

New Features of a Smectic-*A*–Crystal-*B* Phase Transition in a Homologous Series of Liquid Crystals

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The components L_j of the Lorentz tensor and the polarizability density of molecules G in the smectic-*A* and crystalline-*B* phases have been determined for homologues of the series of alkyl-*p*-(4-alkoxybenzylideneamino-)cinnamates. The quantity $L_j(G)$ in both phases is a linear (quadratic) function of the orientational order parameter of molecules S , which is invariant (noninvariant) with respect to the *A*–*B* transition, which is manifested in the form of jumps δL_j and δG and enhancement of the $G(S)$ dependence. An increase in the length of terminal molecular chains and weakening of interlayer correlation of molecules are accompanied by strengthening of the *A*–*B* transition of the first order and $G(S)$ dependences in both phases together with an increase in δL_j and δG . Change δG and dependence $G(S)$ in the *B* phase are related to change in the conformation (flattening) of aromatic molecular cores.

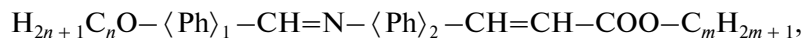
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1. Crystalline smectics-*B* [1] with the long-range intra- and interlayer positional order of molecules are characterized by a crossover between two- and three-dimensional melting at a phase transition to the smectic-*A* phase [2] with the liquid-like positional order of molecules in layers and the quasi-long-range one-dimensional positional order of layers. The character of the *A*–*B* transition, as well as the degree of the manifestation of three-dimensional ordering of molecules in the *B* phase, depends on the degree of interlayer correlation of molecules. In view of the determination of the molecular nature of the *A*–*B* transition, there is a question concerning the effect of the intralayer order of molecules in both phases on the molecular polarizability tensor γ and dipole–dipole interactions between molecules under variation of interlayer correlation of molecules. An answer to this question can be obtained from the refractometry of liquid crystals of one homologous series with the *A*–*B* transition in which the degree of the interlayer correlation of molecules depends on the length of terminal molecular chains, which are in a conformational disordered state.

For uniaxial orthogonal phases *A* and *B*, the components $\varepsilon_j = 1 + 4\pi N f_j \gamma_j$ of the relative permittivity for light waves polarized along ($j = \parallel$) and across ($j = \perp$) the optical axis \mathbf{n} are related to the number N of mole-

cules per unit volume, ensemble-averaged components γ_j of the molecular polarizability, components $f_j = 1 + L_j(\varepsilon_j - 1)$ of the local field tensor, and components L_j of the Lorentz tensor ($\text{Tr} L = 1$). In the visible transparency range, $\varepsilon_j = n_j^2$, where n_j are the refractive indices of the liquid crystal. The anisotropy of the tensor L characterizes the anisotropy of the dipole–dipole interaction between molecules and is an indicator of the local anisotropy of the medium at mesoscopic scales [3]. For layered molecular media similar to the *A* and *B* phases, the contribution of interlayer dipole–dipole interaction between molecules to the components L_j is negligibly small compared to the contribution from the intralayer interaction [4]. For this reason, the components L_j are indicators of the intralayer order of molecules in the *A* and *B* phases when L_j is determined from the experimental data [5] without a priori assumptions about the properties of the tensors γ , L , and f .

In this work, the indicated approach is used to study the components L_j and polarizability density $G_j = N \gamma_j$ in the *A* and *B* phases of homologues of the series of alkyl-*p*-(4-alkoxybenzylideneamino-)cinnamates (*nO.mC*)



where $\langle \text{Ph} \rangle_{1,2}$ are the phenyl rings.

2. For the *A* and *B* phases with the optical axis \mathbf{n} perpendicular to molecular layers, the orientational order of the longitudinal axes \mathbf{l} of molecules with respect to \mathbf{n} is characterized by the quantity $S = \langle 3 \cos^2 \theta - 1 \rangle / 2$, where θ is the angle between axes \mathbf{l} and \mathbf{n} , and the triangular brackets mean averaging over the molecular ensemble. For uniaxial liquid crystals, molecules can be treated as uniaxial without loss of generality of the determination of the components L_j . The tensor γ can be characterized by the longitudinal (γ_l) and transverse (γ_t) components or by the mean value $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$ and anisotropy $\Delta\gamma = \gamma_l - \gamma_t$. For the *A* and *B* phases with $\Delta\varepsilon = (\varepsilon_{\parallel} - \varepsilon_{\perp}) \propto \Delta\gamma S > 0$, the components L_{\perp} and $L_{\parallel} = 1 - 2L_{\perp}$ are expressed [5] in terms of the parameters $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ and $Q = \Delta\varepsilon/(\bar{\varepsilon} - 1)$ and the quantities

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_0, \quad (1)$$

$$b_1 = \frac{2r_0Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1[(6 + Q)/Q]^2,$$

which depend on the temperature T and light wavelength λ . The component $L_{\perp}(T)$ is given by the expression [5]

$$L_{\perp} = L_{\perp k} - \frac{\bar{\varepsilon} + 2}{12(\bar{\varepsilon} - 1)} \quad (2)$$

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

where $L_{\perp k} = (3 + 2Q)/[3(3 + Q)]$ and the function $b(\lambda, T)$ depends on the unknown function $\bar{\gamma}(\lambda, T)$. When the $n_j(\lambda, T)$ values are known for a discrete set λ_i ($i = 1, 2, \dots, p$) in the visible range, the function $b(\lambda, T)$ in the interval $\lambda_1 - \lambda_p$ is approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \dots + a_q(T)\lambda^q. \quad (3)$$

The quantity $L_{\perp}(T)$ is independent of λ . The $q + 2$ unknowns ($L_{\perp}^{(q)}$, a_0 , a_1 , \dots , a_q) correspond to the temperature T . They are determined from the system of $q + 2 = p$ equations (2); each equation corresponds to one of the values λ_i . The degree of the approximation used in Eq. (3) is determined by the accuracy of the experimental values $n_j(\lambda, T)$ and the width of the approximation range $\lambda_1 - \lambda_p$.

The refractive indices $n_j(\lambda_i, T)$ for the *A* and *B* phases of the 2O.2C, 3O.2C, 4O.3C, 8O.3C, and 8O.5C homologues were measured with an accuracy of 5×10^{-4} in [6] and were tabulated at values $\lambda_1 = 0.5461 \mu\text{m}$, $\lambda_2 = 0.5893 \mu\text{m}$, and $\lambda_3 = 0.6438 \mu\text{m}$. For all homologues, the quantity $\Delta\varepsilon(\lambda_i, T)$ changes stepwise at the temperature T_{AB} of the *A*-*B* phase transition of the first order characteristic of the crystal *B* phase of the 2O.2C liquid crystal [7] and other deriva-

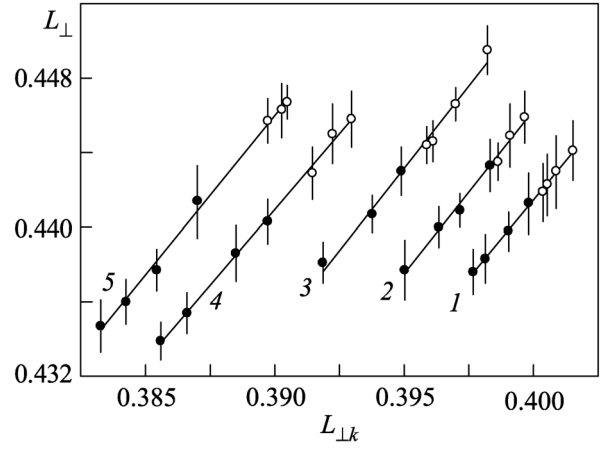


Fig. 1. Dependences (4) in the (closed circles) *A* and (open circles) *B* phases of (1) 2O.2C, (2) 3O.2C, (3) 4O.3C, (4) 8O.3C, and (5) 8O.5C homologues at $\lambda = 0.5893 \mu\text{m}$. Plots marked by $N = 2-5$ are shifted upward by $0.004(N - 1)$.

tives of azomethines [1]. At a given accuracy of $n_j(\lambda_i, T)$ values and narrow range $\lambda_1 - \lambda_3$, parameters $L_{\perp}^{(1)}(T)$ vary irregularly. The quantities $\langle L_{\perp}^{(0)}(T) \rangle$ averaged over the $L_{\perp}^{(0)}(T)$ values for three pairs of references λ_i from the set λ_1 , λ_2 , and λ_3 vary regularly and are adequate to the accuracy of the $n_j(\lambda_i, T)$ values. Thus, $L_{\perp}(T) = \langle L_{\perp}^{(0)}(T) \rangle$ should be accepted.

3.1. With a decrease in T , an increase in $L_{\perp}(T)$ in the *A* phase changes to a jump $\delta L_{\perp}(T_{AB})$ and a subsequent increase in the *B* phase. For each homologue $nO.mC$ at a given λ value, the functions $L_{\perp}(T)$ and $L_{\perp k}(T, \lambda)$ are related to each other as

$$L_{\perp}(T) = \alpha(\lambda)L_{\perp k}(T, \lambda) + \beta(\lambda). \quad (4)$$

These dependences are shown in Fig. 1 at the value $\lambda = \lambda_2$, which corresponds to all spectrum-dependent quantities presented below. The vertical bars in the figure are the standard deviations of the $L_{\perp}^{(0)}(T)$ values from $\langle L_{\perp}^{(0)}(T) \rangle$. Relation (4) is invariant with respect to the *A*-*B* transition. For homologues $nO.mC$, the coefficients in Eq. (4) depend on the length of terminal chains of molecules and are related with a high accuracy as $\beta = (1 - \alpha)/3$. In particular, $\alpha = 1.7092$, $\beta = -0.2366$, and $(1 - \alpha)/3 = -0.2364$ for 8O.5C. Therefore, it follows from Eq. (4) that

$$\alpha = (L_{\perp} - 1/3)/(L_{\perp k} - 1/3) \approx \text{const}. \quad (5)$$

Since $Q \ll 3$, $L_{\perp k} - 1/3 \propto Q$ and, in view of Eq. (5), $L_{\perp} - 1/3 \propto Q$. Then, there is the relation

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

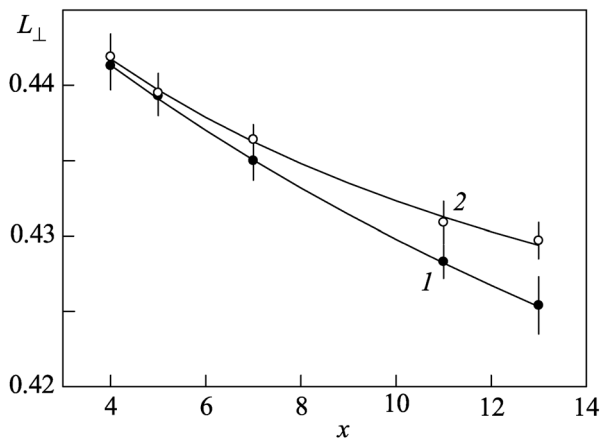


Fig. 2. Dependences $L_{\perp}(x)$ at $T = T_{AB}$ in the (1) A and (2) B phases of $nO.mC$ homologues. The solid lines are approximations by function (8).

where the correction σ to the anisotropy $\Delta f = f_{\parallel} - f_{\perp}$ has the form [5]

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

The substitution of $\Delta f = Q(\bar{\varepsilon} - 1)(1 - \alpha)/3$ shows that the dependence of σ on $\Delta T = T - T_{AB}$ is weak because $Q \ll 3$. In particular, for the 8O.5C liquid crystal, $\sigma = 0.270$ and 0.285 at $\Delta T = 35.6$ and -29.9 K, respectively. For $nO.mC$ homologues, change in $\sigma(\Delta T) = \sigma_0 + \sigma_1 \Delta T$ in the A and B phases is insensitive to the $A-B$ transition, and $\sigma_0(x)$ increases monotonically from $\sigma_0(4) = 0.270$ to $\sigma_0(13) = 0.278$ with an increase in $x = n + m$. Thus, for each $nO.mC$ homologue, the proportionality $L_{\perp} - 1/3 \propto Q \propto S$ relates an increase in $L_{\perp}(T)$ in both phases at a decrease in T and the jump δL_{\perp} to an increase in the orientational order parameter S of molecules because of an increase in the packing density of molecules in layers. This is in agreement with a monotonic increase in the thickness of molecular layers in both phases of the 2O.2C liquid crystal at a decrease in T and the $A-B$ transition [8].

3.2. The quantity δL_{\perp} and the character of the $A-B$ transition are determined by the length of chains x . The quantity δL_{\perp} is an indicator of the difference in the intralayer order of the A and B phase (which determines the character of the $A-B$ transition) and the manifestation of this difference in the dipole-dipole interaction between molecules. Figure 2 shows the $L_{\perp}(x)$ dependences at $T = T_{AB}$ in the A and B phases. The absence of even-odd alternation in change in $L_{\perp}(x)$ indicates the conformationally disordered state of the terminal chains of the $nO.mC$ molecules in both phases [9]. This explains the relation $l > d$ [8] between the length l of the $nO.mC$ molecules at *trans*-conformation of chains and the thickness d of the molecular layers in the monolayer A and B phases. For the 2O.2C

homologue with short terminal chains and strong interlayer correlation between molecules, a small δL_{\perp} value indicates a weak $A-B$ transition of the first order, which corresponds to the thermodynamic data reported in [10, 11]. With an increase in x and weakening of interlayer correlation between molecules owing to the conformational disordering of chains, the enhancement of the $A-B$ phase transition of the first order is accompanied by an increase in δL_{\perp} .

A decrease in $L_{\perp}(x)$ and $Q(x)$ with an increase in x in both phases of $nO.mC$ homologues is due to a decrease in the ratio $\Delta\gamma/\bar{\gamma}$ at the elongation of the terminal chains of molecules and is similar to a decrease in $L_{\perp}(m)$ for the smectic- A phase of 2O.mMC homologues [9], which differ from $nO.mC$ in the replacement of the $CH=CH$ fragment by the $CH=C(CH_3)$ fragment. A decrease in $L_{\perp}(x)$ is also similar to a decrease in L_{\perp} at a decrease in $\Delta\gamma/\bar{\gamma}$ because of the replacement of π -conjugated phenyl rings in the molecular core by saturated cyclic fragments [5, 12, 13]. Dependences $L_{\perp}(x)$ in both phases are well approximated by the function [9]

$$F(x) = (Cx + D)/(x + E), \quad (8)$$

which describes variation of the $\Delta\gamma/\bar{\gamma}$ value in homologous series of liquid crystals [12]. At $x = 0$, the values $L_{\perp}^{(A)}(0) = 0.452$ and $L_{\perp}^{(B)}(0) = 0.454$ for the A and B phases correspond to weak crystallization of the A phase and the $A-B$ phase transition close to a phase transition of the second order. Indeed, enthalpy of the $A-B$ transition even for the 1O.2C homologue with the monotropic B phase [14] is half of that for this transition in the 2O.2C liquid crystal [11].

The enthalpy of the $A-B$ transition increases with x [11]. The limit $x \rightarrow \infty$ corresponds to the $L_{\perp}(\infty)$ value for molecules in the form of long polymethylene chains or for molecules that do not include aromatic π -conjugated fragments (e.g., in the case of replacement of phenyl rings in the core by cyclohexane rings). For the smectic- A phase of $nO.mC$ homologues, the value $L_{\perp}^{(A)}(\infty) = 0.371 \pm 0.014$ coincides within the error with a similar value of 0.368 ± 0.014 for the A phase of 2O.mMC homologues [9], as well as with values $L_{\perp} = 0.363-0.374$ for bilayer lipid membranes, multilayer Langmuir films of cadmium arachidate [5], and the A phase of cholesterol ethers of fatty acids [13].

For the B phase, the value $L_{\perp}^{(B)}(\infty) = 0.409 \pm 0.009$ gives $\delta L_{\perp}(\infty) = 0.038 \gg 0.004 = \delta L_{\perp}(13)$ and corresponds to strong manifestation of the intralayer crystalline order in the dipole-dipole interaction between molecules as compared to the A phase. This corresponds to the unrealistically strong $A-B$ transition of the first order at weak interlayer correlation between molecules and explains why the crystal B phase for nonamphiphilic and nonpolar mesogenic molecules

with cyclohexane rings and/or other saturated cyclic fragments in the core is a neighbor of the nematic or isotropic phase [15, 16]. This situation is similar to that observed for 4-butoxybenzylidene-4'-octylaniline with the nematic, smectic-*A*, and crystalline-*B* phases, where an increase in the entropy of the *A*–*B* transition at an increase in the pressure is accompanied by the narrowing of the interval of the *A* phase, which disappears at the end critical point, after which the crystal-*B*–nematic transition line remains [2].

3.3. The components $G_j = N\gamma_j = \gamma_j/v$ of the polarizability density, where v is the volume per molecule in the medium, are used to determine the molecular nature of the *A*–*B* transition [9]. The most accurately determined quantity $G = N\bar{\gamma}$ is given by the expression

$$G = \frac{3(\bar{\varepsilon} - 1)}{4\pi(\bar{\varepsilon} + 2)(b + r_0)}. \quad (9)$$

For each *nO.mC* liquid crystal, an increase in G in the *A* phase at a decrease in T changes to the jump $\delta G(T_{AB})$ and to a subsequent increase in the *B* phase. Change in $G(T)$ in each phase is best approximated by the function

$$G = G_0 + G_2(\Delta\varepsilon)^2. \quad (10)$$

These dependences at $\lambda = \lambda_2$ are shown in Fig. 3. Since $\Delta\varepsilon \propto S$, the function $G(S)$ is quadratic. Functions (10) are noninvariant with respect to the *A*–*B* transition, because the coefficient $G_2^{(B)}$ in the *B* phase for each *nO.mC* homologue is larger than the coefficient $G_2^{(A)}$ in the *A* phase. An increase in x and the enhancement of the *A*–*B* transition of the first order are accompanied by a monotonic increase in $G_2^{(A)}$, δG , $G_2^{(B)}$, and $G_2^{(B)} - G_2^{(A)}$.

Dependences $G(x)$ for both phases at $T = T_{AB}$ provide information on the polarizability density of the molecular core, $G_c = \bar{\gamma}_c/v_c$, and methylene fragments of chains, $G_\mu = \bar{\gamma}_\mu/v_\mu$. Here, $\bar{\gamma}_c$ and v_c ($\bar{\gamma}_\mu$ and v_μ) are the mean polarizability and volume of the core of the molecule (methylene fragment of the chain) in the liquid crystal. Since $\bar{\gamma}_c$ and $\bar{\gamma}_\mu$ (v_c and v_μ) are additive for *nO.mC* molecules,

$$\bar{\gamma} = \bar{\gamma}_c + x\bar{\gamma}_\mu, \quad v = v_c + xv_\mu. \quad (11)$$

For this reason, the function $G(x)$ is reduced to function (8) with $C = G_\mu$ and $D/E = G_c$. The $G(x)$ dependences for both phases of *nO.mC* liquid crystals at $T = T_{AB}$ are well approximated by function (8) with the parameters $G_\mu^{(A)} = 0.074 \pm 0.005$, $G_\mu^{(B)} = 0.075 \pm 0.002$, $G_c^{(A)} = 0.108 \pm 0.034$, and $G_c^{(B)} = 0.107 \pm 0.024$. The invariance of G_μ at the *A*–*B* transition indicates that the conformationally disordered state of terminal

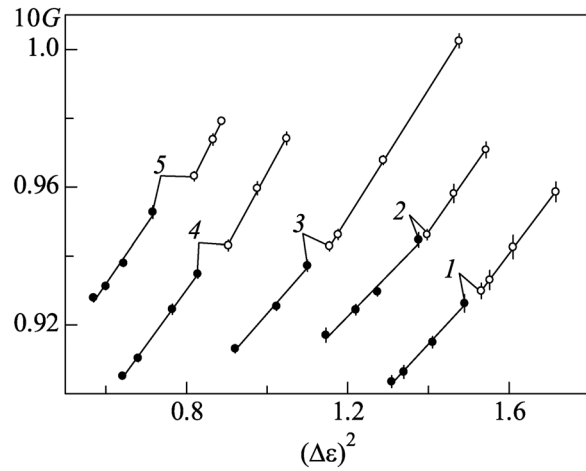


Fig. 3. Dependences (10) in the (closed circles) *A* and (open circles) *B* phases of (1) 2O.2C, (2) 3O.2C, (3) 4O.3C, (4) 8O.3C, and (5) 8O.5C homologues at $\lambda = 0.5893 \mu\text{m}$. Plots marked by $N = 2-5$ are shifted upward by $0.03(N-1)$.

chains is the same in both phases. The relation $G_c > G_\mu$ promotes the intralayer segregation of molecular cores and chains in the *A* and *B* phases with a decrease in the temperature. The invariance of G_c at the *A*–*B* transition shows that the degrees of segregation of molecular cores in these phases at $T = T_{AB}$ are close to each other.

Dependence (10) is similar to the quadratic dependence $\bar{\gamma}(S)$ in the nematic phase of 4-methoxybenzylidene-4'-butylaniline (MBBA) [17]. It is due to change in the oscillator strengths $f_{\pi\pi}(S)$ and $f_{n\pi}(S)$ of long-wavelength electronic transitions $\pi-\pi^*$ and $n-\pi^*$, which are polarized along the long axis *I* of the molecule, because of the interactions between molecules and change in the conformation of the molecular core. The compression of molecules in layers is accompanied by a decrease in the angle φ_N between the CH=N fragment and phenyl ring $\langle \text{Ph} \rangle_2$ of the molecular core. This leads to an increase in the parameter $Q_2 = \langle \cos^2 \varphi_N \rangle = \eta_0 + \eta_2 S^2$ of the conformational state of molecules of the liquid crystal [18]. The relations $f_{\pi\pi} \propto Q_2$ and $f_{n\pi} \propto 1 - Q_2$ result in the quadratic dependences $f_{\pi\pi}(S)$ and $f_{n\pi}(S)$, which contribute to the quadratic dependences $\gamma_1(S)$, $\Delta\gamma(S)$, and $\bar{\gamma}(S)$. For the *A* and *B* phases, the quadratic dependence $Q_2(S)$ holds in the case of different coefficients $\eta_{0,2}$ in different phases.

The approximation of the dependences $G_{||}(\lambda)$ and $G(\lambda)$ for *nO.mC* homologues in the range $\lambda_1-\lambda_3$ by the function

$$Y(\lambda) = Y_b + P\lambda^2/(\lambda^2 - \lambda_r^2) \quad (12)$$

at each temperature point gives close values $\lambda_r(G_{||}) \approx \lambda_r(G)$. For all *nO.mC* homologues in the *A* phase, the

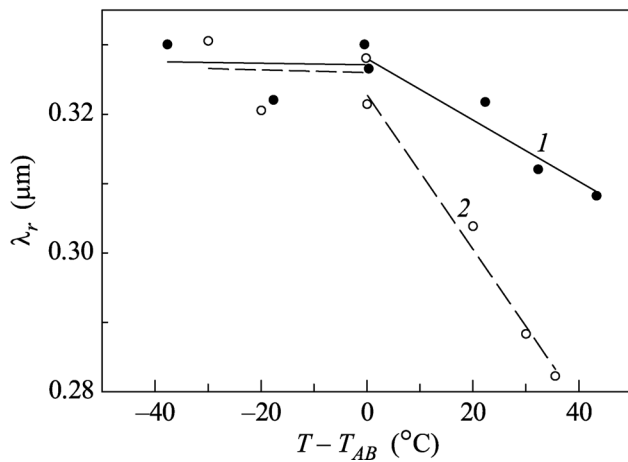


Fig. 4. Temperature dependences of λ_r for the functions $G_{\parallel}(\lambda)$ of form (12) in the A and B phases of (1) 3O.2C and (2) 8O.5C homologues. The solid and dashed lines are interpolations.

$\lambda_r(T)$ dependences are regular and close to similar quantities $\lambda_r(\gamma_i) \approx \lambda_r(\bar{\gamma})$ and maxima of the electronic absorption bands of MBBA for the $\pi-\pi^*$ and $n-\pi^*$ transitions [17]. Figure 4 shows the temperature dependences of the quantities $\lambda_r(G_{\parallel})$ for the 3O.2C and 8O.5C homologues with the minimum and maximum δG values. The spread of the quantities $\lambda_r(G_{\parallel})$ in both phases is due to inaccuracy of the $n_j(\lambda_i)$ values. The spread of the $L_{\perp}(T)$ values in Fig. 1 is not manifested in the scale of Fig. 4. An increase in $\lambda_r(G_{\parallel})$ in the A phase with a decrease in the temperature indicates the shift of long-wavelength electronic absorption bands owing to the enhancement of interactions between molecules at the intralayer segregation of molecular cores and terminal chains. The maximum (minimum) derivative $|d\lambda_r/dT|$ for 8O.5C (3O.2C) correlates with the maximum (minimum) $G_2^{(A)}$ value. For the 8O.5C liquid crystal, the $A-B$ transition is accompanied by a small jump $\lambda_r(G_{\parallel})$ as compared to the total change in $\lambda_r(G_{\parallel})$ within the A phase. For other $nO.mC$ homologues, $\lambda_r(G_{\parallel})$ does not change in this transition. This confirms a close degree of segregation of molecular cores in the A and B phases near T_{AB} . The invariance of $\lambda_r(G_{\parallel})$ and $\lambda_r(G)$ in the B phase for all $nO.mC$ liquid crystals indicates change in $\delta G(T_{AB})$ and an increase in $G(S)$ in this phase owing primarily to an increase in $Q_2(S)$, which slightly affects $\lambda_r(G_{\parallel})$ and $\lambda_r(G)$ [17]. The flattening of molecular cores in the case of their pseudo-hexagonal packing in layers of the B phase [19] is in agreement with a short average intermolecular distance d_w in layers of 2O.2C and 8O.5C homologues [7, 8] as compared to the width of the phenyl ring, as well as in agreement with the absence of the free rotation of molecules about their longitudinal axes **I**.

A decrease in the angle φ_N at the $A-B$ transition for $nO.mC$ homologues is accompanied by the enhancement of electronic conjugation of the fragments of the core, an increase in γ_i , $\Delta\gamma$, and $\bar{\gamma}$, and the enhancement of the molecular attraction stabilizing the B phase. This is promoted by the softness of the benzylideneaniline core with respect to change in Q_2 owing to the interactions between molecules in liquid crystals as compared to the cores of molecules of other chemical classes [20]. In particular, in the term $\Delta F_Q = (\Delta Q_2)^2/2\chi_Q$ in the free-energy density of liquid crystals [18], $\chi_Q = 0.80$ and $0.07 \text{ cm}^3/\text{J}$ for MBBA and alkylcyanobiphenyls, respectively [20]. The introduction of substituents into the $\langle \text{Ph} \rangle_2$ ring, which lead to an increase in the angle φ_N and a decrease in χ_Q , is accompanied by a decrease in the thermostability of the B phase or by its disappearance [20]. This behavior explains why mesogenic derivatives of benzylideneaniline tend to form the crystalline- B phase [1, 16].

4. The above results expand the known capabilities of refractometry in studying the $A-B$ transition [6, 21]. When the $n_j(\lambda)$ values are known in a quite wide transparency range, the quantities $L_j(T)$ and $G_j(\lambda, T)$ determined in terms of these values are sensitive indicators of the intralayer ordering of molecules and interactions between molecules. Relations (4), (8), (10), and (12) provide new information on interactions between molecules in both phases, the molecular nature of the $A-B$ transition, and the dependence of the character of this transition on the degree of interlayer correlation of molecules in the homologue series. At the $A-B$ transition, the structural order of molecules changes consistently with the conformational state of molecular cores. This circumstance allows a unified consideration of the structural, physical, and chemical aspects of this transition.

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