

Effect of noncentrosymmetry of mesogenic molecules on the macroscopic properties of nematic liquid crystals

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A molecular-statistical description of orientational ordering is presented, in which account can be taken of the effect of singularities of the local symmetry and of the short-range order on the macroscopic characteristics of the mesophase. An interpretation of the anomalous thermostability of nematics with noncentrosymmetric molecules is given, and it is also theoretically predicted that in such systems the correlation between the rotational-viscosity activation energy and the thermal stability should be the inverse of that in the familiar Diogo-Martins model. The latter conclusion is experimentally confirmed for mesophases made up of centrosymmetric particles (molecules or associates).

§1. INTRODUCTION

A molecular-statistical theory of nematic liquid crystals is usually developed by starting with a specification of some form of energy E_{ij} of the paired intermolecular interaction. The most general expression for this energy is an expansion in a complete system of generalized spherical functions (Wigner D -functions).^{1,2}

In the average intermolecular field approximation (AIFA),³ the orientational ordering in nematics is described by orientational-order parameters η_L defined by a system of self-consistency equations

$$\begin{aligned} \eta_L &= \langle P_L(\cos \theta) \rangle \\ &= \left\{ \int_{-1}^1 P_L(\cos \theta) \exp[-V(\theta)/kT] d \cos \theta \right\} \\ &\quad \times \left\{ \int_{-1}^1 \exp[-V(\theta)/kT] d \cos \theta \right\}^{-1}. \end{aligned} \quad (1.1)$$

Here $V(\theta)$ is a model potential (pseudopotential) usually written in the form

$$V(\theta) = - \sum_L v_L \eta_L P_L(\cos \theta), \quad (1.2)$$

where θ is the angle between the long axis of the molecule and the axis of the predominant molecular orientation (director).

In a number of studies, to take into account the features of the short-range order, other approximations were also used. These include the cluster approximation,⁴ various variants of the Bethe-Peierls approximation,⁵ the traditional correlation-function method of the theory of liquids,⁶⁻⁸ various chain models,^{9,10} and others. These, however, only refined the quantitative characteristics of the phase transitions. The qualitative relations between the coefficients of the expansion of E_{ij} (or of V) in Legendre polynomials, on the one hand, and the macroscopic properties of the mesophase, on the other, remained similar to those obtained in the AIFA.

In view of the ensuing computational difficulties, E_{ij} was specified only in a very simple form such as

$$E_{ij}(\theta_{ij}) = \sum_L c_L P_L(\cos \theta_{ij})$$

with $L = 2$ or $L = 2.4$; this is valid only for $r_{ij} \gtrsim l$ (l is the molecule length) and does not reflect the qualitative singularities of the interaction of the neighboring molecules in the mesophase.

The limitations of the available approaches can in our opinion be illustrated by the experimental data of Ref. 11. When one of the benzene rings of 4-alkylphenyl-4' alkylbenzoate is replaced by a cyclohexane or bicyclooctane ring, the thermal stability of the mesophase increases, notwithstanding the definite lowering of the anisotropy of the polarizability and the lack of an increase of the geometric anisometry.¹² A rise in the temperature T_i of the transition from a nematic to an isotropic liquid corresponds in this case to enhancement of the noncentrosymmetry of the molecules. Quantum-mechanical calculations¹³ show that for molecules of this type a most essential role is played in the expression for E_{ij} by terms with odd Legendre polynomials, of the type $c_1 P_1(\cos \theta)$. At the same time in Refs. 14 (Bethe-Peierls approximation) and¹⁵ (AIFA) it is concluded that allowance for the terms with P_{2n-1} in the absence of long-range translational order exerts practically no influence on the orientational ordering, thus contradicting the experimental data.¹¹

The purpose of the present paper is an attempt, accepting on the whole as the first-order approximation the AIFA, which has given good account of itself,⁷ to ascertain the qualitative changes of the macroscopic characteristics which can result from additional allowance for the local symmetry of the long-range order, and which are connected with the singularities of the construction of the molecules in specific nematics.

§2. DISTRIBUTION FUNCTION OF ANISOMETRIC MOLECULE IN THE MESOPHASE

We define an n -particle distribution function $F^{(n)}(x_1 \dots x_n)$ as

$$F^{(n)}(x_1 \dots x_n) = \frac{N!}{(N-n)!} \frac{\int dx_{n+1} \dots dx_N \exp(\beta U_N)}{\int dx_1 \dots dx_N \exp(\beta U_N)}, \quad (2.1)$$

where N is the total number of molecules in the ensemble, $x_i \{ \mathbf{r}_i, o_i \}$ is the set of phase variables that describe the position and orientation of the i th molecule, $\beta = 1/kT$, and

$$U_N = \sum_{1 \leq i < j \leq N} E_{ij}(x_i, x_j).$$

For a single-particle distribution function in the superposition approximation, the solution of the BBGKY equations can be represented in the form

$$F^{(1)}(x_i) = \frac{1}{Z} \exp \left\{ -\beta \int dx_j E_{ij}(x_i, x_j) F^{(1)}(x_j) g^{(2)}(x_i, x_j) \right\}, \quad (2.2)$$

where

$$Z = \frac{1}{N} \int dx_i \exp \left\{ -\beta \int dx_j E_{ij}(x_i, x_j) F^{(1)}(x_j) g^{(2)}(x_i, x_j) \right\}, \quad (2.3)$$

$g^{(2)}(x_i, x_j)$ is a two-particle correlation function, the determination of which calls for solution of the next equation of the BBGKY chain with a three-particle correlation function.

Neglecting completely the correlations between the molecules, i.e., putting $g^{(2)}(x_i, x_j) = 1$, we obtain

$$F^{(1)}(x_i) = \frac{1}{Z} \exp \left\{ -\beta \int E_{ij}(x_i, x_j) F^{(1)}(x_j) dx_j \right\}. \quad (2.4)$$

This corresponds to the known average molecular field approximation in the models of the type of the Maier-Saupe theory.³ At the same time it is possible, retaining the statistical independence of the molecules (i.e., remaining in the framework of the AIFA for the orientational part of the distribution function⁷) to take into account the correlations of the positions of the centroids. To this end we consider the correlation function

$$g^{(2)}(x_i, x_j) \equiv g^{(2)}(\mathbf{r}_i, o_i; \mathbf{r}_j, o_j)$$

in the form

$$g^{(2)}(\mathbf{r}_i - \mathbf{r}_j) \equiv g^{(2)}(\mathbf{r}_{ij}).$$

The presence of cylindrical symmetry in the system allows us to express the angular dependence of $g^{(2)}(\mathbf{r}_{ij})$ in the form

$$g^{(2)}(\mathbf{r}_{ij}) = \sum_{\mathbf{L}} g_{\mathbf{L}}^{(2)}(r_{ij}) P_{\mathbf{L}}(\cos \vartheta_{ij}), \quad (2.5)$$

where r_{ij} and ϑ_{ij} are polar coordinates of the center of gravity of the j th molecule in the i th coordinate system. The concrete form of the coefficients $g_{\mathbf{L}}^{(2)}(r_{ij})$ can be obtained by numerical calculation in analogy with Ref. 8 and is not our present purpose.

Averaging $E_{ij}(\mathbf{r}_i, o_i; \mathbf{r}_j, o_j)$ over all the values of r_{ij} and over the orientations of the j th molecule we obtain in the particular case of axial-symmetry molecules, with (2.2) (2.5) taken into account, an expression for the orientational part of the distribution function $F^{(1)}$ in the form

$$F^{(1)}(\theta) = \frac{1}{Z} \exp[-\beta V(\theta)], \quad (2.6)$$

where

$$Z = \frac{1}{N} \int dx \exp[-\beta V(\theta)],$$

$$V(\theta) = - \sum_{\mathbf{L}} \sum_{\mathbf{M}} v_{LM} \eta_{\mathbf{L}} P_{\mathbf{M}}(\cos \theta) \quad (2.7)$$

is the pseudopotential of the i th molecule and differs from the pseudopotential in the AIFA (1.2) in that it contains crossover terms with $L \neq M$.

Note that the pseudopotential (2.7) was first introduced in Ref. 6 specifically to take into account the local cylindrical symmetry of the nematic mesophase within the AIFA framework, but neither a detailed proof nor calculations with its aid were given.

The crossover terms in (2.7) have a two-fold meaning. On the one hand they permit, as was indeed proposed in Ref. 16, the taking into account the local symmetry of the nematic mesophase. On the other hand, the molecule centroid correlations connected, e.g., with the short-range translational order, make also their own contribution to $g_{\mathbf{L}}^{(2)}(r_{ij})$, and hence to the crossover terms (2.7). It becomes thus possible, without complicating the formalism and merely by renormalizing the coefficients v_{LM} , to take into account a number of mesophase features connected with the short-range order and not describable formally in the AIFA. By way of an example illustrating the capabilities of the method, we consider a nematic made up of noncentrosymmetric molecules.

§3. MODEL CALCULATIONS OF ORIENTATIONAL ORDERING IN A MESOPHASE MADE UP OF NONCENTROSYMMETRIC MOLECULES

For the concrete calculations we confine ourselves to the terms with P_2, P_4 , and P_1 in the pseudopotential (2.7). We recognize next that in real nematic mesophases $\eta_1 \equiv 0$ always. Furthermore, we use the fact that in accord with the experimental data $\eta_4 \approx a_1 \eta_2$ in first-order approximation¹⁷ (in the general case we can assume $\eta_4 = a_1 \eta_2 + a_2 \eta_2^2 + \dots$). We have ultimately

$$V(\theta) = -v\eta [P_2(\cos \theta) + \delta_1 P_1(\cos \theta) + \delta_4 P_4(\cos \theta)], \quad (3.1)$$

where

$$\eta_2 \equiv \eta_1, \quad v = v_{22} \left(1 + a_1 \frac{v_{42}}{v_{22}} \right), \quad \delta_1 = \frac{v_{21}}{v} \left(1 + a_1 \frac{v_{41}}{v_{21}} \right),$$

$$\delta_4 = \frac{v_{24}}{v} \left(1 + a_1 \frac{v_{44}}{v_{24}} \right).$$

We note that an expression

$$V(\theta) = v\eta [P_2(\cos \theta) + R(\theta)],$$

similar in form to (3.1) was introduced by us in Ref. 18 as the starting model potential for the description of cholesteric mesophases and made possible the description of a number qualitative features of the helical twist.

After substituting (3.1) in (1.1) and numerical calculations we obtain $\eta(T)$ curves for different values of the parameters δ_1 and δ_4 , and also the characteristics $t_i \equiv kT_i/v$ and $\eta_i \equiv \eta(T_i)$ of the transition from a nematic to an isotropic liquid, as functions of δ_1 and δ_4 (Figs. 1 and 2).

We note the following qualitative features of the results.

1. The character of the $\eta(T/T_i)$ dependence for differ-

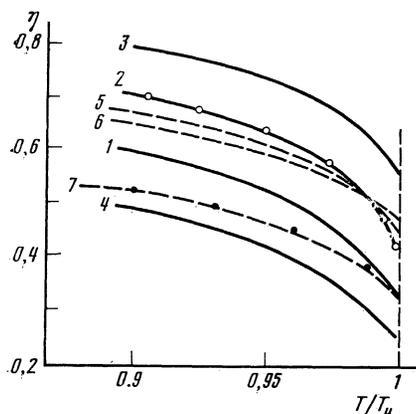


FIG. 1. Temperature dependence of the orientational order parameter for model systems with the following parameter values: 1 — $\delta_1 = 0$, $\delta_4 = 0$; 2 — $\delta_1 = 0$, $\delta_4 = 0.1$; 3 — $\delta_1 = 0$, $\delta_4 = 0.2$; 4 — $\delta_1 = 0$, $\delta_4 = -0.1$; 5 — $\delta_1 = 0.6$, $\delta_4 = 0$; 6 — $\delta_1 = 1.0$, $\delta_4 = 0$; 7 — $\delta_1 = 1.0$, $\delta_4 = -0.12$; light circles—experimental data for pazoxyanisole,¹⁰ dark circles—experimental data for cholesteryl-*o*-fluorobenzoate.²⁰

ent δ_4 at $\delta_1 = 0$, as well as the influence of δ_4 on η_i and t_i , are similar to the results^{3,16} obtained by solving the self-consistency equations with account taken of η_2 and η_4 and using the pseudopotential (1.5). Comparison with the experimental data for dialkyloxyazoxybenzenes,¹⁹ the centrosymmetric shape of whose molecules excludes a possible contribution of the term with P_1 , shows that the corresponding model dependence (Fig. 1, curve 2), just as in Refs. 3 and 11, describes accurately enough the experimental data; the influence of δ_4 on η_i and t_i is also similar to that in Refs. 3 and 16.

2. The effect of δ_1 on the orientational order has a qualitatively different character. Thus, with increasing δ_1 , the decrease of η with temperature becomes all the more smoother, i.e., $|d\eta/d(T/T_u)|$ decreases. [We note that cholesterine esters, the noncentrosymmetry of whose molecules is obvious, is characterized by just such a variation of η with temperature²⁰ (Fig. 1, curve 7).]

Next, the change of η with increasing δ_1 is nonmonotonic; at $\delta_1 \sim 1$ the function $\eta_i(\delta_1)$ (Fig. 2) goes through a maximum and then decreases asymptotically to zero (this is natural, since a second-order phase transition should take place in the system at $\gamma \gg 1$, Ref. 21). At small δ_1 the forces connected with P_1 are thus insufficient to produce a tenden-

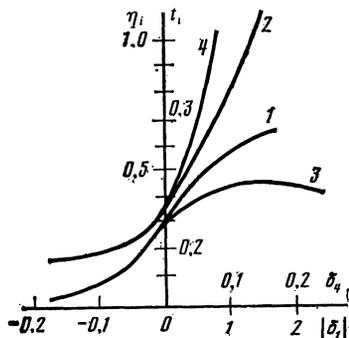


FIG. 2. Dependence of the orientational order parameter and of the relative temperature at the isotropic-transition point on δ_1 and δ_4 : 1 — $\eta_i(\delta_4)$, 2 — $t_i(\delta_4)$, 3 — $\eta_i(\delta_1)$, 4 — $t_i(\delta_1)$.

cy toward further “antiparallel” order, and the term with P_1 leads only to additional orientational ordering, acting in analogy with the term containing P_4 for the corresponding $\delta_4 > 0$.

3. We note finally the increase of t_i with increasing $|\delta_1|$. This means that, other conditions being equal, nematics with noncentrosymmetric molecules should have higher isotropic-transition temperatures, in agreement with the experimental data.¹¹ It is probably possible to interpret similarly also the anomalously high values of T_i for substituted cholesterine benzoates.²²

§4. EXPERIMENTAL INVESTIGATIONS OF ROTATIONAL VISCOSITY IN MODEL SYSTEMS

In accordance with the known theory of Diogo and Martins,²³ the rotational viscosity coefficient γ_1 is determined by the frequency ν_0 of the hoppers of the nematic between two equilibrium positions with $\theta = 0$ and 180° :

$$\gamma_1 = \nu_0^{-1} (kT/\pi^2 V^*), \quad (4.1)$$

where V^* is the molecular volume at temperature T .

For real nematics, in the absence of pre-transition phenomena connected with the tendency to translational ordering, and far from T_i , the activation energy E_a of the rotational viscosity is proportional to the constant ν in the Maier-Saupe pseudopotential, meaning that a correlation should exist between E_a and T_i . On the other hand, for a potential of the type (3.1), which has (at $\delta_1 > 0$) an absolute minimum at $\theta = 0^\circ$ and a local minimum at $\theta = 180^\circ$, the value of ν_0 should increase with increasing δ_1 (the contribution made to η by a molecule with an orientation corresponding to a local minimum of the pseudopotential is analogous to that of a molecule at the absolute minimum; at the same time, the probability of hopping over from this potential is substantially higher). This means that for noncentrosymmetric molecules described by a pseudopotential of type (3.1) the correlation between E_a and T_i should be the reverse of that of “ordinary” nematogenic molecules described by a pseudopotential of the Maier-Saupe type. To verify experimentally this consequence of the developed model, we investigated the rotational viscosity of a number of systems (see Table I).

The coefficient γ_1 was determined from the relaxation time t of the Fréedericksz transition (S -effect) in a planarly oriented NLC deformed by an electric field,²⁴ using the relation

$$\ln(\varphi_0/\varphi) = 2\pi^2 K_{11} t / l^2 \gamma_1,$$

where $\varphi = \Phi/2\pi$, Φ is the phase delay of monochromatic linearly polarized light incident perpendicular to the layer, l is the thickness of the NLC layer,

$$\varphi_0 \approx (d\varphi/dU|_{U=U_{thr}}) (U - U_{thr})$$

is the initial phase, and U_{thr} is the threshold voltage of the S -effect. The elastic constant K_{11} for each temperature was determined from the threshold voltage and dielectric anisotropy, measured under the same conditions. We described the experimental procedure in detail earlier in Ref. 24. The NLC layer thickness was measured by an interference method and

TABLE I.

Designation	Components	Composition, mol. fract.
Mixture A	<chem>C1=CC=C(C=C1)C(=O)Oc2ccc(OCC)cc2</chem>	5/11
	<chem>C1=CC=C(C=C1)C(=O)Oc2ccc(OCC)cc2</chem>	5/11
	<chem>C1=CC=C(C=C1)C(=O)Oc2ccc(OCC)cc2</chem>	1/11
Mixture B	<chem>C1=CC=C(C=C1)C(=O)Oc2ccc(OCC)cc2</chem>	5/11
	<chem>C1=CC=C(C=C1)C(=O)Oc2ccc(OCC)cc2</chem>	5/11
	<chem>C1=CC=C(C=C1)C(=O)Oc2ccc(OCC)cc2</chem>	1/11
Mixture C	<chem>C1=CC=C(C=C1)N=Nc2ccc(OCC)cc2</chem>	2/3
	<chem>C1=CC=C(C=C1)N=Nc2ccc(OCC)cc2</chem>	1/3
FCH-7	<chem>C1=CC=C(C=C1)C#N</chem>	-

was about 60 μm . The measurement cell temperature was maintained constant with $\pm 0.1^\circ\text{C}$. The error in the determination of γ_1 did not exceed 7–10%. The dependences of $\log \gamma_1$ on T^{-1} for mixtures A and B are shown in Fig. 3. They are well approximated by straight lines (except for the region near T_i), whose slopes were used to determine E_a accurate to ± 0.010 eV.

The most important results of the experiments are the following.

1. On going from the mixture A to the mixture B (see Table I), i.e., from a system made up of centrosymmetric molecules to a system made up principally of noncentrosymmetric ones (in each of the mixtures we introduced 9% of *n*-

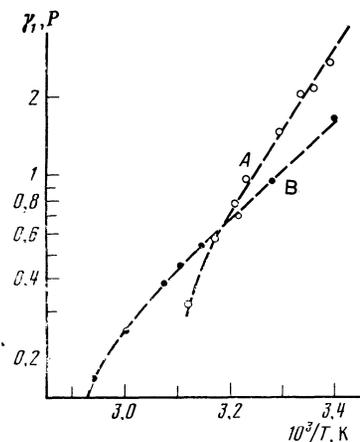


FIG. 3. Temperature dependences of the rotational-viscosity coefficient γ_1 for mixtures A and B.

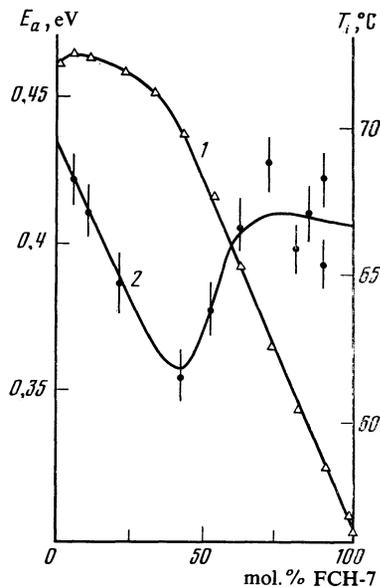


FIG. 4. Dependence of the macroscopic characteristics of the mixture C + FCH-7 mixture on the molar concentration of the FCH-7: 1— T_i , 2— E_a .

cyanophenyl ester of *n*-hexylbenzoic acid to make the anisotropy of the dielectric constant positive) T_i increases from 47.6 to 73.6 $^\circ\text{C}$; the energy E_a decreases in this case from 0.561 to 0.393 eV, and the coefficient γ_1 from 2.17 to 1.3.7 P.

2. Figure 4 shows the concentration dependences of γ_1 (25 $^\circ\text{C}$), E_a , and T_i for a mixture of azoxy compounds (mixture C, Ref. 25) and 4(4-*n*-heptyltranscyclohexane) of benzonitril (FCH-7). At an approximate FCH-7 molar concentration 40–45% a maximum deviation of T_i from additivity and a minimum of E_a are observed. It is natural to attribute this²⁶ to the fact that the particles of each of the components are centrosymmetric (the molecules of the azoxy compounds and the FCH-7 associates, Refs. 27 and 28); at the same time, the associates of the mixed composition produced in the mixture are undoubtedly noncentrosymmetric. In this case δ_1 in (3.1) increases and, as a consequence, an increase of T_i and a decrease of E_a are noted compared with the additive behavior of these parameters.

§5. CONCLUSION

Thus, the aggregate of the results obtained in §§3 and 4 shows that the noncentrosymmetry of the mesogenic molecules (the difference between the “heads” and “tails” of the particles making up the mesophase) exert a substantial influence on the macroscopic properties of NLC (particularly on the thermal stability and rotational viscosity). Allowance for the noncentrosymmetry of the molecules (one approach for which is proposed in this paper) is, in our opinion, an indispensable condition for an adequate molecular-statistics description of the nematic mesophase.

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- ¹J. R. Sweet and W. A. Steele, *J. Chem. Phys.* **47**, 3022 (1967).
- ²L. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum* [in Russian], Nauka, 1975.
- ³P. J. Wojtowicz, *RCA Rev.* **35**, 118 (1974).
- ⁴R. Van der Haegen, J. Debruyne, R. Luyckx, and H. N. W. Lekkerker, *J. Chem. Phys.* **73**, 2469 (1980).
- ⁵J. G. J. Ypma and G. Vertogen, *J. Phys.* **37**, 557 (1976).
- ⁶A. Wulf, *J. Chem. Phys.* **55**, 4512 (1971).
- ⁷Y. M. Shih, Y. R. Lin-Liu, and C. W. Woo, *Phys. Rev.* **A14**, 1895 (1976).
- ⁸M. A. Lee and C. W. Woo, *Phys. Rev.* **A16**, 750 (1977).
- ⁹P. Sheng and P. J. Wojtowicz, *Phys. Rev.* **A14**, 1883 (1976).
- ¹⁰L. Longa, *Acta Phys. Pol.* **A60**, 513 (1981).
- ¹¹N. Carr, G. W. Gray, and S. M. Kelly, *Mol. Cryst. Liq. Cryst.* **66**, 267 (1981).
- ¹²W. H. deJeu, *Physical Properties of Liquid Crystalline Substances*, Gordon & Breach, N. Y. (1980); [Russ. transl.], Mir, 1982.
- ¹³K. Tokita, K. Fujimara, S. Kondo, and M. Takeda, *Mol. Cryst. Liq. Cryst.* **64**, 171 (1981).
- ¹⁴J. G. J. Ypma and G. J. Vertogen, *J. Phys.* **37**, 1331 (1976).
- ¹⁵P. J. Photinos and A. Saupe, *Phys. Rev.* **A13**, 1926 (1976).
- ¹⁶R. L. Humphries, P. G. James, and G. R. Luckhurst, *J. Chem. Soc. Faraday Trans. II*, p. 1031 (1972).
- ¹⁷E. M. Aver'yanov, A. Vaitkyavichyus, A. Ya. Korets, R. Sirutkaitis, A. V. Sorokin, and V. F. Shabanov, *Zh. Eksp. Teor. Fiz.* **76**, 1791 (1979) [*Sov. Phys. JETP* **49**, 910 (1979)].
- ¹⁸G. S. Chilaya and L. N. Lisetskii, *Usp. Fiz. Nauk* **134**, 297 (1981) [*Sov. Phys. Usp.* **24**, 496 (1981)].
- ¹⁹E. G. Hanson and Y. R. Shen, *Mol. Cryst. Liq. Cryst.* **36**, 193 (1976).
- ²⁰P. J. Collings, T. J. McKee, and J. R. McColl, *J. Chem. Phys.* **65**, 3520 (1976).
- ²¹S. Chandrasekhar, *Liquid Crystals*, Camb. Univ. Press, 1977.
- ²²V. G. Tishchenko and R. M. Cherkashina, in: *Cholesteric Liquid Crystals* [in Russian], Novosibirsk, Inst. Teor. Appl. Math. Sib. Div. USSR Acad. Sci., 1976, p. 26.
- ²³A. C. Diogo and A. F. Martins, *Mol. Cryst. Liq. Cryst.* **66**, 133 (1981).
- ²⁴V. G. Chigrinov and M. F. Grebenkin, *Kristallografiya* **20**, 1240 (1975) [*Sov. Phys. Crystallogr.* **20**, 747 (1975)].
- ²⁵M. I. Barnik, S. V. Belyaev, M. F. Grebenkin, *et al.*, *ibid.* **23**, 805 (1978) [**23**, 460 (1978)].
- ²⁶Yu. A. Fialkov, A. N. Zhitomirskii, and Yu. A. Tarasenko, *Physical Chemistry of Non-aqueous Solutions* [in Russian], Khimiya, 1973.
- ²⁷H. Schad and M. A. Osman, *J. Chem. Phys.* **75**, 880 (1981).
- ²⁸A. J. Leadbetter and A. I. Metra, *J. Mol. Cryst. Liq. Cryst. Lett.* **72**, 51 (1981).

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