

Features of the orientational order of molecular fragments and character of the nematic–smectic-*A* phase transition in liquid crystals

E. M. Aver'yanov, P. V. Adomenas, V. A. Zhuikov, and V. Ya. Zyryanov

L. V. Kirenski Institute of Physics, Siberian Branch of the Academy of Sciences of the USSR, Krasnoyarsk
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The orientational order of the molecular spines and of the end fragments of the flexible chains of molecules in uniaxial liquid crystals is investigated. Orientational melting of end fragments, induced by isotropic-liquid–smectic-*A* or nematic–smectic-*A* phase transitions, is observed for the first time. Within the framework of the Landau–de Gennes theory an interpretation of the experiment is given and it is shown that the melting of the end fragments exerts a strong influence on the interaction of the order parameters of these phases and on the position of the tricritical point on the line of nematic–smectic-*A* transitions.

1. INTRODUCTION

The nematic–smectic-*A* (*N*–*A*) phase transition in liquid crystals (LC) has been intensively studied, experimentally and theoretically, in recent years. Although there has been progress in the theoretical description of the critical behavior of LC in the region of the *N*–*A* transition,¹ a number of experimentally observable features of this transition still remain unexplained at the molecular level. For example, the *N*-phase range $\Delta = 1 - T_{NA}/T_{NI}$, corresponding to the appearance of a tricritical point (TCP) on the *N*–*A* transition line, depends on the nature of the materials investigated and varies from values $\Delta_T \cong 0.1$ (Ref. 2) close to the prediction of the McMillan model theory³ to anomalously small values $\Delta_T \cong 10^{-2}$ – 10^{-3} (Ref. 4–6). Since the nematic order parameter and the susceptibility of the *N* phase of known LC are universal functions of the temperature that depend only weakly on the molecular properties,⁷ the variation of Δ_T indicates the nonuniversality of the McMillan parameter T_{NA}/T_{NI} for characterizing transitions of the *N*–*A* type and indicates the presence of additional restrictions, dependent on features of the molecular structure, on the character of the interaction of the order parameters of the *N* and *A* phases. The microscopic causes of these restrictions are not yet clear, although the presence of the restrictions for a smectic phase of the *C* type follows from recent calorimetric investigations of the vicinity of the *NAC* point.⁸

On the other hand, the reason for the broad region of values $\Delta > \Delta_T$ in which, for LC with similar molecular structures, crossover from tricritical behavior in the region of the *N*–*A* transition to critical behavior corresponding to the three-dimensional *XY* model⁹ is not clear.

In the framework of the model theoretical approach of Ref. 3 and the phenomenological theoretical approach of Ref. 9 the variation of Δ_T implies a strong dependence of the coupling of the orientational order and the one-dimensional translational order of the molecules,^{3,10} or of the coupling constant of the interaction of the corresponding order parameters,^{9,11} on those features of the molecular structure that determine the nature of the smectic mesomorphism.

Since the condensation of the smectic density wave is due to the strong interaction of the molecules through the flexible end chains, it is important to elucidate the influence of the latter on the stability of the smectic phase and on the coupling of the order parameters of the *N* and *A* phases.

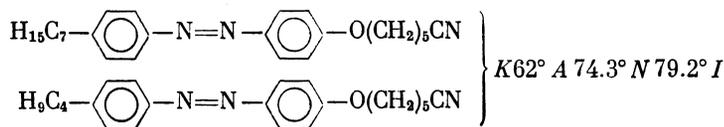
A feature of flexible chains is their conformational mobility, which manifests itself in the differences in the experimentally measured orientational order parameters $S_i = \langle 3\cos^2\theta_i - 1 \rangle / 2$ for fragments of the flexible chain, both in absolute magnitude and in their temperature dependence (Refs. 12–14) (θ_i is the angle between the physically distinct axis of the *i*th fragment of the chain and the LC director, and the brackets $\langle \dots \rangle$ denote averaging over all the molecules of the sample).

The conformational mobility of the chains depends on the temperature and on features of the molecular order,^{15–17} the change in the orientational order of the end fragments of the chain being qualitatively different from the behavior of the other fragments and of the rigid molecular spine, even in transitions between smectic phases.^{12,18} Therefore, the role of the flexible chains of the molecules in the above-mentioned features of *N*–*A* transitions can be elucidated by an experimental investigation of the orientational order of the end fragments of the chains in the *N* and *A* phases.

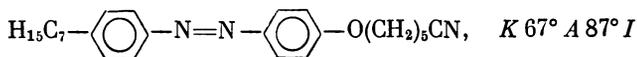
In the present paper we study the orientational order of the rigid molecular spines and of the end fragments of the flexible chains in a smectic LC of the *A* type and in a liquid-crystal mixture with *N* and *A* phases. Orientational melting of the end fragments in the *N*–*A* transition is observed for the first time, and its influence on features of the given transition is elucidated. In Sec. 2 we describe the substances investigated and the experimental techniques. Section 3 contains a discussion of the results, a phenomenological interpretation of them, and a description of their consequences.

2. OBJECTS OF THE INVESTIGATION AND EXPERIMENTAL METHODS

The experiment was carried out on a 50:50 wt.% mixture (LC-1) of



and on the pure component (LC-2)



with phase transitions at the indicated temperatures ($^\circ\text{C}$) from the crystal (K) to the A phase to the N phase to the isotropic liquid (I). In their molecular structure and the lengths of their flexible chains these substances are similar to the LC studied earlier^{2,4,5} with an N - A transition close to the TCP. In LC-1 the effective molecule has flexible chains of different lengths while in LC-2 the lengths of the chains are equal, and this makes it possible to elucidate the influence of the asymmetry of the molecules on the orientational order of the end groups in the smectic- A structure. In the straightened conformation of the chains the end fragment $\text{C}\equiv\text{N}$ is oriented parallel to the long axis of the molecular spine, and this rules out change of its orientation in the N phase because of steric interactions with its surroundings, as was observed previously by NMR at the end methyl groups of the alkyl (alkoxy) chains with an even (odd) number of carbon atoms.¹²⁻¹⁴ Unlike the previously studied substances with a broad N -phase range^{12,14,17} and an almost second-order N - A phase transition, the chosen substances permit us to hope for a reliable separation of the contributions of the nematic and smectic order to the change of orientational order of the end fragments of the chains in the A phase.

At the same time, the chosen substances make it possible to solve the previously posed question of the anisotropy of the local field at a weakly ordered end fragment of the flexible chain of a molecule. An experimental solution of this problem is at present urgent for the development of a molecular-statistical approach to the study of local-field effects in LC and for the elucidation of the role of intermolecular correlations of different types in the formation of a local field.^{20,21}

The orientational order parameter S_e of the end fragments of the chains and the components $L_{\parallel,\perp}$ of the Lorentz tensor in the N phase of LC-1 were found from the dichroic ratios $N_2 = D_{\perp}/D_{\parallel}$ and $N_3 = D_{\parallel}/D_i$ of the integral optical densities $D_{\parallel,\perp,i}$ of the isolated infrared-absorption band ($\nu_{\max} = 2245 \text{ cm}^{-1}$) pertaining to the stretching vibration of the $\text{C}\equiv\text{N}$ bond, by solving the following system of two equations²²:

$$S_e = 1 - N_2 g_2 = (N_3 g_3 - 1)/2, \quad \text{Sp } L = 1. \quad (1)$$

Here the correction factors

$$g_2 = \frac{\rho_i n_{\perp}^b}{\rho n_i^b} \left(\frac{f_i}{f_{\perp}} \right)^2, \quad g_3 = \frac{\rho_i n_{\parallel}^b}{\rho n_i^b} \left(\frac{f_i}{f_{\parallel}} \right)^2 \quad (2)$$

depend on the densities ρ and ρ_i of the liquid-crystalline and isotropic phases, the background refractive indices $n_{\parallel,\perp,i}^b$ of the LC in the investigated absorption band, and the components of the local-field tensor

$$f_{\parallel,\perp} = 1 + L_{\parallel,\perp} [(n_{\parallel,\perp}^b)^2 - 1]. \quad (3)$$

The values of S_e in the A phases of LC-1 and LC-2 were found from (1)–(3) from the dichroism N_2 for a fixed value $L_{\perp} = 0.395$.

The order parameter S_s of the rigid molecular spines in LC-1 and LC-2 was found from the dichroism N_2 of the doublet band ($\nu_{\max} = 1585$ and 1600 cm^{-1}) associated with the benzene-ring vibration polarized along the $\text{N}\dots\text{O}$ direction. The ratio of the optical densities of the bands of the doublet at the maxima does not depend on the temperature of the mesophase, and the values of N_2 found from the maxima of the individual bands and from the integrated intensity of the doublet coincide within the limits of the experimental error. For the N phase of LC-1 we used in (1)–(3) the ex-

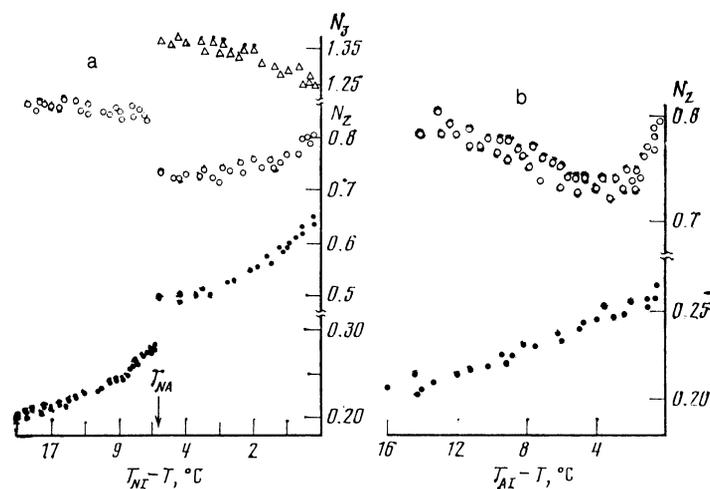


FIG. 1. Temperature dependences of the dichroic ratios $N_2 = D_{\perp}/D_{\parallel}$ and $N_3 = D_{\parallel}/D_i$ of the optical densities of the absorption bands associated with the vibrations of the $\text{C}\equiv\text{N}$ group (Δ, \circ) and of the benzene ring (\bullet) in LC-1 (a) and LC-2 (b).

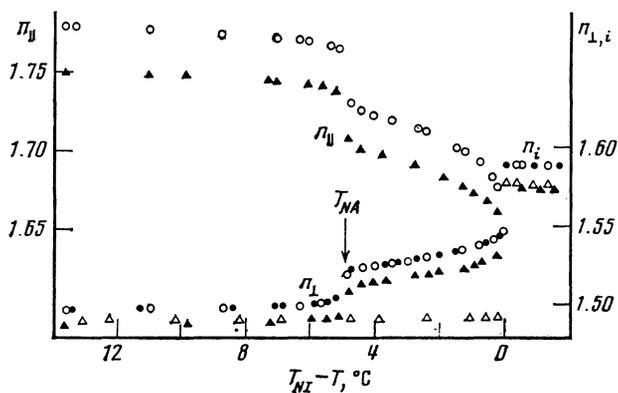


FIG. 2. Temperature dependences of the refractive indices $n_{\parallel,i}$ in LC-1 (○, ●, ▲) and LC-2 (△), measured by the wedge method (○, ▲) and on a refractometer (●, △) at $\lambda = 589$ nm (○, ●, △) and 735 nm (▲).

perimental values of $L_{\parallel,1}$, and for the A phases of LC-1 and LC-2 we took $L_{\perp} = 0.395$. The method of the spectral measurements is similar to that described earlier.^{19,22} The results of the measurements on several newly prepared samples are presented in Fig. 1.

The refractive indices $n_{\parallel,i}$ of LC-1 in the N and A phases were measured by the wedge method¹⁹ for $\lambda = 589$ and 735 nm. The control measurements of $n_{\perp,i}$ for LC-1 and LC-2 at $\lambda = 589$ nm were made on a refractometer. These data are given in Fig. 2. The background parameters $n_{\parallel,i}^b$ within the absorption bands investigated were calculated from the experimental values of $n_{\parallel,i}$ in the same way as in Ref. 19. The nematic order parameter $S \sim (n_{\parallel}^2 - n_{\perp}^2)$ (Ref. 9) for LC-1 was normalized to the quantity S_s at $\Delta T = T_{NI} - T = 14$ °C in the A phase, and the values of S for the two values of λ coincide.

The measurements of S_e (S_s) were performed in sandwich cells of fluorite with a planar (in the N phase) and homeotropic (in the N and A phases) orientation of the molecules, with an LC layer thickness of 30 (5) μm . The error in the thermostating of the samples was ± 0.1 °C. The temperature dependences of the order parameters S , S_s , and S_e are given in Fig. 3.

3. DISCUSSION AND INTERPRETATION OF THE EXPERIMENTAL RESULTS

The situation realized here, with measurement of the local field at the weakly ordered end fragment $C \equiv N$ of the flexible chain, is intermediate between the use for this purpose of a spherically symmetric optical probe²³ and the use of an optical marker rigidly connected with the molecular spine.^{19,22} The values found for L_{\perp} agree well, both in magnitude and in the dependence of L_{\perp} on $n_{\parallel} - n_{\perp}$, with the data of analogous measurements in other pure and impure LC.^{19,22,23} This implies that the same local field acts on different fragments of the molecules in the N phase and, evidently, is connected with the absence of correlation in the arrangement of the centers of gravity of the molecules along the director. To interpret this result in the framework of the molecular statistical theory of Refs. 20 and 21 it is necessary to develop the theory further to take account of both the nonlocal character of the molecular polarizability and many-particle intermolecular correlations.

The values of S and S_s are in good agreement with each other in the entire range of existence of the N and A phases, this being a consequence of the high polarizability of the molecular spine in the substances investigated and of the relatively small contribution of the polarizability of the flexible chains to the birefringence of the LC.¹⁶ As $T \rightarrow T_{NA}$ one observes in the N phase the previously predicted¹¹ pretransi-

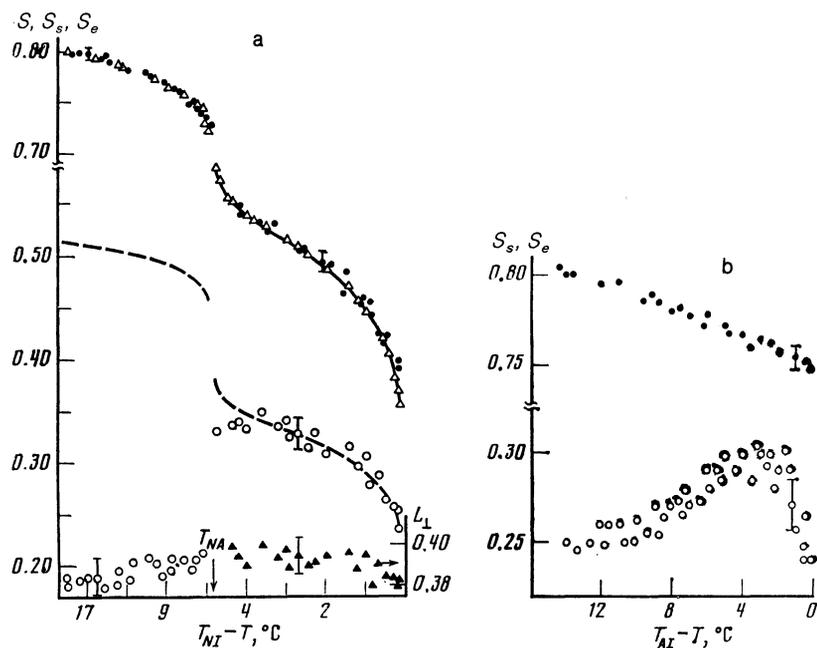


FIG. 3. Temperature dependences of the nematic order parameter S (△), the orientational order parameter S_s of the rigid spines (●), the orientational order parameter S_e of the end fragments of the flexible chains of the molecules (○), and the component $L_{\perp,1}$ (▲) of the Lorentz tensor in LC-1 (a) and LC-2 (b). The solid curve in Fig. 3a is an interpolation of the data for S and S_s , and the dashed line is the dependence $S_e(S)$ calculated from (5) for LC-1 with $\lambda_1 \chi = 0.642$.

tional increase of S due to fluctuations of the smectic order, and this indicates the proximity of the N - A transition in LC-1 to a TCP. We note that the value $\Delta = 0.014$ for the given LC is close to the values of Δ_T for the previously investigated substances with a TCP.⁴⁻⁶ At the N - A transition the increase of S by an amount ~ 0.14 occurs in a temperature interval of $\sim 0.2^\circ\text{C}$, which gives an upper bound on the width of the possible two-phase region. More definite conclusions about the character of this transition can be made only on the basis of precise calorimetric data. In the N phase the end $C \equiv N$ fragments of the chains are much less ordered than the rigid spines of the molecules. With increase of S the parameter S_e increases, but near T_{NA} this increase slows down, and at the N - A transition S_e decreases sharply to values smaller than $S_e(T = T_{NI})$. With decrease of the temperature of the A phase one observes a lowering of S_e , while S increases markedly. Thus, the N - A transition is accompanied by orientational melting of the end fragments of the flexible chains, and the contributions of the orientational and translational order of the LC molecules to the change of S_e are opposite in sign.

In the the A phase of LC-2 the parameter S_e is also appreciably lower than S , and has a nonmonotonic temperature dependence. Except for a narrow interval of temperatures near T_{AI} , S_e decreases with decrease of the temperature of the A phase, as in LC-1. However, the values of S_e in the A phase of LC-2 are appreciably higher than in LC-1, although the parameters S_e for these substances practically coincide. If we take into account that the translational order of the molecules in the A phase of LC-2 should be higher than that in LC-1 (Ref. 3), this difference in the values of S_e implies that the influence of the smectic ordering on the orientational melting of the end fragments of the chains is weaker for molecules with two equally long flexible chains than for molecules with flexible chains of different lengths.

The data obtained here, and also the results of Refs. 12-18, point to the necessity of introducing several orientational order parameters, associated with the distinct fragments of conformationally unstable molecules, in order to describe the thermodynamic behavior of LC in the region of a phase transition and to take into account specifics of the structure of the mesogenic molecules in features of these phase transitions. In particular, for an adequate description of the observed molecular transformations in the N - A transition it is necessary to take into account not only the macroscopic order parameter S , which essentially describes the orientational order of the rigid molecular spines ($S \sim S_s$), but also features of the order of the flexible molecular chains. Although the contribution of the chains to the modulus of S is small,¹⁶ their contribution to the energy of the steric and dispersion intermolecular interactions, and especially to the entropy of the LC, can be significant because of the large number of possible conformational states of flexible chains.

As a first step toward the interpretation of the experimental data—a step that takes into account the different character of the ordering of the molecular fragments in the phase transitions—we can take the phenomenological approach based on the inclusion in the LC thermodynamic potential of contributions associated with the ordering of

these fragments and with the interaction of the order parameters corresponding to them.²⁴ Then the expansion of the LC thermodynamic potential near the N - A transition, according to the Landau-de Gennes theory,⁹ is written in the form

$$\Delta\Phi = \frac{1}{2}A_1S^2 - \frac{1}{3}B_1S^3 + \frac{1}{4}C_1S^4 + \frac{1}{2}A_2\psi^2 + \frac{1}{4}C_2\psi^4 - \lambda_0S\psi^2 + \frac{1}{2\chi}S_e^2 - \lambda_1S_eS + \lambda_2S_e\psi^2. \quad (4)$$

Here $A_1 = a_1(T - T_{NI}^*)$, $A_2 = a_2(T - T_{NA})$, ψ is the amplitude of the density wave of the smectic layers, λ_0 is the coupling constant of the bare interaction of the order parameters S and ψ (the bare interaction does not include the effect of the end fragments of the molecules on the N - A transition), χ is the susceptibility of the LC phase to chain ordering and $\lambda_{0,1,2} > 0$. In (4) it has been taken into account that the ordering of the chains of the molecules is a consequence of the ordering of the molecular spines, and χ is independent of the inverse susceptibility $1/\chi$ obtained in comparison with the dependence A obtained in the lowest-order invariants description of the parameters S and ψ with S_e .

Minimizing (4) with respect to S_e gives

$$S_e = \chi(\lambda_1S - \lambda_2\psi^2), \quad (5)$$

$$\Delta\Phi = \Delta\Phi_S + \frac{1}{2}A_2\psi^2 + \frac{1}{4}(C_2 - 2\lambda_2^2\chi)\psi^4 - (\lambda_0 - \lambda_1\lambda_2\chi)S\psi^2, \quad (6)$$

where $\Delta\Phi_S$ differs from (4) by the renormalized value $T_{NI} = T_{NI}^* + \lambda_1^2\chi/a_1$. As can be seen from Fig. 3, the dependence (5) gives a good description of the variation of S_e with S in the N phase of LC-1 for the fixed value $\lambda_1\chi = 0.642$ found from the experimental values of S_e and S at $\Delta T = 0.2^\circ\text{C}$. Near the N - A transition, as $T \rightarrow T_{NA}$ the expected and observed dependences $S_e(S)$ differ, indicating orientational melting of the end fragments as a result of fluctuations of the smectic order. In the A phase of LC-1 the values of S_e calculated from (5) are much higher than the experimental values. Comparison of the calculation with experiment for S_e when $\Delta T = 19^\circ\text{C}$ and the estimate $\psi^2 \cong 0.1$ (Ref. 11) give $\lambda_2/\lambda_1 \cong 5$, i.e., the order of the end fragments of the chains is much more sensitive to features of the smectic order than to features of the nematic order. It is not accidental, therefore, that the character of the order of the end fragments of the chains differs qualitatively from that for the rigid molecular spines even in phase transitions between smectic phases.^{12,18}

The nonmonotonic variation of S_e in the A phase of LC-2 can be understood if we take into account the small value of $\psi(T = T_{AI})$, corresponding to weak modulation of the density of the LC by the smectic wave.¹¹ In fact, for $T \lesssim T_{AI}$, because of the large values of S , the contribution of the first term in (5) to the variation of S_e is dominant. With lowering of the temperature of the A phase ψ grows, and, because of the strong inequality $\lambda_1 \ll \lambda_2$, the increase of S_e is replaced by a decrease.

With increase of the width Δ of the nematic range the parameter $S(T_{NA})$ increases, the value of $\psi(T_{NA})$ at the first-order phase transition decreases,³ and orientational melting of the end fragments should be manifested to a lesser

degree than for the LC-1 investigated here. For continuous $N-A$ transitions we should expect fluctuational melting of the end fragments at $T \approx T_{NA}$, with a continuous change of S_e at $T = T_{NA}$ and with a possible slowing of the growth (or with a decrease) of S_e in the A phase. This corresponds to the observed variation of S_e in the liquid crystal 8CB (Ref. 14), for which the $N-A$ transition, according to calorimetric data, has been identified as continuous.^{6,25}

As can be seen from (6), the orientational melting of the end fragments of the chains in the $N-A$ transition leads to two effects that influence the character of the given transition: to a decrease of the coupling constant $\lambda = \lambda_0 - \lambda_1 \lambda_2 \chi$ of the order parameters S and ψ , and to a decrease of the coefficient C_2 multiplying ψ^4 . The decrease of λ should lead to a decrease of Δ_T (Refs. 9, 11). In fact, the orientational melting of the end fragments of the molecules stabilizes the smectic structure, hindering the diffusion of molecules from layer to layer, and a continuous $N-A$ transition can be realized at low values of S , i.e., for small values of Δ . It is obvious that the orientational melting of the flexible chains involves an increase of the free volume per chain in the transition from the nematic to the smectic structure. Therefore, strong melting of the end fragments in the $N-A$ transition should be expected for molecules of three types: molecules for which, by virtue of features of the chemical structure of the spine, the cross-sectional area of the spine is appreciably greater than that of the flexible chains; molecules with two flexible chains of different lengths; molecules that have one flexible chain and a strongly polar spine and tend to form associates and bilayer smectic structures. The latter two types of substances correspond to the previously investigated liquid crystals 10S5 (Ref. 4), OOHCS (Ref. 5), and 9CB (Ref. 6) with anomalously small values of Δ_T . At the same time, for molecules with two chains of the same length the melting of the end fragments in the $N-A$ transition is manifested appreciably more weakly (e.g., LC-2), and the increase of λ and Δ_T corresponds to this. Such substances were investigated in Ref. 2. Thus, features of the molecular structure that were not taken into account in the model theory of Ref. 3 can have a substantial effect on the interaction of the order parameters of the N and A phases and on the position of the TCP on the $N-A$ -transition line.

Decrease of the coefficient of ψ^4 in (6) causes the second-order $N-A$ transition to approach the TCP. It is possible, therefore, that for liquid crystals of the above-indicated types with the expected (and observed¹⁴) orientational melting of the end fragments there is a broad region of values of $\Delta > \Delta_T$ with crossover from tricritical behavior.^{4-6,25,26} The crossover behavior of liquid crystals with molecules of the other type has not been investigated in detail.

In conclusion we note that orientational melting of the end fragments of molecules, similar to that studied here, should also occur in $N-C$ transitions with an analogous effect on the character of the given transition. It is possible that the recently discovered^{8,27} proximity of the point of in-

tersection of the $N-A$, $N-C$, and $A-C$ transition lines (the NAC point) to a tricritical point is connected with this, since the investigated liquid-crystalline mixtures consisted of molecules with flexible chains that were asymmetric in length.

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