

Orientalional order and critical behavior of a discoid nematic liquid crystal

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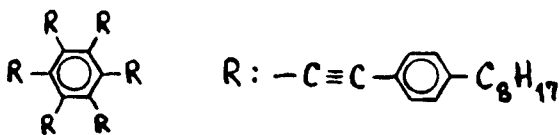
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First experimental data on the orientational order of the molecules in a discoid nematic liquid crystal are reported. These results are dramatically at odds with the results of a numerical simulation for rigid disk-shaped molecules. The N_D-I phase transition is simultaneously close to an isolated Landau critical point and to the tricritical point, as in ordinary calamite nematic liquid crystals with Planckian molecules. This result indicates that conformational degrees of freedom of the molecule play an important role in the features of the N_D-I transition. © 1995 American Institute of Physics.

1. In contrast with the huge number of theoretical and experimental studies which have been carried out on the structure and physical properties of discotic columnar phases $D_{h,r,t}$, no experimental information is available on the orientational order of discoid nematic liquid crystals N_D or on the features of their N_D-I phase transition to an isotropic liquid.¹ For rigid disk-shaped molecules, a numerical simulation^{2,3} predicts high values of the orientational order parameter, $S=0.7-0.95$, in the N_D phase—values approaching those in the D_h phase. These simulations also predict a weak $S(T)$ dependence with a large jump S_c at the point T_c of the N_D-I transition. In the isotropic phase of a discoid nematic liquid crystal, on the other hand, the reciprocal susceptibility has the behavior⁴ $\chi^{-1} \sim (T-T^*)$ with $T_c-T^* \approx 1$ K, as for ordinary calamite nematic liquid crystals with a weak, first-order $N-I$ transition and low values of S_c (Ref. 5). Experimental data on $S(T)$ in real nematic liquid crystals N_D would be of much interest for (1) testing these simulation results, (2) clarifying the applicability of the Landau–de Gennes for describing the N_D-I transition,⁶ and (3) determining the role played for conformational degrees of freedom of flexible molecular chains, whose presence is necessary for a manifestation of discotic mesomorphism in real entities.¹

In this letter we are reporting first experimental data on the $S(T)$ dependence. We clarify the questions raised above. We also report features of the critical behavior of $S(T)$, the correlation radius ξ of fluctuations in S , and the linear [$\chi \equiv S' = (\partial S / \partial h)_{T, h \rightarrow 0}$] and quadratic [$S'' = (\partial^2 S / \partial h^2)_{T, h \rightarrow 0}$] susceptibilities of a nematic N_D with respect to the field h , which is the conjugate of the modulus of S .

2. To determine $S(T)$ we used precise data on the refractive indices $n_{e,o}(\lambda = 589$ nm) (Ref. 7) in the N_D phase of the nonpolar liquid crystal:



Here we have the value $T_c = 372.66$ K; there are no low-temperature D phases. We introduce the parameters $A = 3(\gamma_t - \gamma_l)/(\gamma_l + 2\gamma_t)$ and $Q = \epsilon_a/(\bar{\epsilon} - 1)$, where $\hat{\gamma}$ is the molecular-polarizability tensor, the l axis is normal to the plane of the molecule, $\epsilon_j = n_j^2$, $\epsilon_a = \epsilon_o - \epsilon_e$, and $\bar{\epsilon} = (\epsilon_e + 2\epsilon_o)/3$. Using the anisotropy of the local field of the light wave in a liquid crystal,⁸ we can write the modulus S of the tensor order parameter $S_{ij} = S(r_i r_j - \delta_{ij}/3)$ ($r_{i,j}$ are components of the director \mathbf{r}) as follows:

$$SA = Q \frac{1 + (\bar{\epsilon} - 1)(P - 1)/3\bar{f}}{1 + \epsilon_a(P - 1)(1 + 2Q/3)/9\bar{f}} \equiv Q(1 + \sigma). \quad (1)$$

Here σ is a correction for the anisotropy of the local field, $P = \tau/\tau_k$, τ is the anisotropy of the Lorentz tensor of the liquid crystal,⁸

$$\tau_k = Q/9(1 - Q/3), \quad \bar{f} = (\bar{\epsilon} - 2\epsilon_a\tau + 2)/3. \quad (2)$$

As for calamite nematic liquid crystals, the $Q(T)$ dependence is described by the Haller approximation⁹ over the entire temperature range $\Delta T = 40$ of the N_D phase:

$$Q(T) = Q_0(1 - T/T_n)^{\beta_n}, \quad (3)$$

with the parameter values $Q_0 = Q(T=0) = 0.687$, $T_n - T_c = 0.7$ K, and $\beta_n = 0.255$. With $A = \text{const}$, the ratio $Q(T)/Q_0$ gives us the $S(T)$ dependence in the approximation of an isotropic local field with $\sigma = 0$. Substitution of Q_0 into (2) yields $\tau_{k0} = 0.099$ and the parameter value²⁾ $\tau_0 = 0.235$. Since we have⁸ $\tau(T)/\tau_k(T) = \text{const}$, we have $P = \tau_0/\tau_{k0}$ in (1) and $\tau = P\tau_k$ in (2).

Figure 1 shows the temperature dependence $AS(T)$ (1) and $S(T)$; the anisotropy of the local field has been taken into account here. The $AS(T)$ dependence can be approximated well by Eq. (3) with the parameter values $AS_0 = 0.943$, $T_n - T_c = 0.7$ K, and $\beta_n = 0.247$. With $S_0 = 1$, incorporating the anisotropy of the local field renormalizes the parameter A but has only a slight effect on β_n and the values of S in the N_D phase, since the $\sigma(T)$ dependence in (1) is weak.

It can be seen from Fig. 1 that the values of S in the N_D phase are approximately the same as those for calamite nematic liquid crystals, and well below those expected on the basis of the numerical simulation.^{2,3} For the liquid crystal under consideration, the molecules have a rigid, strongly polarized aromatic core, and the polarizability of the flexible C_nH_{2n+1} end chains contribute negligibly to the parameter A . The resulting values of S thus characterize the orientational order of rigid molecular cores. For a given liquid crystal, the value of T_c lies at temperatures at which the flexible chains of the molecules are orientationally melted, and their elongation within the homologous series does affect the value of T_c for calamite nematics.¹⁰ In the N_D phase, with a larger free volume corresponding to the peripheral flexible chains, their orientational order lowers the energy

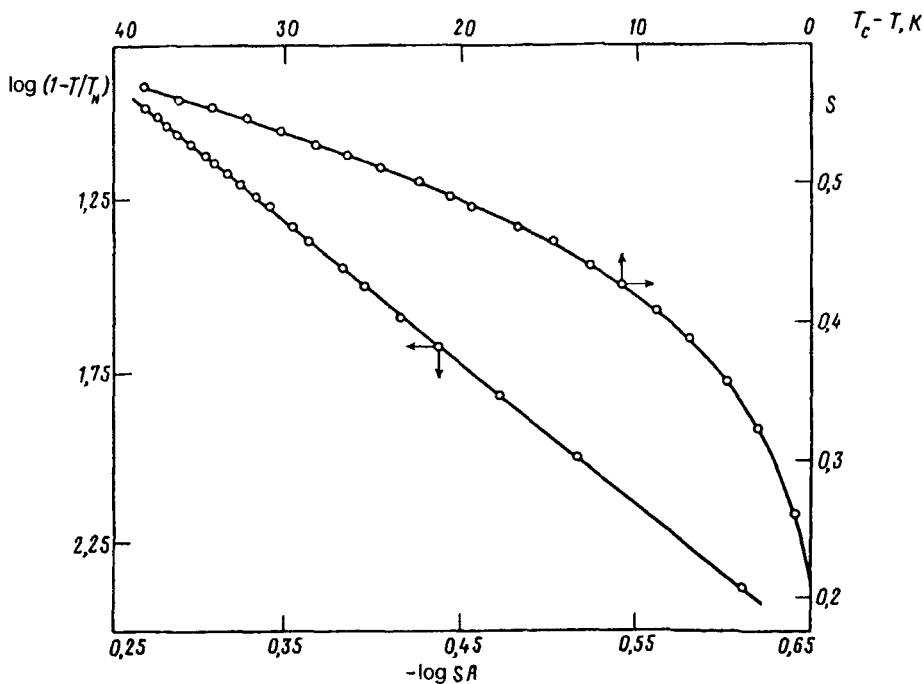


FIG. 1. Temperature dependence of the orientational-order parameter of the molecules, S (at right and above), and of the product AS [see Eq. (1); at left and below] in the nematic phase N_D . The points are experimental. The solid curves were calculated from Eqs. (3) and (7) (at right and above) and by interpolation (at left and below).

of the anisotropic dispersive and steric intermolecular interactions and increases the entropy of the N_D phase. These events probably also lead to low values of S in comparison with those expected for rigid molecules.^{2,3}

At the same time, low values of S in the N_D phase in comparison with the values of S in the $D_{h(0,d)}$ phases¹⁻³ agree qualitatively with the proposition that the N_D - D transition is always a first-order phase transition^{1,6} and that the D phase can form only at high values of S (Ref. 6). We would accordingly expect both a substantial jump in S at the N_D - D transition and higher values of S in the N_D phase of entities which have low-temperature $D_{h(0,d)}$ phases.

Interrelated changes in the conformational mobility of the chains (the anisotropy of the molecular shape) and S in the N_D phase should be manifested in the temperature dependence $S(T)$ and in the nature of the N_D - I transition or the functional dependence $\Delta\Phi(S)$ of the thermodynamic-potential density of the N_D phase.

3. Working in the Landau-de Gennes theory, and using the results of Refs. 4-6, we choose the potential $\Delta\Phi(S)$ in the form

$$\Delta\Phi(S) = \frac{1}{2} a(T - T^*)S^2 + \frac{1}{3} BS^3 + \frac{1}{4} CS^4 + \frac{1}{6} DS^6. \quad (4)$$

This form of the potential makes it possible to incorporate a possible proximity of the N_D-I transition to an isolated Landau critical point ($B=0$) and to the tricritical point ($C=0$). We switch to the variable $y=S/S_1$ and introduce the parameter

$$R=(4y_c^3-9y_c+4)/(4-3y_c), \quad (5)$$

where $S_1=S(T_1)$, T_1 is the limiting stability temperature of the N_D phase, and $y_c=y(T_c)$. The conditions $\Phi_S''(T_c)>0$ and $D\geq 0$ impose the restrictions $y_c\leq 4/3$, $R>0$, and $1/R\geq 0$. The expansion coefficients in (4) can be written

$$\frac{a}{D}=\frac{S_1^4 R}{T_1-T^*}, \quad \frac{B}{D}=2S_1^3(1-R), \quad \frac{C}{D}=S_1^2(R-3). \quad (6)$$

We thus see that the parameter R determines the magnitude and sign of the coefficients B and C and also the nature of the N_D-I transition. Using (6), we write the equation of state

$$y^4+(R-3)y^2+2(1-R)y+(T-T^*)R/(T_1-T^*)=0, \quad (7)$$

from which we find the expression

$$\beta_1=\frac{(y-1)[(y+1)^2+R-1]}{2y[2y(y+1)+R-1]} \quad (8)$$

for the effective power β_1 in the approximation $S=S_0 t^{\beta_1}$, where $t=1-T/T_1$. We obviously have $\beta_1(T)/(T_1-T)=\beta_n/(T_n-T)$, and at $(T_1-T)\gg(T_n-T_1)$ the condition $\beta_1(T)\approx\beta_n$ holds. Setting $\beta_1(T_c-32.8\text{ K})=\beta_n=0.247$ in (8), and using $y=y_c S/S_c$, $S_c=0.212$, and $R=R(y_c)$, we find a fourth-degree equation for y_c . The physical root of this equation is $y_c=1.284$. This value corresponds to the values $S_1=0.165$, $R=6.094$, and the following parameter values in (4) and (6):

$$aT_c/D=1.09, \quad B/D=-0.046, \quad C/D=0.084. \quad (9)$$

Substituting R into (7) for the extreme points $T=T_c$ and $T_c-38.2\text{ K}$, we find $T_c=T^*=1.33\text{ K}$ and $T_1-T_c=0.21\text{ K}$. These figures are typical of nematic liquid crystals N and N_D (Refs. 4 and 5). It can be seen from Fig. 1 that for intermediate values $0<\Delta T<38.2\text{ K}$ equation of state (7) leads to a theoretical $S(T)$ which agrees with the experimental results and also with approximation (3) for $S(T)$, when we incorporate the anisotropy of the local field and use the value $\beta_n=0.247$. At $T=0$ we find $S_0=1.012$ from (7), in excellent agreement with the value $S_0=1$, in view of the relative extrapolation interval $[(T_c-38\text{ K})/(38\text{ K})=8.8\gg 1]$.

The Landau-de Gennes thus gives a quantitative description of the $S(T)$ dependence over the entire interval of the N_D phase, and it justifies the use of the Haller approximation, (3). The coefficients in (9) for potential (4) are anomalously small (smaller by a factor of about 4 than the MBBA coefficients⁵), and the N_D-I transition is simultaneously close to an isolated Landau critical point and the tricritical point. Over the entire range of the mesophase, the $S(T)$ dependence is determined by the temperature dependence, as can be seen from the value $\beta_n\approx 0.25$. At this point, the reason why B is small is not clear, since in the case at hand there is no biaxiality factor of the polarizability tensor $\hat{\gamma}$ or of the molecular shape, which leads to a lowering of B for calamite

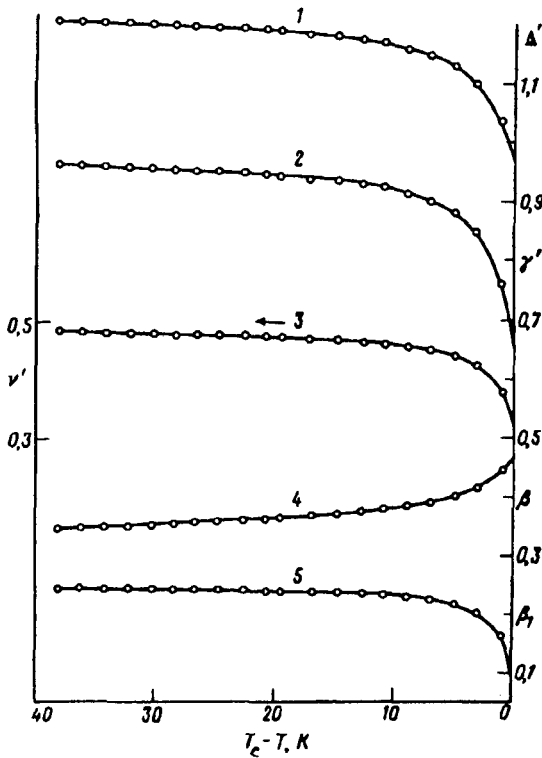


FIG. 2. Temperature dependence of the effective powers Δ' (1), γ' (2), ν' (3), β (4), and β_1 (5) as calculated with $R=6.094$ from Eqs. (8) and (10) and experimental values of $y=y_c S/S_c$ (points) and with values of y satisfying equation of state (7) (solid curves).

liquid crystals and to a possible change in the nature of the $I-N-S_A$ transitions from first to second.^{5,11} A natural cause of a small value of C , as in calamite nematic liquid crystals, might be mutually consistent changes in S and the effective flexibility of the molecular chains.⁵

4. The effective powers β , γ' , and Δ' , defined by

$$S=S_1+(S_0-S_1)t^\beta, \quad \chi \sim t^{-\gamma'}, \quad S''/S' \sim t^{-\Delta'}$$

are given by

$$\gamma' = 1 - \frac{1}{2y} + \frac{(y^3-1)(4y+R-1)+y^2(y-1)(R+3)}{2y[2y(y+1)+R-1]^2}, \quad (10)$$

$$\Delta' = 2\gamma' - \frac{3\beta_1 y(10y^2+R-3)}{10y^3+3y(R-3)+2(1-R)}$$

for potential (4) and by the expression $\beta=\beta_1 y/(y-1)$, which does not depend on the form of $\Delta\Phi(S)$. When a gradient term $g(\nabla S)^2/2$ is incorporated in (4), one can find, in

the usual way, an expression for the correlation radius $\xi = (g\chi)^{1/2} \sim t^{-\nu'}$ of equilibrium fluctuations of the modulus of S with an effective power $\nu' = \gamma'/2$. With $T = T_1$ and $y = 1$, we find $\beta_1 = 0$, $\beta = 0.5$, $\gamma' = 0.5$, $\nu' = 0.25$, and $\Delta' = 1$, from (8) and (10). Figure 2 shows a temperature dependence of these exponents in the N_D phase at $T \leq T_c$. In the interval $T_c < T < T_1$, the exponent Δ' varies in a nonmonotonic way, going through a minimum. At $T = 0$ we have $\beta_1 = 0.253$, $\beta = 0.303$, $\gamma' = 0.998$, $\nu' = 0.499$, and $\Delta' = 1.246$. Far from T_c these parameters vary slightly and are close to the tricritical values: $\beta_1 = 0.25$, $\gamma' = 1$, $\nu' = 0.5$, and $\Delta' = 1.25$ (Ref. 5), while we have $\beta(T) > 0.25$.

5. These results demonstrate the extensive capabilities of refractrometry for studying N_D phases. They confirm the suggestion¹ that conformational degrees of freedom of the molecules play an important role in the particular features of the phase transitions in discotic liquid crystals. They demonstrate the validity of the Landau-de Gennes theory for describing the N_D -I transition. They demonstrate general features of the N_D -I and N -I transitions. They do not resolve the question of why the coefficient $B < 0$ in (4) is small. In order to test the results of the numerical simulation, it will be necessary to study the orientational order of discotics with N_D and D phases.

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²The details of determining τ_0 from independent experimental data will be published separately.

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