STRUCTURAL AND THERMODYNAMIC CONSEQUENCIES
OF THE INTERACTION OF CONFORMATIONAL DEGREES
OF FREEDOM OF AZOMETHINES IN THE NEMATIC PHASE

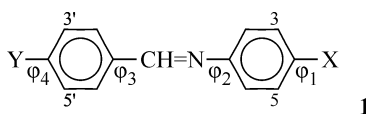**E. M. Aver'yanov**   UDC 532.783:548.0

The interaction of the conformational degrees of freedom of azomethines in the nematic phase, which is induced by electronic donor-acceptor properties of the terminal substituents of the benzylideneaniline core is studied. These degrees of freedom related to the rotation angles φ_k around the bonds between the substituent and the aniline ring (φ_1) and also between the CH=N bridge and the aniline ring (φ_2) are characterized by the parameters $Q_k = \langle \cos^2 \varphi_k \rangle$. It is found that the interaction of these degrees of freedom is manifested in the linear dependence $Q_2(Q_1)$. Within the phenomenological theory the effect of this interaction on changes δ_k in the Q_k values during the nematic liquid crystal–isotropic liquid phase transition is revealed along with the temperature T_{NI} and character of this transition. The derivation of previously established empirical dependences $T_{\mathrm{NI}}(Q_k)$ is presented in the presence of direct and indirect steric effects of side substituents affecting the Q_k values. A diverse combination of δ_k signs in the nematic phase, which is a prerequisite for the conformational polymorphism of the nematic phases of azomethines, is shown.
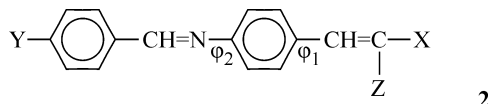
INTRODUCTION

Azomethine derivatives with a moiety shown below

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form thermotropic liquid crystals (LCs) of different types [1, 2] with a wide range of practical applications. Technological characteristics of these materials depend on the internal rotation angles φ_k determining the degree of moiety conjugation and the electronic structure of molecules, the anisotropy of polarizability and intermolecular interactions. In compounds **1**, the angle φ_2 between the planes of the CH=N bridge and the phenyl ring depends on the strength of the donor-acceptor electronic properties of X, Y moieties and can change from 0° to 90°, and the angle φ_3 is insensitive to the electronic properties of the

X, Y moieties [2-8]. At X=H the strengthening of the donor (acceptor) properties of the Y moiety leads to an increase (decrease) in φ_2. At Y=H the strengthening of the donor (acceptor) properties of the X moiety causes a decrease (increase) in φ_2.

The dependence of φ_2 on the donor-acceptor properties of the X, Y moieties leads to the dependence of φ_2 on the degree of conjugation of these moieties with the phenyl rings. Two cases are possible here. In the first of them the X (or Y) moiety is directly bonded to the ring and has the structure of the NO_2, NH_2, $N(CH_3)_2$, $COOH$, $C(O)OC_nH_{2n+1}$ type. The rotation of X (Y) relative to the phenyl ring plane is characterized by the angle φ_1 (φ_4). A change in the latter due to the steric effect of the Z substituent at sites 3 or/and 5 (3′ or/and 5′) changes the degree of X (Y) conjugation with the ring and the angle φ_2. Hence, the direct steric effect of the Z substituent (a change in φ_1 or φ_4) is accompanied by the indirect steric effect of this substituent (a change in φ_2). In the second case, the X moiety is bonded to the phenyl ring through the bridging group passing on the conjugation as in compound **2**.

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The direct steric effect of the bulk Z substituent increases the angle φ_1 and decreases the X conjugation with the ring. In the donor (acceptor) X moiety this results in an increase (decrease) in the angle φ_2: the indirect steric effect of the Z substituent.

In both cases, the relation φ_2 (φ_1) can be considered as the interaction of the conformational degrees of freedom. In the scientific and applied aspects it is interesting to reveal the effect of this interaction on the conformational state of molecules, the temperature and character of phase transitions in the structurally ordered environments at a competitive effect of the anisotropic intermolecular interactions and the intramolecular electronic effects on the $\varphi_{1,2}$ values. The aim of this work is to study the interaction effect of the conformational degrees of freedom in compounds **1** and **2** on the conformational state of molecules in the nematic phase, the temperature T_{NI}, and the character of the nematic–isotropic liquid (N–I) phase transition.

INTERACTION OF MOLECULAR CONFORMATIONAL DEGREES OF FREEDOM IN LCs

In the statistical molecular ensemble of LC the internal rotation barriers of fragments for typical mesogenic molecules are comparable with the energy of intermolecular interactions or thermal motion [2]. For a separate molecule the internal rotation angles $\varphi_k(\mathbf{r},\Omega)$ of the moieties fluctuate together with the position $\mathbf{r}$ and orientation Ω of the molecule with respect to its nearest anisotropic coordination environment or axes of the macroscopic anisotropy of LCs related to the long-range orientation order of molecules. The φ_k values calculated for the isolated molecules [8] are not directly associated with the values measured experimentally [2], which complicates the use of the theoretical dependence φ_2 (φ_1) for the interpretation of the experiment. For the pairs of molecular moieties with relative rotation angles φ_k at the energy equivalence of the $[\pm\varphi_k]$ and $[\pi\pm\varphi_k]$ states the parameters of the conformational state of the molecular ensemble are the values $\langle\cos^{2n}\varphi_k\rangle$, where $\langle\ldots\rangle$ mean the statistical averaging over the ensemble [2, 7]. The $\langle\cos^{2n}\varphi_k\rangle$ values characterize the physical properties of the medium, which depend on the conformational state of molecules and are determined by different physical methods [9, 10]. Therefore, for the type **1** molecules it is natural to consider the relationship $Q_2(Q_{1,4})$ between the values $Q_k=\langle\cos^2\varphi_k\rangle$ on which the measured properties of molecules (e.g., oscillator strengths of molecular transitions and polarizability tensor components [2], ^{1}H and ^{13}C NMR chemical shifts [4-6]), and transition temperatures between LC phases depend [2, 7]. With regard to that two substituents at the X and Y sites of the molecule of **1** give an additive contribution to the measured Q_2 value [5, 6] and the effect of X is much stronger than that of Y (as in the onefold substitution [4]), it is possible to limit ourselves to the relationship $Q_2(Q_1)$.

Since the dependence $Q_2(Q_1)$ is determined by the electronic conjugation of the X moiety (the CH=CZ moiety in **2**) with the phenyl ring, we use the expansion of the function $Q_2(Q_1)$ with respect to the degrees Q_1 in vicinity of the point
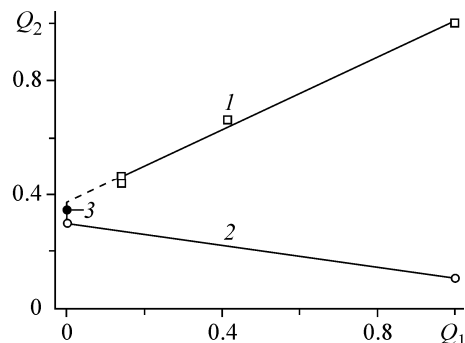
Fig. 1. Dependence (1) for derivatives **1** in solution with $X = N(CH_3)_2$, $Y = NO_2$ (*1*) and $X = C(O)O–CH_3$, $Y = H$ (*2*), the Q_{2i} value in the isotropic phase of nematic LC of MBBA (**1**, $X = C_4H_9$, $Y = OCH_3$) (*3*). (See comments in the text).

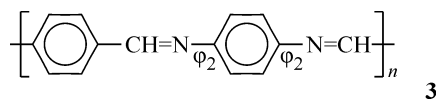$Q_1 = 0$ for which this conjugation is absent. In the linear approximation we have the relationship

$$Q_2 = Q_2^{(0)} + \kappa Q_1 \tag{1}$$

with the coefficients $Q_2^{(0)} = Q_2(Q_1 = 0)$, $\kappa = (dQ_2/dQ_1)_{Q_1=0}$. In this case it is possible to neglect a possible weak dependence of the coefficient κ on the phase state of the medium and the degree of ordering of a separate phase. For the donor (acceptor) X substituents in the molecules of **1** and **2** we have $\kappa > 0$ ($\kappa < 0$).
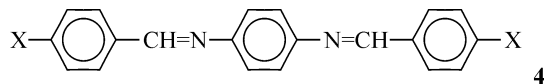
Formula (1) is confirmed by the linear dependence $Q_{2i}(Q_{1i})$ shown in Fig. 1 for the molecules of **1** with $X = N(CH_3)_2$, $Y = NO_2$ in solution on varying Q_{1i} due to the CH_3 substituents at 3,5-sites of the aniline ring in the absence of substituents at 3′,5′-sites of the benzylidene ring [2, 11]. For the X (Y) moiety the angle φ_1 (φ_4) characterizes a deviation of the normal to the phenyl ring plane from the plane passing through the C_{Ar}–N bond and the symmetry axis of the lone pair of the N atom. At $Q_{1i} = 0.140$ a smaller (larger) Q_{2i} value in Fig. 1 corresponds to the presence (absence) of two additional CH_3 substituents at 3′,5′-sites of the benzylidene ring and the value $Q_{4i} = 0.165$ ($Q_{4i} = 1$). A minor decrease in Q_{2i} at a substantial decrease in Q_{4i} indicates a weak effect of the strong acceptor $Y = NO_2$ on the Q_{2i} value determined by the strong donor $X = N(CH_3)_2$ and the Q_{1i} value. According to Fig. 1 data, for $X = N(CH_3)_2$ we have $\kappa = 0.636$. The extrapolation of dependence (1) to $Q_{1i} = 0$ gives the value $Q_{2i}^{(0)} = 0.372$ close to the value $Q_{2i} = 0.345 \pm 0.033$ for nematic LC of *p*-methoxybenzylidene-*p*′-butylaniline (MBBA) in the isotropic phase [12].

When the value $Q_{2i}^{(BA)} = 0.297$ is used for the dissolved benzylideneaniline molecules (**1**, X=Y=H) [4] as a reference of $Q_{2i}^{(0)}$ from formula (1) it follows that the value $\kappa = -0.297$ corresponds to the extremely strong acceptor X ($Q_{1i} = 1$, $Q_{2i} = 0$). For the molecule of **1** in solution with $Y = H$ and a strong acceptor $X = C(O)O–CH_3$ ($Q_{1i} = 1$, $Q_{2i} = 0.106$ [2, 4]), which is typical of mesogenic derivatives of **1** and **2**, the use of $Q_{2i}^{(0)} = Q_{2i}^{(BA)}$ yields $\kappa = -0.191$ and $|\kappa| \ll 1$.

Relationship (1) is relevant for polyazomethines $[–(Ar_1)–CH=N–(Ar_2)–N=CH–]_n$ with various aromatic cyclic $Ar_{1,2}$ moieties [13-16]. The experimental Q_2 values are unknown for them, although they determine the characteristics of the electronic structure, which are important for applications in optoelectronics [14–16]. For the most known polymer [15, 16]

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the value $Q_{1i} = Q_{2i}$ must be close to the value $Q_{2i} = 0.513$ in the isotropic phase of nematic LCs consisting of molecules

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$$X - \langle\bigcirc\rangle - CH=N - \langle\bigcirc\rangle - N=CH - \langle\bigcirc\rangle - X$$

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with substituents X = H, CH_3, OCH_3, Cl, Br, and I [7]. This Q_{2i} value is noticeably higher than the $Q_{2i}^{(BA)}$ value due to the mutual effect of the azomethine moieties through the phenyl ring. The quantum chemical calculation for the isolated molecule of polymer **3** also gives a smaller value of φ_2 [15] than that for benzylideneaniline. For compounds **3** and **4** with $Q_1 = Q_2$ we obtain from formula (1)

$$\kappa = (Q_2 - Q_2^{(0)})/Q_2. \tag{2}$$

The use of the values Q_{2i} and $Q_{2i}^{(0)} = Q_{2i}^{(BA)}$ instead of Q_2 and $Q_2^{(0)}$ yields $\kappa = 0.421$, i.e. the N=CH group is a weaker donor than the substituent X = $N(CH_3)_2$ in the molecule of **1**.

MOLECULAR CONFORMATIONS AND FEATURES OF THE N–I TRANSITION

Let us consider the consequences of relation (1) for the N–I transition within the phenomenological approach [12]. In the nematic phase with relatively close molecular packing the anisotropic intermolecular interactions (close packing effects, anisotropic dispersion interactions) determine the presence of the long-range orientational order of long molecular axes of **l** with respect to the **n** macroscopic axis of their preferred orientation (director). The orientational ordering of molecules is characterized by the value $S = \langle 3\cos^2\theta - 1 \rangle/2$ [17], where θ is the angle between the **l** and **n** axes. The same intermolecular interactions are responsible for the changes $\delta_1 = Q_1 - Q_{1i}$, $\delta_2 = Q_2^{(0)} - Q_{2i}^{(0)}$ in Q_1 and $Q_2^{(0)}$ parameters with respect to their equilibrium Q_{1i} and $Q_{2i}^{(0)}$ values in the isotropic phase. Therefore the changes $\delta_{1,2}$ can be considered as a consequence of the dependence $Q_k(S)$. In the arbitrary system of coordinates the tensor parameter of the order of the nematic **S** has the components $S_{ij} = S(3n_in_j - \delta_{ij})/2$, where $n_{i,j}$ are the components of the **n** director in this system of coordinates [17]. In the *xyz* system of coordinates of the **n**||*z* director the diagonal tensor **S** has the components $S_{xx} = S_{yy} = -S/2$, $S_{zz} = S$. The dependences $Q_k(S)$ determined by the relationship of the tensor **S** with the Q_k parameters minimize the density of the free energy of the nematic [12]

$$\Delta F = \Delta F_S + \Delta F_Q + \Delta F_{SQ}. \tag{3}$$

The summand ΔF_S reflecting the orientational ordering of molecules in the absence of the relation between **S** and Q_k has the form [17]

$$\Delta F_S = a(T - T_0^*)S^2/2 - BS^3/3 + CS^4/4 + \dots \tag{4}$$

with constant coefficients B, C, … in a narrow range of the nematic phase. The contribution ΔF_Q is associated with the changes δ_k. Unlike the molecules with one actual conformational degree of freedom [12], in the case considered here the function $\Delta F_Q(\delta_k)$ with the minimum at $\delta_k = 0$ is given in the lowest approximation by the positively determined quadratic form

$$\Delta F_Q = \delta_1^2/2\chi_1 + \delta_1\delta_2/\chi_m + \delta_2^2/2\chi_2 \tag{5}$$

with the coefficients $\chi_k > 0$ and $\chi_m^2 > \chi_1\chi_2$. Due to the noncritical character of changes δ_k with respect to the nematic ordering of molecules it is possible to neglect the temperature dependence of the coefficients $\chi_{k,m}$. The summand $\propto \delta_1\delta_2$ takes into account the correlation between δ_1 and δ_2 due to the intermolecular interactions. The summand ΔF_{SQ} is determined by the relationship of the tensor **S** with the scalar parameters Q_k. In the lower order with respect to S and Q_k the function $\Delta F_{SQ}(I_k)$ depends on the invariants $I_k = Q_k\text{Sp}(\mathbf{S}^2) = 3Q_kS^2/2$ and has the form $\Delta F_{SQ} = -2(\mu_1I_1 + \mu_2I_2)/3$. With regard to (1) this function consists of two parts

$$\Delta F_{SQ}(Q_{ki}) = -S^2[\mu_1^*Q_{1i} + \mu_2Q_{2i}^{(0)}], \tag{6}$$

$$\Delta F_{SQ}(\delta_k) = -S^2[\mu_1^* \delta_1 + \mu_2 \delta_2], \tag{7}$$

where $\mu_1^* = \mu_1 + \kappa\mu_2$. The substitution of the summand $\Delta F_{SQ}(Q_{ki})$ into (3) and its inclusion in ΔF_S (4) give

$$T^* = T_0^* + (2/a)[\mu_1^* Q_{1i} + \mu_2 Q_{2i}^{(0)}]. \tag{8}$$

The experimental difference in the temperatures T_{NI} and T^* is about one degree [17], and dependence (8) is also valid for T_{NI}. The linear dependence $T_{NI}(Q_{1i})$ with $\mu_1 > 0$ corresponds to the experimental data for mesogenic cinnamic acids and their ethers and also other compounds with $\kappa = 0$ [2, 18] in which the conformation of the aromatic core does not depend on the conjugation of the X moiety with the core and the Q_{1i} value. At a fixed Q_{1i} value the linear dependence $T_{NI}(Q_{2i})$ with $\mu_2 > 0$ is confirmed by the known data for the mesogenic derivatives of azomethines on variation of the Q_{2i} parameter in the whole range of the alteration $Q_{2i} = 0 - 1$ due to the donor-acceptor properties of the terminal substituents [7]. According to the experimental data [2, 18], the derivative $\partial T_{NI}/\partial Q_{ki} \propto \mu_k/a$ is zero in the absence of the effect of angles φ_k on the electronic conjugation of the molecular moieties and polarizability. Thus, in (8) we have $\mu_k > 0$ regardless of the electronic nature of the X substituents.

For mesogenic derivatives **2** in formula (8) the $T_0^*(Z)$, $Q_{1i}(Z)$ values depend on the Z substituent. When the H atom is replaced by the Z substituent the change $\Delta Q_{1i} = Q_{1i}(H) - Q_{1i}(Z)$ is accompanied by the change $\Delta T_0^*(H–Z) = T_0^*(H) - T_0^*(Z)$ and the total change

$$\Delta T^*(H–Z) = \Delta T_0^*(H–Z) + (2/a)\mu_1^* \Delta Q_{1i}. \tag{9}$$

With regard to $T_{NI} \approx T^*$ this relationship can be rewritten in the following form:

$$\Delta T_{NI}(H–Z) = \Delta T_{NI}^{(g)}(H–Z) + \Delta T_{NI}^{(s)}(Q_{1i}) + \Delta T_{NI}^{(s)}(Q_{2i}), \tag{10}$$

found experimentally [2, 7]. The positive value of $\Delta T_{NI}^{(g)}(H–Z) \equiv \Delta T_0^*(H–Z)$ is due to the geometric effect of the Z substituent reflecting a combined manifestation of the following factors: a decrease in the anisotropy of the molecular form because of an increase in the lateral dimension of the molecules; an increase in the average intermolecular distance in the direction perpendicular to the **n** director; a resulting decrease in the anisotropy of intermolecular interactions providing the stability of LCs. In the absence of the Q_k effect on the electronic conjugation of the molecular moieties and the polarizability of molecules ($\mu_k = 0$) the equality is satisfied $\Delta T_{NI}(H–Z) = \Delta T_{NI}^{(g)}(H–Z)$ [2, 18]. The positive value of $\Delta T_{NI}^{(s)}(Q_{1i}) = 2\mu_1 \Delta Q_{1i}/a$ is caused by the direct steric effect of the Z substituent: a decrease in Q_{1i}. The value $\Delta T_{NI}^{(s)}(Q_{2i}) = 2\mu_2 \Delta Q_{2i}/a$ is related to the indirect steric effect of the Z substituent: a change in $\Delta Q_{2i} = \kappa \Delta Q_{1i}$ due to the relationship $Q_2(Q_1)$. For the donor X substituents with $\kappa > 0$ and $\Delta T_{NI}^{(s)}(Q_{2i}) > 0$ the direct and indirect steric effects of the Z substituent lead to an increase in $\Delta T_{NI}(H–Z)$. For the acceptor X substituents with $\kappa < 0$ and $\Delta T_{NI}^{(s)}(Q_{2i}) < 0$ the positive contribution of $\Delta T_{NI}^{(s)}(Q_{1i})$ to the $\Delta T_{NI}(H–Z)$ value is partially or completely compensated by the negative contribution of $\Delta T_{NI}^{(s)}(Q_{2i})$. This explains the anomalously low $\Delta T_{NI}(H–Z)$ values for mesogenic azomethines of type **2** with the acceptor X moieties [2, 7], including $\Delta T_{NI}(H–Z) = 0$. A comparison of formulas (9) and (10) shows that the relationship $\Delta T_{NI}(H–Z) < \Delta T_{NI}^{(g)}(H–Z)$ for the molecules of **2** with X acceptors [2, 7] corresponds to the inequality $\mu_1^* = (\mu_1 - |\kappa|\mu_2) < 0$. With regard to $|\kappa| \ll 1$ from here the relation $\mu_2 \gg \mu_1$ follows.

The minimization of the $\Delta F_Q + \Delta F_{SQ}(\delta_k)$ sum with respect to $\delta_{1,2}$ gives the relationships

$$\delta_1 = S^2 \frac{\chi_1(\mu_1^* - \mu_2\chi_2/\chi_m)}{1 - \chi_1\chi_2/\chi_m^2}, \quad \delta_2 = S^2 \frac{\chi_2(\mu_2 - \mu_1^*\chi_1/\chi_m)}{1 - \chi_1\chi_2/\chi_m^2}. \tag{11}$$

Allowable signs of δ_k values are listed in Table 1. They are determined by the signs of the μ_1^*, χ_m coefficients and the condition $\chi_m^2 > \chi_1\chi_2$. In addition to the table data at $\kappa < 0$ for $\mu_1^* = 0$ and $\chi_m > 0$ ($\chi_m < 0$) we have $\delta_1 < 0$, $\delta_2 > 0$ ($\delta_k > 0$).

TABLE 1. Allowable Signs of the δ_k, δ_2^* Values in the Molecules of **1**, **2** at Different Signs of the Coefficients μ_1^*, χ_m, and κ

$\mu_1^* > 0$						$\mu_1^* < 0,\ \kappa < 0$				
$\chi_m > 0$				$\chi_m < 0$		$\chi_m > 0$		$\chi_m < 0$		
δ_1	δ_2	δ_2^*		δ_1	δ_2	δ_1	δ_2	δ_1	δ_2	δ_2^*
		$\kappa > 0$	$\kappa < 0$							
—	+	$\delta_2 - \kappa\lvert\delta_1\rvert$	+			—	+	—	+	+
0	+	+	+					**0**	+	+
+	+	+	$\delta_2 - \lvert\kappa\rvert\delta_1$	+	+	+	+	+	+	$\delta_2 - \lvert\kappa\rvert\delta_1$
+	**0**	+	—					—	**0**	+
+	—	$-\lvert\delta_2\rvert + \kappa\delta_1$	—					—	—	$-\lvert\delta_2\rvert + \kappa\delta_1$

The measured value $Q_2 = Q_{2i} + \delta_2^*$ involves the summands $Q_{2i} = Q_{2i}^{(0)} + \kappa Q_{1i}$, $\delta_2^* = \delta_2 + \kappa\delta_1$. The allowable signs of δ_2^* are given in Table 1 along with the expressions for δ_2^* when their sign is determined by the particular δ_k and κ values. The correlation of δ_1 and δ_2^* values due to the relationship $Q_2(Q_1)$ modifies the $\delta_2^* \neq \delta_2$ values and induces the $\delta_2^* \neq 0$ values at $\delta_2 = 0$. The largest number of possible combinations of the signs of δ_1 and δ_2^* occurs at μ_1^*, $\chi_m > 0$ for the donors and sufficiently weak X acceptors, and also at μ_1^*, $\chi_m < 0$ for sufficiently strong X acceptors. A diverse combination of the signs of δ_1 and δ_2^* is caused by the correlation between δ_1 and δ_2 due to the intermolecular interactions ($1/\chi_m \neq 0$) and the relationship $Q_2(Q_1)$. When $1/\chi_m = 0$ the number of possible combinations of the signs of δ_1 and δ_2^* decreases. At $\mu_1^* > 0$ and $\kappa > 0$ ($\kappa < 0$) we have $\delta_k > 0$ and $\delta_2^* > 0$ ($\delta_2^* = \delta_2 - \lvert\kappa\rvert\delta_1$). At $\kappa < 0$ and $\mu_1^* < 0$ ($\mu_1^* = 0$) we obtain $\delta_1 < 0$ and $\delta_2^* > 0$ ($\delta_1 = 0$, $\delta_2^* > 0$). Different combinations of the signs of δ_1 and δ_2^* demonstrate the possibility of the conformational polymorphism of nematic azomethines, i.e. the existence of stable or metastable nematic modifications with one of the allowed combinations of the signs of δ_1 and δ_2^*.

A comparison of the table data with a combination of the signs of δ_1 and δ_2^* observed in the experiment makes it possible to judge about the sign of χ_m. The variant $\delta_1 \approx 0$, $\delta_2^* > 0$ [2, 12] corresponding to the value $\chi_m > 0$ corresponds to the nematicой phase of MBBA with a weak donor $X=C_4H_9$. For the molecules of **2** with $X=C(O)O–C_2H_5$, $Y=OCH_3$, $Z=H$ on passing from the solution to the crystal we have $\delta_1 = 0$ and $\delta_2^* > 0$ [19], and at $Z = CH_3$ δ_1, $\delta_2^* > 0$ correspond to the same transition [20]. With regard to the acceptor nature of X and $\mu_1^* < 0$ for these compounds [7] from the table data we obtain $\chi_m < 0$.

The substitution of $\delta_{1,2}$ (11) into (5), (7) reduces functional (3) to the one-parameter form

$$\Delta F_S = a(T - T^*)S^2/2 - BS^3/3 + C^*S^4/4 + \dots \qquad (12)$$

with coefficients T^* (8) and $C^* = C - \Delta C$, where

$$\Delta C = \frac{2}{1 - \chi_1\chi_2/\chi_m^2}[(\mu_1^*)^2\chi_1 + \mu_2^2\chi_2 - 2\mu_1^*\mu_2\chi_1\chi_2/\chi_m]. \qquad (13)$$

For the μ_1^*, χ_m values with the same (different) sign the latter summand in brackets is negative (positive). At μ_1^*, $\chi_m > 0$ the taking into account of the inequalities $[(\mu_1^*)^2\chi_1 + \mu_2^2\chi_2] > 2\mu_1^*\mu_2(\chi_1\chi_2)^{1/2}$, $\chi_m > (\chi_1\chi_2)^{1/2}$ yields $\Delta C > 0$. At μ_1^*, $\chi_m < 0$ the replacement of these values by their absolute ones in formula (13) and the mentioned inequalities leads to the same result. A decrease in C^* and the possibility of a change in the sign of C^* for the negative one indicates the necessity to take into account the following terms of series (12) for the adequate description of the experimental dependences $S(T)$ by the

theoretical dependence $S^*(T)$ minimizing functional (12). This is confirmed by the approximation of the dependence $S(T)$ for MBBA (μ_1^*, $\chi_m > 0$) with the function $S^*(T)$ for series (12) with the summand $\propto S^6$ [21].

CONCLUSIONS

The above arguments give evidence of the efficiency of the use of parameters of the conformational state of molecules $Q_k = \langle \cos^2 \varphi_k \rangle$ in nematic LC in the analysis of the interaction of the conformational degreees of freedom and its effect on the LC properties. Unlike the fluctuating $\varphi_k(\mathbf{r}, \Omega)$ values for separate molecules, the measured Q_k values for the interacting conformational degrees of freedom are related by simple expressions. For azomethines the interaction of two actual degrees of freedom are expressed by relationship (1) that makes it possible to range the X donors and acceptors in derivatives **1** and **2** by the values of the coefficient κ.

For nematic LC the taking into account of relationship (1) within the phenomenological theory allowed us to derive empirically found expressions (8) and (10) for the temperature T_{NI} of the N–I transition and its changes $\Delta T_{NI}(\text{H–Z})$ in the presence of the direct and indirect steric effects of the side Z substituents in the molecules of type **2**. The correlation between the changes δ_k in the Q_k parameters in the nematic phase, which is caused by the intramolecular electronic properties of the X substituent and the intermolecular interactions, results in the possibility of the conformational polymorphism of the nematic phases of azomethines, which depends on the competition of these factors. The self-consistent change in the parameter of the orientational order of molecules S and the δ_k values in the nematic phase is manifested in a change in the dependence $S(T)$ and the quadratic dependence $\delta_k(S^2)$, which is the consequence of the symmetry of the nematic phase and the absence of the invariant $\text{Sp}\mathbf{S} = 0$. The approach developed here can be used for the study of smectic LCs and other statistically ordered environments of azomethines.

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