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Correlation of the Molecular Structure of Discotic Nematic Liquid Crystals with Their Orientational Order and Specific Features of the Nematic–Isotropic Phase Transition

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Abstract—The orientational order parameter S of molecules in high-temperature discotic nematic liquid-crystal phases of triphenylene derivatives is investigated as a function of the length of side flexible molecular chains at different temperatures. It is established that the orientational order parameters S in the range of the transition from the nematic phase to the isotropic liquid phase (the N_D – I transition) are smaller than those predicted from the molecular-statistical theory and computer simulation. It is shown that the N_D – I transition is close to both the isolated Landau point and the tricritical point (regardless of the chemical structure of the molecules and the anisotropy of dispersion intermolecular interactions). Consistent explanations are offered for a number of experimental findings, such as the anomalously small changes in the enthalpy and entropy upon the N_D – I transition (as compared to those revealed upon the N – I transition in calamitic nematic liquid crystals), the anomalously strong response of the isotropic phase of discotic nematic liquid crystals to external fields (thermodynamically conjugate to the order parameter S) and the long relaxation times of this response, and the formation of cybotactic discotic molecular clusters in the isotropic phase in the vicinity of the N_D – I transition. © 2004 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

The phase transition from a discotic nematic phase to an isotropic liquid phase (the N_D – I transition) in liquid crystals consisting of disk-shaped molecules is one of the most intriguing phenomena in the physics of liquid crystals. This transition has been the subject of extensive experimental studies [1–12], molecular-statistical theoretical investigations [13–17], and computer simulation [18–23]. Disk-shaped molecules forming a discotic nematic phase consist of a planar central aromatic core with a relatively large radius and radial flexible aliphatic chains of specific length [24, 25]. In a uniaxial nonpolar homogeneously oriented discotic nematic phase, the preferred axes \mathbf{l} of disk-shaped molecules are normal to the molecular planes and are predominantly oriented along the director \mathbf{n} . The degree of orientational ordering in liquid-crystal molecules is characterized by the order parameter $S = \langle 3 \cos^2 \theta - 1 \rangle / 2$, where θ is the angle between the vectors \mathbf{l} and \mathbf{n} and the brackets $\langle \dots \rangle$ indicate statistical averaging.

Discotic nematic liquid crystals are characterized by anomalously small changes in the enthalpy $\Delta H = 0.02$ – 0.6 kJ/mol upon the N_D – I phase transition [3–8, 12] as compared to the enthalpy change $\Delta H = 1$ – 6 kJ/mol [26] observed upon the N – I phase transition in calamitic nematic liquid crystals, which consist of rodlike or lath-like molecules. From the Landau–de Gennes expansion

for the thermodynamic potential of a nematic liquid crystal into a series in powers of the parameter S , that is,

$$\Delta \Phi = a(T - T^*)S^2/2 - BS^3/3 + CS^4/4 + ES^5/5 + DS^6/6 + \dots, \quad (1)$$

we obtain the following expression:

$$\Delta H = aS_{NI}^2 T_{NI}/2, \quad (2)$$

where T_{NI} is the temperature of the N_D – I phase transition ($T_{NI} > T^*$) and $S_{NI} = S(T_{NI})$. Hence, it follows that the smallness of the change in the enthalpy ΔH can be associated either with the small values of S_{NI} and the similarity of the N_D – I phase transition to the second-order transition or with the smallness of the factor a . Both variants lead to a number of physical consequences. Since the specific features of the N_D – I phase transition are governed by the structural features of disk-shaped molecules, this problem can be solved by analyzing the available data on the influence of molecular properties on the temperature dependence of the orientational order parameter $S(T)$. There are only a few works devoted to the investigation of the dependence $S(T)$ for discotic nematic liquid crystals with the use of refractometry [6, 9–11] and IR spectroscopy [12].

In this work, the dependence $S(T)$ for the discotic nematic phase of two high-temperature triphenylene

derivatives was investigated using the anisotropy of diamagnetic susceptibility of these compounds. Consideration was given to the structural features of the chosen molecules and their ordering, which are responsible for the strong coupling of the orientational and conformational degrees of freedom of molecules in the discotic nematic phase. A correlation was revealed between the dependence $S(T)$ and molecular properties. The results obtained were compared with those predicted from the molecular-statistical theory and computer simulation. Consistent explanations were offered for the known features of the N_D -I phase transition.

2. OBJECTS OF INVESTIGATION AND THEIR SPECIFIC FEATURES

Owing to the relatively dense molecular packing in the nematic phase, the shape of the molecules determines the anisotropy of their local coordination environment. In calamitic nematic liquid crystals, the vector \mathbf{n} is perpendicular to the direction of the shortest intermolecular distance which is comparable to the transverse size of rodlike molecules. At the same time, in the discotic nematic liquid crystals, the vector \mathbf{n} is aligned parallel to the direction of the shortest intermolecular distance which is comparable to the thickness of disk-shaped molecules. This difference in the local anisotropy of the calamitic nematic and discotic nematic phases, along with the structural-chemical features of discotic molecules, accounts for the fact that the conformational state of side chains of these molecules in the discotic nematic phase has a more profound effect on the order parameter S and the dependence $S(T)$ as compared to that in the calamitic nematic phase.

The loose structure of discotic molecules with the statistical symmetry axis $C_n \parallel \mathbf{l}$ ($n \geq 3$) is characterized by large-sized holes between side chains of the molecules, which is a prerequisite for a high conformational mobility of the chains. As the chain length increases, the free volume per chain of a discotic molecule increases rapidly, which also enhances their conformational mobility.

In the discotic nematic phase, the planar aromatic cores of the molecules are equivalent to the planes restricting the conformational mobility of the chains of neighboring molecules along the director. However, the mobility in the directions normal to the director remains sufficiently high and is restricted only by steric repulsion of adjacent chains of the same molecule or by the engagement of chains of the neighboring molecules. An increase in the degree of orientational order of molecular axes \mathbf{l} with respect to the director \mathbf{n} or in the order parameter S leads to a decrease in the number of conformational states responsible for the deviation of the chains from the core plane. This favors an increase in the anisotropy of the molecular shape and enhances anisotropic steric intermolecular interactions. On the other hand, the thermal conformational mobility

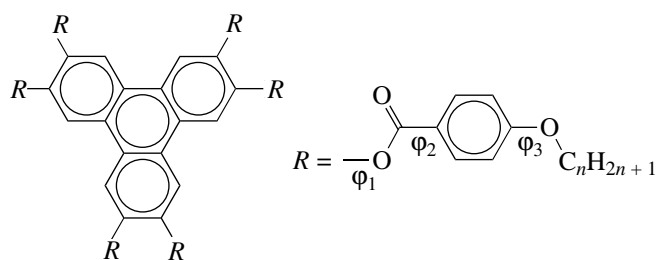


Fig. 1. Structure of n OBT molecules.

of the chains results in a decrease in their contribution to the energy of the anisotropic intermolecular interaction and has a disordering effect on the molecular cores. The above factors are responsible for the interrelation between the orientational order of molecules and the conformational state of their chains in the nematic phase. In turn, this interrelation should manifest itself in the dependence of the magnitude and the temperature behavior of the order parameter S on the chain length, especially in the case when the mesophase has a high temperature corresponding to a high thermal mobility of the molecular chains.

On this basis, the compounds of the homologous series of 2,3,6,7,10,11-hexakis(4- n -alkyloxybenzoyloxy)triphenylenes (n OBT) at $n = 6$ and 11 [1] were chosen as the objects of our investigation. The structure of n OBT molecules is shown in Fig. 1.

The molecules of these compounds with an identical number of side chains differ from those studied earlier in [9–11] in terms of the point group of statistical symmetry C_3 , the chemical structure, the polar properties of the aromatic cores, and the free volume per chain in an individual molecule. For each fragment R , the angle ϕ_1 between the plane of the triphenylene core and the plane of the O(O)C bridging group varies from 61° to 81° [7]. The angle $\phi_2 = 0$ between the plane of the O(O)C electron-acceptor fragment and the phenyl ring provides the π conjugation of this fragment to the phenyl ring and the electron-donor alkoxy chain. This results in an increase in the anisotropy of molecular polarizability. The distribution function $f(\phi_3)$ has a maximum at the angle $\phi_3 = 0$ [7]. Therefore, for the methylene chain fragments that are adjacent to the molecular core and predominantly adopt a *trans* conformation, the carbon backbone lies in the plane making the angle $\phi_4 = \phi_1$ with the plane of the triphenylene core. As the length of the chains increases, their side fragments deviate from the core plane. This leads to an increase in the thickness of the molecule and a decrease in the anisotropy of the molecular shape. The anisotropy of steric intermolecular interactions also decreases.

Among the known compounds [25], the 6OBT homolog has one of the highest temperature discotic nematic phases. The nematic phase of the 11OBT

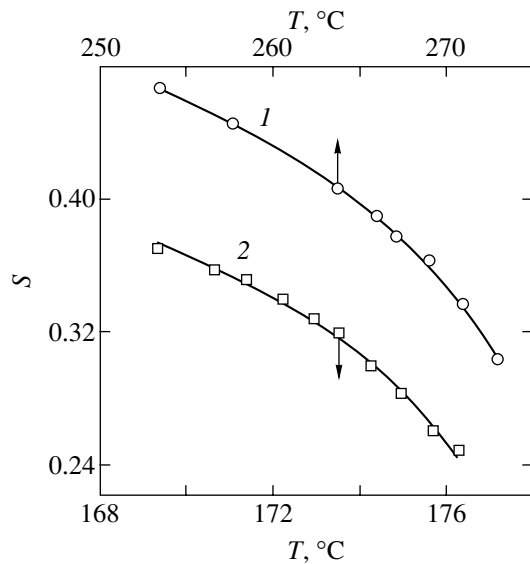


Fig. 2. Temperature dependences of the order parameter S in the discotic nematic phase for n OBT homologs at $n = (1)$ 6 and (2) 11. Solid lines represent the results of interpolation according to relationships (3) and (4).

homolog is also observed at temperatures considerably above the limiting temperature $T_l = T_{NI}(n \rightarrow \infty) \approx 60^\circ\text{C}$ at which the molecular chains do not affect the phase transition point T_{NI} for this homologous series [27]. For all homologs of the n OBT series, the inequality $T_{NI}(n) > T_l$ holds true and an increase in n is accompanied by a monotonic decrease in the temperature $T_{NI}(n)$. This implies a decrease in the anisotropy of intermolecular interactions that stabilize the nematic order of molecules. There is a scatter in the data available in the literature on the phase transition temperatures $T_{NI}(n)$ for compounds of the n OBT series [1, 5, 12, 24, 25]; however, this scatter is not related to the anisotropic properties of the discotic nematic phase on the scale of the reduced temperature $\Delta T = T_{NI} - T$.

3. ORIENTATIONAL ORDER OF THE NEMATIC PHASE AND SPECIFIC FEATURES OF THE N_D - I PHASE TRANSITION

The molecules under consideration are statistically uniaxial, and the anisotropy $\Delta\chi_m = (\chi_{\parallel}^m - \chi_{\perp}^m) < 0$ of the diamagnetic susceptibility tensor of a discotic nematic liquid crystal is determined only by the order parameter S [11]. The components χ_{\parallel}^m and χ_{\perp}^m correspond to the magnetic field directions parallel and perpendicular to the director. For the 6OBT and 11OBT homologs, there are data on the dependence of the specific diamagnetic anisotropy $\Delta\chi_m(T)$ for the discotic nematic phase oriented in a magnetic field [1]. These dependences were obtained from the relationship $\Delta\chi_m = 3(\chi_i^m - \chi_{\perp}^m)$ under

the assumption that the diamagnetic susceptibility χ_i^m in the isotropic phase coincides with the average diamagnetic susceptibility in the nematic phase $\bar{\chi}_m = (\chi_{\parallel}^m + 2\chi_{\perp}^m)/3$, which does not depend on the temperature and the degree of molecular ordering. Since the contribution of alkyl chains to the anisotropy of diamagnetic polarizability of the studied molecules is negligible [28], the dependences $\Delta\chi_m(T)$ can be used to determine the order parameter S :

$$S(T) = \Delta\chi_m(T)/\Delta\chi_{m0}. \quad (3)$$

Here, the value of $\Delta\chi_{m0} = \Delta\chi_m(T = 0, S = 1)$ can be determined from the approximate relationship

$$\Delta\chi_m(T) = \Delta\chi_{m0}(1 - T/T_H)^\beta, \quad (4)$$

which was theoretically justified in terms of expansion (1) [9–11]. Here, we have $T_H > T_{NI}$. Figure 2 shows the dependences $S(T)$ thus calculated with parameters $\Delta\chi_{m0} = -(1.267 \pm 0.027) \times 10^{-7} \text{ cm}^3/\text{g}$, $T_H = 550 \pm 0.27 \text{ K}$, and $\beta = 0.241 \pm 0.007$ for the 6OBT compound and $\Delta\chi_{m0} = -(0.811 \pm 0.082) \times 10^{-7} \text{ cm}^3/\text{g}$, $T_H = 451 \pm 0.38 \text{ K}$, and $\beta = 0.248 \pm 0.027$ for the 11OBT compound. The order parameters for each homolog at the highest temperatures correspond to the values of S_{NI} [1]. It can be seen from Fig. 2 that the dependences $S(T)$ are approximated well by expressions (3) and (4). For identical differences $\Delta T = T_{NI} - T$, the order parameter S for the 11OBT homolog with long chains is smaller than that for the 6OBT homolog with short chains (especially at temperatures close to the phase transition point T_{NI}). This indicates that the thermal mobility of chains has a disordering effect on the orientational order of the molecular cores in the range of the N_D - I phase transition. For the intermediate homolog 8OBT of the studied series with the phase transition temperature $T_{NI} = 238^\circ\text{C}$ and a wide range of existence of the nematic phase, the order parameters $S(\Delta T)$, which were obtained from the data on the dichroism of the IR absorption band at frequency $\nu = 1603 \text{ cm}^{-1}$ for homeotropically oriented samples, vary in the range from 0.27 to 0.6 [12]. For identical differences ΔT , these order parameters fall in the range between the corresponding values for the 6OBT and 11OBT homologs. Therefore, an increase in the chain length of the n OBT homologs leads to a monotonic decrease in the order parameter S in the range of the N_D - I phase transition. A similar decrease in the order parameter S with an increase in the chain length was observed earlier for the low-temperature reentrant discotic nematic phase of truxene derivatives [29] and, most likely, can be considered a general property of discotic nematic liquid crystals.

The values of $\beta = 0.24$ – 0.25 for the above homologs are close to those determined for the previously studied liquid crystals [6, 9–11] with a different molecular

structure and different parameters $A = 3(\gamma_l - \gamma_t)/(\gamma_l + 2\gamma_t)$, where γ_l and γ_t are the longitudinal (along the **l** axis) and transverse components of the molecular polarizability, respectively. The parameter A characterizes the relative anisotropy of the molecular polarizability and dispersion intermolecular interactions in the nematic phase. The close values of β indicate that the steric intermolecular repulsion plays a decisive role in the orientational ordering of discotic nematic liquid crystals, as is the case with calamitic nematic liquid crystals.

The experimental values of the order parameter $S(\Delta T)$ for the homologs under consideration and the compounds studied earlier in [6, 9–12] are considerably smaller than the parameters predicted from the Maier–Saupe molecular-statistical theory [13], especially in the vicinity of the phase transition temperature T_{NI} . The approaches based on generalizing this theory with a more detailed analysis of the anisotropic intermolecular interactions [14–16] and intermolecular correlations of short-range order [17] lead to overestimated values of $S(\Delta T)$ and do not offer correct interpretation of the experimental data. The molecular dynamics simulation of a system of particles in the form of oblate ellipsoids of revolution [21–23] predicts the sequence of the $I-N_D-Col_{hd}$ phase transitions with the order parameter $S_{NI} = 0.5–0.7$ and large values of $S = 0.7–0.95$ for the discotic nematic phase. These results differ significantly from the experimental data. Therefore, the experimentally observed features in the dependence $S(\Delta T)$ for discotic nematic liquid crystals cannot be explained without considering the structural features of real discotic molecules and intramolecular degrees of freedom in the framework of the molecular-statistical theory and in the computer simulation.

The sequence of the $I-N_D-Col_{hd}$ phase transitions was also predicted by the Monte Carlo method for an athermal system of disk-shaped particles (cut spheres with diameter D_s and thickness L) at $L/D_s < 0.14$ [20]. However, in this system, the N_D-I phase transition is a weak first-order transition with the order parameter $S_{NI} = 0.3–0.4$. For a system of N disk-shaped particles in a volume V with $L = 0$ and an effective density $\rho = ND_s^3/V$ [18, 19], the order parameter $S_{NI} \approx 0.37$ corresponds to the temperature of the N_D-I phase transition at $\rho = \rho_{NI}$ and the dependence $S(\rho)$ in the discotic nematic phase is approximated well by the relationship $S \sim (\rho - \rho_1)^\beta$, where $\beta = 0.23 \pm 0.03$. Here, the quantities ρ_1 and β are similar to the quantities T_H and β in formula (4). The small difference between the calculated and experimental values of β confirms the above assumption regarding the role played by the steric intermolecular interactions in the ordering of the discotic nematic phase.

Therefore, when changing over from models of ellipsoidal molecules with a three-dimensional shape ($D = 3$) [17, 21–23] to models of disk-shaped molecules

with a small thickness (dimension $D \approx 2$) [18, 19], the calculated parameters S_{NI} and β approach the experimental values. The loose structure of discotic molecules with large-sized holes between radial side chains suggests that the shape of these molecules has a dimension $D < 2$. The value of D depends on statistical symmetry of molecules, the structure of the molecular core, the number of flexible chains, and their length. This ensures a mutual penetration of the chains of neighboring molecules in the nematic phase (similar to engaged gears) and hinders the rotation of molecules about the **l** axes and their sliding relative to one another in planes normal to the director. This type of intermolecular correlation, which is not taken into account or described in any of the known theoretical approaches or computer simulation, corresponds to the high viscosity of discotic nematic liquid crystals, which exceeds the viscosity of calamitic nematic liquid crystals by one or two orders of magnitude [4].

The experimental dependences $S(\Delta T)$ for calamitic and discotic nematic liquid crystals over the entire range of existence of the mesophase are described with a high accuracy in terms of expansion (1) with inclusion of the terms up to S^6 [9–11]. Note that, at $B \neq 0$, the contribution from the term $\sim S^5$ is insignificant. Since the values of β for discotic nematic liquid crystals are close to 0.25, both coefficients B and C in expansion (1) are small; i.e., the N_D-I phase transition is close to the isolated Landau point ($B = 0$) and the tricritical point ($C = 0$). The smallness of the coefficients B and C for discotic liquid-crystal molecules can be due to the dimension of these molecules ($D < 2$) and the interrelation between the orientational order of the molecules and the conformational state of their flexible chains. The former factor is associated with the mutual penetration and engagement of the neighboring molecules located in the plane normal to the director. This factor brings about the formation of molecular associates with an effective biaxial shape, which leads to a decrease in the coefficient B [30]. The interrelation between the order parameter S and the conformational mobility of chains provides a decrease in the coefficient C [11].

The order parameters S_{NI} for the discotic nematic liquid crystals considered in this paper and studied earlier in [6, 9–12] are smaller than those for calamitic nematic liquid crystals. However, the difference is insignificant. Therefore, the anomalously small changes in the enthalpy ΔH [expression (2)] upon the N_D-I phase transition, as compared to the enthalpy change observed upon the $N-I$ phase transition, are determined primarily by the smallness of the factor a for the discotic nematic liquid crystals. In turn, the smallness of the factor a suggests a considerable bare correlation length ξ_0 for equilibrium thermal fluctuations of the order parameter S . For the isotropic phase, the bare correlation length can be represented in the form $\xi_{0i} = (L/aT^*)^{1/2}$ [10]. In the one-constant approximation of the elasticity theory, the parameter L and the

elastic modulus K of the nematic liquid crystal are related by the expression $K = 2S^2L$ [28]. Since the elastic moduli (like the order parameters S) for calamitic and discotic nematic liquid crystals are close to each other [3–5], the correlation length ξ_{0i} for the discotic nematic liquid crystals should be severalfold greater than $\xi_{0i} \approx 6 \text{ \AA}$ for the calamitic nematic liquid crystals [31] and should be comparable to the diameter of disk-shaped molecules.

According to the x-ray scattering data [1, 4], the mean intermolecular distance along the director \mathbf{n} in the discotic nematic phase $d_{\parallel} \approx 4.5 \text{ \AA}$ is substantially smaller than the molecular diameter. Structurally, from the inequality $\xi_{0i} \gg d_{\parallel}$ for discotic nematic liquid crystals, it follows that the isotropic and nematic phases should contain cybotactic molecular clusters with a strong correlation of several molecules along the director \mathbf{n} . This is confirmed by the x-ray scattering data obtained for n OBT homologs with polar molecules [1] and other liquid crystals with nonpolar molecules [4]. The latter circumstance implies that the polarity of discotic molecules is not a controlling factor in the formation of cybotactic clusters.

The small values of the enthalpy change ΔH indicate a small change in the entropy $\Delta \Xi = \Delta H/T_{NI}$. In turn, the smallness of the entropy change $\Delta \Xi$ means that cybotactic clusters consisting of several molecules rather than individual molecules serve as structural units upon the N_D - I phase transition. Moreover, this transition is attended by an insignificant transformation of the local structure of the material. This inference is consistent with the aforementioned consequences of the smallness of the factor a .

The factor a characterizes the susceptibility $\chi_i = (\partial^2 \Phi / \partial S^2)_{S=0}^{-1} = [a(T - T^*)]^{-1}$ of the isotropic phase of the nematic liquid crystal to external actions and determines the amplitude of anomalous changes in the anisotropic properties of this phase in response to external fields (thermodynamically conjugate to the order parameter S) as the temperature of the I - N_D phase transition is approached [10, 11]. Furthermore, the smallness of the factor a indicates long relaxation times $\tau \sim \chi_i$ [32] for anisotropic properties induced by external fields in the isotropic phase for a fixed difference $T - T^*$. This explains not only the anomalously high birefringence $\Delta n \sim \chi_i$, which is induced by shear flow in the isotropic phase of the discotic liquid crystal [8] with an anomalously small value of $\Delta H = 20 \pm 10 \text{ J/mol}$, but also the large Kerr constant $B \sim \chi_i$ for the electric birefringence Δn_E in the isotropic phase of the discotic nematic liquid crystal in the vicinity of the phase transition temperature T_{NI} and the long relaxation time $\tau \sim \chi_i$ for the quantity Δn_E as compared to the relaxation time characteristic of calamitic nematic liquid crystals [4].

4. CONCLUSIONS

Thus, the above analysis of the experimental data on the properties of discotic and calamitic nematic liquid crystals has demonstrated that the difference in their properties and the specific features of the N_D - I phase transition are associated with the structural features of loose discotic molecules and can be consistently explained in terms of the smallness of the factor a in expansion (1).

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