NA}^{(-)}$ (*1*) and in the nematic phase at temperature $T_{NA}^{(+)}$ (*2*, dashed line). The solid line shows our approximation by Eq. (9).

The $L_\perp(n)$ function in the smectic phase decreases monotonically with an increase in *n*. The absence of notable $L_\perp(n)$ alternation is correlated with the same experience for the *S*(*n*) dependence at $T = T_{NA}^{(-)}$ according to the NMR data [12] and is due to an increase in the conformational flexibility (orientational melting) of the terminal alkyl chains of the molecules upon the transition from the nematic to smectic A phase [2, 13, 14]. As a result, the contribution of the chains to the anisotropy of the molecular shape, the value of Δγ, and the anisotropy of the sterical and dispersion intermolecular interactions that determine the value of *S* in the smectic phase, is substantially weakened in comparison with the nematic phase.

The reduction in $L_\perp(n)$ upon an increase in *n* in the smectic phase is not associated with the alteration of

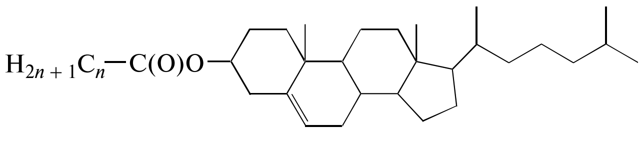
$S(n)$, since the $S(n)$ values in the smectic A at $T = T_{\mathrm{NA}}^{(-)}$ remain unchanged when the character of the N–SmA transition changes from a weak to a strong first order transition and to the I–SmA transition [12]. The $\sigma(n)$ values in (6) for homologues LC1.*n* at $T = T_{\mathrm{NA}}^{(-)}$ and λ = 0.5893 μm change irregularly from an average value of 0.284 with a standard deviation of 0.004. Since a reduction in $L_\perp(n)$ is accompanied by a decrease in $L_{\perp k}(n)$ and $Q(n)$, the probable cause of this effect is a reduction in the ratio $\Delta\gamma/\bar{\gamma}$ upon elongation of the alkyl chain, as follows from (6). This is natural for molecules of LC1.*n*, the core of which is comprised of a longitudinal chain of aromatic fragments connected by a π-electronic conjugation [2]. A reduction in $L_\perp(n)$ is similar to a decrease in $L_\perp$ with decreasing $\Delta\gamma$, due to variations in the electronic structure of the molecules at fixed S [2–4, 7, 8].

This can be verified by comparing the limiting value $L_\perp(n \to \infty)$ with the $L_\perp$ value for the multilayered Langmuir films of cadmium arachidate (Cd-A) [3], which have a smectic A structure where the long alkyl chains of the molecules $[\mathrm{CH_3{-}(CH_2)_{18}{-}C(O)O^-}]_2\mathrm{Cd^{++}}$ are perpendicular to the molecular layers. As is shown in Fig. 2, the monotone dependence $L_\perp(n)$ at $T = T_{\mathrm{NA}}^{(-)}$ is well approximated by the function

$$F(n) = C\frac{D+n}{E+n}, \qquad (9)$$

which describes the change in the ratio $\Delta\gamma/\bar{\gamma}$ over a homologous series of LCs [2] and approximates the $T_{\mathrm{NI}}(n)$ dependence for homologues LC1.*n* with an accuracy of 0.2° [15]. The value $L_\perp(n \to \infty) = C = 0.368 \pm 0.014$ obtained with allowance for errors in the $L_\perp(n)$ values agrees with the value $L_\perp^{(1)} = 0.365$ (0.356) for Cd-A films on glass (polymethylmethacrylate) substrates [3].

On the other hand, a value of $L_\perp(n \to \infty)$ in a smectic A phase should conform to the value $L_\perp$ for molecules with long alkyl chains, if the core of such molecules does not contain aromatic fragments. At the same time, we should expect a weak dependence of $L_\perp(n)$ on the alkyl chain length for such molecules in this phase. Convenient objects for verifying these assumptions are the cholesteryl esters of fatty acids:



(LC2.*n*)

The refraction indices at the values $\lambda = \lambda_{1-5}$ (λ_{2-5}) from the set $\lambda_1 = 0.4358$, $\lambda_2 = 0.5086$, $\lambda_3 = 0.5461$, $\lambda_4 = 0.5893$, and $\lambda_5 = 0.6438$ μm for the cholesteric and smectic A phases of these homologues with $n = 8$ (9–11, 13) were tabulated in [16]. This allowed us to determine the values $L_\perp^{(3)} = 0.362$ (LC2.8) and $L_\perp^{(2)} = 0.360$ (LC2.9), 0.361 (LC2.10–LC2.13) in the smectic phase at temperature T_{ChA} of the cholesteric–SmA transition. These values of $L_\perp(n)$ do not depend on n and agree with the $L_\perp$ values for Cd-A and $L_\perp(n \to \infty)$ for LC1.*n*. The $L_\perp(n)$ dependence is also absent in the cholesteric phase of homologues LC2.*n*, which do not have a smectic phase [8], and in the cholesteric phase of related molecules where alkyl chains are replaced by alkoxyl chains [17].

THE $\bar{\gamma}(S, n)$ DEPENDENCES AND THEIR CONSEQUENCES

In our method, the functions $b(T, \lambda)$ and $\bar{\gamma}(T, \lambda)$ are determined consistently with the functions $L_\perp(T)$ and $\Delta f(T, \lambda) = (L_{\perp k} - L_\perp)(\bar{\varepsilon} - 1)(3 + Q)$, and the signs of Δf and b coincide. The value and sign of Δf impose limitations on $\bar{\gamma}$. Let us demonstrate this by considering the equation [2]

$$\bar{\varepsilon} - 1 = 4\pi N(\bar{\gamma}\bar{f} + 2S\Delta\gamma\Delta f/9), \qquad (10)$$

where $\bar{f} = (f_\parallel + 2f_\perp)/3 = (\bar{\varepsilon} + 2)[1 - A(1 - r_0)]/3$. The inequalities $L_\perp > L_{\perp k}$, $A > 1$, and $\Delta f < 0$ are valid for the nematic and smectic A phases of homologues LC1.*n* in the visible range, in consideration of which Eq. (10) leads to the inequality $(\bar{\varepsilon} - 1) < 4\pi N\bar{\gamma}\bar{f}$ and the limitations

$$\bar{\gamma} > \frac{3(\bar{\varepsilon}-1)}{4\pi N(\bar{\varepsilon}+2)[1 - A(1 - r_0)]} > \frac{3(\bar{\varepsilon}-1)}{4\pi N(\bar{\varepsilon}+2)} = \bar{\gamma}_{\mathrm{H}}. \qquad (11)$$

The expression for $\bar{\gamma}_{\mathrm{H}}$ was introduced arbitrarily in place of $\bar{\gamma}$ for molecular crystals [18] and is widely used in the optics of LCs [19–31]. In consequence of the familiar empirical correlation

$$\frac{\bar{\varepsilon}-1}{N(\bar{\varepsilon}+2)} \approx \mathrm{const}, \qquad (12)$$

which is satisfied with a high level of accuracy when the temperature and phase state of uniaxial LCs [2, 19–29, 32] vary, the $\bar{\gamma}_{\mathrm{H}}$ value remains invariable. As follows from (1), the equality $\bar{\gamma} = \bar{\gamma}_{\mathrm{H}}$ is equivalent to the values $b = 1 - r_0 = b_{\mathrm{H}} > 0$, $L_\perp(b = b_{\mathrm{H}}) = L_\perp^{(\mathrm{H})} < L_{\perp k}$, and $\Delta f(L_\perp = L_\perp^{(\mathrm{H})}) = \Delta f_{\mathrm{H}} > 0$, which disagrees with experiments in the visible and IR ranges [2–4, 7, 8, 17]. The use of $\bar{\gamma} = \bar{\gamma}_{\mathrm{H}}$ in (10) and consideration of the inequality $\Delta f_{\mathrm{H}} > 0$ yield $(\bar{\varepsilon} - 1) > 4\pi N\bar{\gamma}_{\mathrm{H}}\bar{f}_{\mathrm{H}}$ where $\bar{f}_{\mathrm{H}} = \bar{f}(A = A_{\mathrm{H}})$. The limitations $A_{\mathrm{H}} > 0$ and $L_\perp^{(\mathrm{H})} > 1/3$ follow from this. The change in $L_\perp^{(\mathrm{H})}(\Delta T)$ agrees with formulas (4) and (5) with a high level of accuracy, but the dependence $A_{\mathrm{H}}(n)$ is very weak (Table 1) and the $L_\perp^{(\mathrm{H})}(L_{\perp k})$ graphs for all the homologues LC1.*n* lie along one line.

Let us examine the behavior of $\bar{\gamma}$ in dependence on the orientational ordering and phase state of the

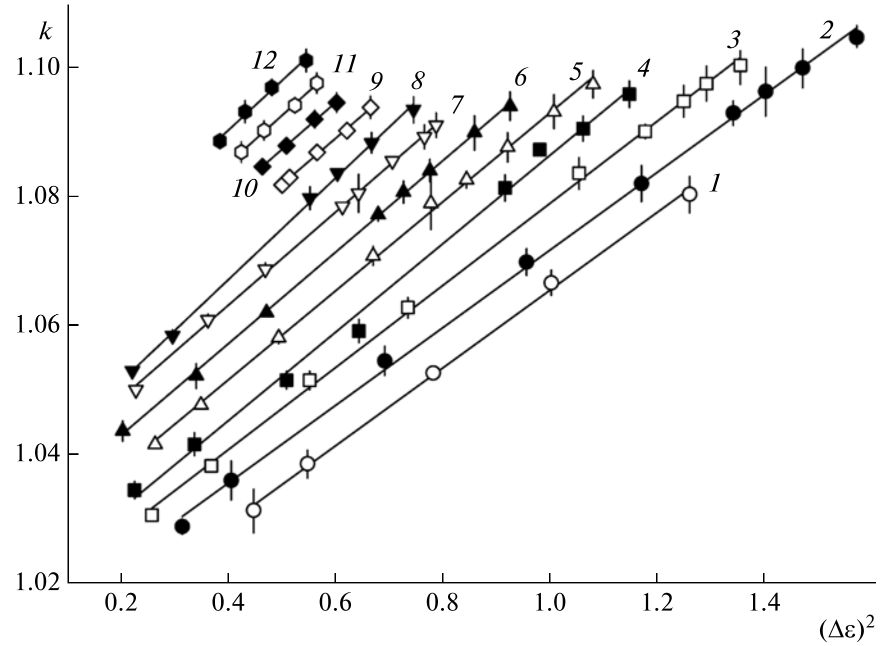


Fig. 3. Dependence of values $\kappa = \overline{\gamma}/\overline{\gamma}_H$ on $(\Delta\varepsilon)^2$ at $\lambda = 0.5893$ μm for LC1.*n* homologues; numbers correspond to the *n* values; straight lines are dependences (15) with coefficients from Table 2. The graphs with $n = 2$–12 are shifted upward by $0.005(n-1)$.

homologues LC1.*n*. As follows from (1), consideration of the expression (11) for $\overline{\gamma}_H$ yields

$$\overline{\gamma} = \overline{\gamma}_H(b + r_0)^{-1}. \qquad (13)$$

Allowing for (12) and the absence of data on the density $\rho \propto N$ for homologues LC1.*n*, we use the normalized value

$$\kappa = \overline{\gamma}/\overline{\gamma}_H = (b + r_0)^{-1} \qquad (14)$$

in place of $\overline{\gamma}$. The variation $\kappa(\Delta T)$ in the LC is associated with the orientational ordering of molecules and its influence on the anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, which is a macroscopic parameter of the nematic order [9] and $\Delta\varepsilon \propto S$ in the linear approximation by S [2]. Given the absence of absolute values of S for the homologues LC1.*n*, it is natural to consider the variation $\kappa(\Delta T)$ as the function $\kappa(\Delta\varepsilon)$. From the phenomenological viewpoint, the value $\overline{\gamma}(I_{1-3})$ in the nematic phase, as an invariant of the γ tensor, is a function of the invariants $I_1 = \mathrm{SpS} = 0$, $I_2 = \mathrm{SpS}^2 \propto S^2$, and $I_3 = \mathrm{SpS}^3 \propto S^3$ of the tensor order parameter of the nematic phase $\mathbf{S} = S(n_i n_k - \delta_{ik}/3)$ [9] where $n_{i,\,k}$ are the components of director $\mathbf{n}$ in an arbitrary coordinate system. Variation $\delta\overline{\gamma}(S)$ in the nematic phase with regard to the $\overline{\gamma}_i$ value in the isotropic phase of LC should therefore start from the summand $\propto S^2$ or $\propto(\Delta\varepsilon)^2$. Dependence $\kappa(\Delta\varepsilon)$ in the lowest order by $\Delta\varepsilon$ is then approximated by the expression

$$\kappa(\Delta\varepsilon) = \kappa_0 + \kappa_2(\Delta\varepsilon)^2. \qquad (15)$$

The κ values calculated using Eq. (14) for homologues LC1.*n* are shown in Fig. 3 as functions of $(\Delta\varepsilon)^2$ at $\lambda = 0.5893$ μm. The graph points correspond to the values $\langle b(\Delta T)\rangle$ obtained from Eq. (2) at $L_\perp(\Delta T) = \langle L_\perp^{(0)}(\Delta T)\rangle$. The standard deviations of the $b(\Delta T)$ values in Fig. 3 correlate with the standard deviations of the $L_\perp^{(0)}(\Delta T)$ values in Fig. 1. The maximum difference between $\overline{\gamma}$

Table 2. Coefficients of Eq. (15) and correlation coefficients R for homologues of the LC1.*n* series at $\lambda = 0.5893$ μm

n	κ_0	κ_2	*R*	*n*	κ_0	κ_2	*R*
1	1.0052	0.0605	0.9984	7	1.0043	0.0726	0.9991
2	1.0065	0.0605	0.9988	8	1.0006	0.0791	0.9988
3	1.0053	0.0639	0.9989	9	1.0063	0.0717	0.9978
4	1.0029	0.0688	0.9958	10	1.0061	0.0730	0.9985
5	1.0040	0.0693	0.9987	11	1.0054	0.0750	0.9984
6	1.0038	0.0713	0.9995	12	1.0046	0.0774	0.9914

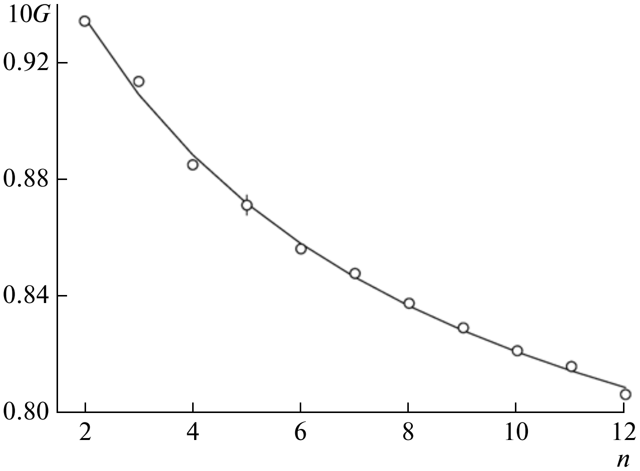


Fig. 4. Dependence of the *G* value (17) on the number *n* of LC1.*n* homologues in the smectic A phase at temperature $T_{\rm NA}^{(-)}$ and λ = 0.5893 μm (dots). The solid line shows our approximation by Eq. (9).

and $\overline{\gamma}_{\rm H}$ for the first homologues LC1.*n* is 10%. As is shown in Fig. 3, the dependences $\kappa(\Delta\varepsilon)$ for all the homologues LC1.*n* in all temperature intervals of the nematic and smectic phases are well approximated by Eq. (15) with the coefficients given in Table 2. The κ_0 value depends on the $\overline{\gamma}(0)$ value, extrapolated to the value $\Delta\varepsilon = 0$. The $\overline{\gamma}(0)$ value for the N–I first order transitions is different from $\overline{\gamma}_i$ due to the limited interval of the change $\Delta\varepsilon \ge \Delta\varepsilon(T_{\rm NI})$ and could be due to differences in the short-range molecular order of the isotropic and LC phases. The κ_0 values approach unity as the $\Delta\varepsilon$ values at $T = T_{\rm NI}$ ($T_{\rm IA}$) become lower and the accuracy level of the extrapolation to $\Delta\varepsilon = 0$ from the nematic (smectic) phase at n = 1–8 (9–12) becomes higher. The difference of κ_0 from unity is considerably less than the relative change in κ upon transition from the isotropic liquid to the LC.

The N–SmA transition of the homologues LC1.*n* is accompanied by jump $\delta\kappa(T_{\rm NA}) = \kappa(T_{\rm NA}^{(-)}) - \kappa(T_{\rm NA}^{(+)})$, due to the appearance of the density wave $\psi = |\psi|\exp(i\varphi)$ of smectic layers [9]. The function $\overline{\gamma}(I_{2,3}, |\psi|)$ in the smectic phase depends on *S* and the magnitude $|\psi|$. The influence of $|\psi|$ on a change in $\overline{\gamma}$ upon the N–SmA and I–SmA transitions and in the smectic phase is revealed through the change in the *S* and $\Delta\varepsilon$ values due to correlation between order parameter **S** and ψ [9]. As a result, dependence (15) for homologues LC1.*n* remains invariant with respect to the N–SmA transition (n = 2–8) and is valid in the presence of a single smectic phase (n = 9–12). This demonstrates one advantage analyzing the $\kappa(\Delta\varepsilon)$ dependence via the measurable $\Delta\varepsilon$ value in the smectic phase instead of the $\kappa(\Delta T)$ dependence with the unknown $|\psi|(\Delta T)$ function. The κ_2 coefficient for homologues LC1.*n* with nematic and smectic phases (with a single smectic phase) increases monotonously with an increase in *n*. The occurrence of this effect can now be observed in earlier-studied nematic LCs **1–5** with different molecular structures ([4], Table 2) upon the lengthening of one (two) terminal chains at transitions **2** → **1** and **5** → **4** (**5** → **3**).

Upon the self-organization of molecules whose chemical and electron properties are non uniform within the molecular volume, the formation of hierarchically organized structures in the absence of specific intermolecular interactions (e.g., complexation, hydrogen bonds) depends on the distribution of polarizability along the molecular volume [2, 14]. A difference in the polarizability densities of the aromatic core and terminal aliphatic chains of mesogenic molecules promotes microlayering of the nematic phase and the formation of smectic phases, with segregation of the molecular cores and chains according to the principle of like dissolves like. With a weak (strong) difference in the polarizability densities of the core and chains, the smectic A has the monolayered structure of $\rm SmA_1$ (or the bilayered structure of $\rm SmA_d$) [14]. Let us define the polarizability density of the *k*-th molecular fragment in a medium by the expression $G_k = \overline{\gamma}_k/v_k$, where $\overline{\gamma}_k$ and v_k are increments of the molecular polarizability and volume related to this particular fragment in a medium. The $G_{\rm c}$ and $G_{\rm ch}$ values for the molecular core and the alkyl chain are important for the homologues of one series, and $G_{\rm ch}$ coincides with the polarizability density G_m of the chain methylene fragment.

In the case of the LC1.*n* molecules considered as the core and the alkyl chain, we should allow for the additivity of the $\overline{\gamma}_m$ values for unconjugated methylene fragments of the chain [1] and the additivity of v_m values for the same fragments in the smectic phases [33–36]. As a result, we obtain

$$\overline{\gamma} = \overline{\gamma}_{\rm c} + n\overline{\gamma}_m, \quad v = v_{\rm c} + nv_m. \tag{16}$$

Here $v = 1/N$ is the volume per one molecule in a medium, and the $\overline{\gamma}_{\rm c}$ and $v_{\rm c}$ values relate to the molecular core. The $\overline{\gamma}_{\rm c}$ and $\overline{\gamma}_m$ values depend on the character and degree of the molecular ordering due to intermolecular interactions, and the volumes $v_{\rm c}$ and v_m depend on the temperature, due to the thermal expansion of the mesophase [33–36]. The polarizability density $G = \overline{\gamma}/v = N\overline{\gamma}$ of the molecules of LC1.*n* in the mesophase is given by the expression

$$G = \frac{3(\overline{\varepsilon} - 1)}{4\pi(\overline{\varepsilon} + 2)(b + r_0)}. \tag{17}$$

In consideration of (16), the dependence $G(n)$ can be reduced to function (9) with parameters

$$C = \overline{\gamma}_m/v_m, \quad D = \overline{\gamma}_{\rm c}/\overline{\gamma}_m, \quad E = v_{\rm c}/v_m. \tag{18}$$

Dependence $G(n)$ for the smectic phase of the homologues LC1.*n* at $T = T_{\rm NA}^{(-)}$ is shown in Fig. 4. It decreases monotonically and is well approximated by function (9), the parameters of which at $\lambda = 0.5893$ μm with allowance for (18) lead to $G_c = \overline{\gamma}_c/v_c = CD/E = 0.1018 \pm 0.0244$ and $G_m = C = 0.0715 \pm 0.0009$. The insignificant difference $G_c > G_m$ is in agreement with the monolayered structure of the smectic phase of the LC1.*n* homologues [37]. The molar volume $V_m = N_A v_m$ (where N_A is the Avogadro number) of a methylene fragment in molecules of the azomethine derivatives with a single alkyl chain in the monolayered smectic A phase at temperatures close to the $T_{NA}(n)$ values for the LC1.*n* homologues varies over the interval $V_m \approx 16.2–17.5$ cm^3/mol [34]. With allowance for the G_m values, we obtain the estimate $\overline{\gamma}_m \approx 1.92–2.08$ Å^3, which is higher than the mean value $\overline{\gamma}_m \approx 1.84$ Å^3 ($\lambda = 0.5893$ μm) for normal alkanes in the liquid state or in solution [1, 32]. The growth of $\overline{\gamma}_m$ in anisotropic media is predetermined by intermolecular interactions and corresponds to the limitations of (11) with allowance for the equality $\overline{\gamma}_i \approx \overline{\gamma}_H$ in the isotropic and LC phases.

CONCLUSIONS

The observed characteristics of the behavior of $L_\perp(\Delta T)$ and $\overline{\gamma}(\Delta T)$ at the I–N–SmA phase transitions and in a homologous series can be divided into two categories: universal (associated with the symmetry of mesophases and character of the corresponding order parameters) and specific (in dependence on the properties of individual homologues). Dependence $L_\perp(\Delta T)$ in the nematic phase for each homologue reflects variations in the orientational order parameter of molecules, S. The quadratic relationships $\overline{\gamma}(\Delta\varepsilon)$ or $\overline{\gamma}(S)$ are general manifestations of the self-organization of molecules and are predetermined by the symmetry of the LC (the absence of invariant $\mathrm{Sp}\mathbf{S} = 0$) regardless of the particular reasons for changes in the γ tensor (e.g., intermolecular interactions and variations in the electronic structure and molecular conformations). Invariance of the linear dependence (4) and the squared relationship $\overline{\gamma}(S)$ with respect to the N–SmA transition demonstrates that the contribution from the smectic ordering to changes in $L_\perp$ and $\overline{\gamma}$ is revealed through a change in S, due to the interaction of the nematic and smectic order parameters $\mathbf{S}$ and ψ, and it is better to use the $\Delta\varepsilon$ scale in the smectic phase than the ΔT scale with the unknown $|\psi|(\Delta T)$ function.

The alternating of $L_\perp(n)$ in the nematic phase at $T = T_{NA}^{(+)}$ is determined by the alternating of $S(n)$, $\Delta\gamma(n)$ and the molecular shape anisotropy due to the relative rigidity of the alkyl chains in the molecules. The absence of alternation in $L_\perp(n)$ in the smectic A phase at $T = T_{NA}^{(-)}$ is associated with the weakness (or absence) of the $S(n)$ dependence owing to the orientational–disordered state of the alkyl chains. The monotone decrease in $L_\perp(n)$ upon an increase in *n* in the smectic phase of the LC1.*n* homologues is determined by the isotropization of the L tensor, along with the reduction of the $\Delta\gamma/\overline{\gamma}$ relation upon the lengthening of the alkyl chain. The obtained value $L_\perp(n \to \infty)$ is in agreement with $L_\perp$ for the Cd-A Langmuir films and the smectic A phase of cholesteryl esters LC2.*n*, the molecules of which do not have aromatic fragments.

The insignificant difference in the polarizability density of the core (G_c) and the alkyl chain ($G_{ch} = G_m$) of the LC1.*n* homologues correlates with the known monolayered type of their smectic A phase. Application of the proposed approach to investigation of LCs with bilayered types of a smectic A phase ($\mathrm{SmA_d}$, $\mathrm{SmA_2}$) may help to ascertain the G_c values corresponding to these types of smectic structure and on the molecular level, and to make clear the quantitative criteria for the hierarchical organization of molecular ensembles.

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