LIQUID CRYSTALS

Influence of Nematic and Smectic Orders on Polarizability of Molecules of Ethyl-*p*-(4-Ethoxybenzylideneamino-)α-Methyl Cinnamate Liquid Crystals

E. M. Aver'yanov

*Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences,
Akademgorodok 50–38, Krasnoyarsk, 660036 Russia*
e-mail: aver@iph.krasn.ru

Abstract—Experimental values of the polarizability tensor γ components of molecules of ethyl-*p*-(4-ethoxybenzylideneamino-)α-methyl cinnamate liquid crystals in the nematic and smectic *A* phases have been obtained. Quadratic dependences of the longitudinal, γ_l, and transverse, γ_t, components, the mean value $\bar{\gamma}$, and anisotropy $\Delta\gamma$ in both phases have been established as functions of the orientational order parameter S of molecules in a maximally wide range of S. The nematic—smectic *A* phase transition with a continuous variation of S manifests itself as kinks in the linear dependences of $\bar{\gamma}$, $\Delta\gamma$, and γ_l on S^2 and does not influence the dependence $\gamma_t(S^2)$. The observed dependences have been derived in the framework of the theory of the nematic—smectic *A* phase transition. The factors responsible for different influences of the orientational and positional orderings of molecules on the polarizability parameters have been determined.

1. INTRODUCTION

Natural and artificial anisotropic molecular ensembles with long-range orientational and quasi-long-range one- or two-dimensional positional orders of molecules show promises as the elemental base of molecular electronics. The general model of such media is represented by smectic *A* and *B* liquid crystals (LC). The self-organization of molecules in them is accompanied by structural changes of the short- and long-range orders and the corresponding intermolecular interactions. This results in a change of the molecular polarizability tensor γ and reflects the change in the polarization, electron structure, and conformation of molecules in the medium [1]. The investigation of the dependence of γ on the character and degree of structural ordering of molecules in an LC makes it possible to elucidate the influence of the self-organization of molecules on their physical and functional properties, to establish the correlation between the conformational, orientational, and positional degrees of freedom of molecules, and to understand the specific features of phase transitions and the molecular nature of the mesomorphism.

The presence of a long-range orientational order of LC molecules and the local anisotropy of LC in the mesoscale impose lower bounds on the mean value $\bar{\gamma} = \mathrm{Sp}(\gamma)/3$ [2], which suggests that γ depends on the phase state of the LC and temperature. The symmetry of uniaxial nematic LC and the corresponding tensor

order parameter **S** with the components $S_{ik} = S(3n_i n_k - \delta_{ik})/2$ ($n_{i,k}$ are the components of the director **n**) [3] lead to quadratic dependences of the longitudinal (γ_l) and transverse (γ_t) components of the tensor γ and the quantities $\bar{\gamma}$ and $\Delta\gamma = \gamma_l - \gamma_t$ on the orientational order parameter of molecules $S = \langle 3\cos^2\theta - 1 \rangle/2$ [4]. Here, θ is the angle between the longitudinal axis of the molecule **l** and the director **n** and angular brackets $\langle ... \rangle$ mean the averaging over a molecular ensemble. In the smectic *A* phase, the rise of the density wave $\psi = |\psi|\exp(i\phi)$ [3] of molecular layers along the director is accompanied by an increase in S [5]. The influence of these specific features of the smectic ordering of molecules on the dependences $\gamma_{l,t}(S)$, $\bar{\gamma}(S)$, and $\Delta\gamma(S)$ has not been studied yet.

An experimental solution of this problem is possible for LC with known values of S, density ρ, and refractive indices $n_j(\lambda)$ for light waves polarized along ($j = \parallel$) and across ($j = \perp$) the director **n**. The presence of spectral dispersion of $n_j(\lambda)$ in the visible transparency region is necessary for determining the components L_j of the Lorentz tensor ($\mathrm{Sp}\,\mathbf{L} = 1$) and components $f_j = 1 + L_j(n_j^2 - 1)$ of the local field tensor by the method of [6], which is independent of model conceptions and a priori assumptions on the properties of molecules and tensors **L** and **f**. The components f_j relate the local field of the light wave $E_j^{(\mathrm{loc})}(\omega) =$

Table 1. Values of $L_\perp$, S, and ρ (g/cm^3) used for determining $\bar{\gamma}$, $\Delta\gamma$, and $\gamma_{l,t}$ for EEMB LC at the given values of $\Delta T = T_{NI} - T$ (°C)

ΔT	$L_\perp$	S	ρ	ΔT	$L_\perp$	S	ρ
1.0	0.3881*	0.325	1.0490	45.0	0.4298 ± 0.0018	0.755	1.0842
3.0	0.3931 ± 0.0017	0.400	1.0516	46.0	0.4350 ± 0.0011	0.795	1.0874
5.5	0.4006 ± 0.0032	0.450*	1.0541*	50.5	0.4364 ± 0.0021	0.832	1.0913
8.0	0.4043*	0.485	1.0568	58.0	0.4378 ± 0.0016	0.870	1.0980
18.0	0.4149 ± 0.0020	0.580	1.0636	72.0	0.4394 ± 0.0008	0.885	1.1099
33.0	0.4238 ± 0.0015	0.678*	1.0751*				

Note: Asterisks mark the values obtained by the interpolation using the formulas presented in this paper.

$f_j(\omega)E_j(\omega)$ polarizing a molecule to the macroscopic field $E_j(\omega)$ of the light wave in the medium [1]. These requirements are satisfied by ethyl-*p*-(4-ethoxyben-zylideneamino-)α-methyl cinnamate (EEBM [7, 8])

$$H_5C_2O-\bigcirc-CH=N-\bigcirc-CH=C(CH_3)-C(O)O-C_2H_5$$

LC with the temperatures $T_{NA} = 77$°C and $T_{NI} = 123$°C of the nematic−smectic A ($N-SmA$) and nematic−isotropic liquid ($N-I$) phase transitions, respectively.

The objectives of this work are to study the dependences $\gamma_{l,t}(S)$, $\bar{\gamma}(S)$, and $\Delta\gamma(S)$ in the nematic and smectic A phases of EEBM, to elucidate the influence of the $N-SmA$ phase transition on these dependences, to interpret the observed changes in the framework of the theory of the $N-SmA$ phase transition [3, 5], and find the reasons of these changes.

2. RESULTS AND DISCUSSION

At $\lambda = 0.5893$ μm and the reference values of $\Delta T = T_{NI} - T$, presented in Table 1, the refractive indices n_j for EEBM are tabulated in [7, 8]. For separate points ΔT, which partially coincide with the reference ones, the values of S measured by the NMR method and the molar volumes $V_m = M/\rho$, where $M = 337.442$ is the molecular weight of EEBM, are presented in [8]. On a continuous variation in S at the point T_{NA} [8] and on the $N-SmA$ phase transition, which is close to a second-order phase transition, the approach to T_{NA} in the nematic phase of EEBM is accompanied by an anomalous increase of S, caused by local critical fluctuations of $\langle|\psi|^2\rangle$ of the smectic order [5, 9]. To exclude this anomaly, when determining the values of S at the reference points $\Delta T = 5.5$ and 33°C, which are far from T_{NA}, the experimental dependence $S(\Delta T)$ for $\Delta T \leq 18$°C was approximated by the function

$$S = S_0(1 - T/T_H)^\beta \qquad (1)$$

with the absolute temperature scale and adjustable parameters $S_0 = 1.138 \pm 0.035$, 0.220 ± 0.009, and $T_H - T_{NI} = 0.33 \pm 0.17$°C. For finding ρ at the points $\Delta T = 5.5$ and 33°C, the linear dependence $\rho(\Delta T)$ in the interval $\Delta T = 3-45$°C was approximated by the formula

$$\rho = \rho_0 + \vartheta\Delta T \qquad (2)$$

with the coefficients $\rho_0 = 1.0499$ g/cm^3 and $\vartheta = 7.634 \times 10^{-4}$ g/(cm^3 K).

The components L_j for EEBM and other homologues of this series were determined in [10], using the refractive indices $n_j(\lambda)$ [7] at $\lambda_1 = 0.5461$ μm, $\lambda_2 = 0.5893$ μm, and $\lambda_3 = 0.6438$ μm for ΔT, partially coinciding with the reference values. For determining the components $L_\perp$ at arbitrary points ΔT with known values of $n_j(\Delta T, \lambda)$, one can use relation [6, 10]:

$$L_\perp(\Delta T) = A(\lambda)L_{\perp k}(\Delta T, \lambda) + B(\lambda), \qquad (3)$$

which is satisfied with high accuracy and is invariant with respect to the $N-SmA-SmB$ phase transitions. Here, $L_{\perp k}(\Delta T, \lambda) = (3 + 2Q)/[3(3 + Q)]$, $Q = (\varepsilon_\parallel - \varepsilon_\perp)/(\bar{\varepsilon} - 1)$, $\varepsilon_j = n_j^2$, and $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$. The values of $L_\perp$ for EEBM at the reference points $\Delta T = 1$ and 8°C were obtained by formula (3) with the use of the values of $n_j(\Delta T, \lambda_2)$ [8] and the known coefficients $A(\lambda_2) = 1.4859$ and $B(\lambda_2) = -0.1526$ [10].

For a uniaxial LC with uniaxial molecules, the polarizability components γ_j averaged over molecular orientations with respect to the director are connected with the components ε_j and L_j by the relation [1]

$$\varepsilon_j = 1 + 4\pi N\gamma_j[1 + L_j(\varepsilon_j - 1)] \quad (j = \parallel, \perp), \qquad (4)$$

where N is the number of molecules in a unit volume. Hence, we find the parameters $\bar{\gamma} = (\gamma_{\parallel} + 2\gamma_{\perp})/3$, $\Delta\gamma = (\gamma_{\parallel} - \gamma_{\perp})/S$, $\gamma_l = \bar{\gamma} + 2\Delta\gamma/3$, and $\gamma_t = \bar{\gamma} - \Delta\gamma/3$. Their dependence on S^2 is shown in the figure. The errors in the values of $\bar{\gamma}$ and γ_t, caused by the error of determination of the component $L_{\perp}$, are not seen in the scale of the figure. In the nematic phase of EEBM, the temperature dependence of the parameters $\bar{\gamma}$, $\gamma_{l,t}$, and $\Delta\gamma$ is approximated well by the function

$$\Gamma = \Gamma_0 + \Gamma_2 S^2 \qquad (5)$$

with the coefficients presented in Table 2. The scatter of $\gamma_{l,t}$ and $\Delta\gamma$ near T_{NI} is caused by the error in the values of S [8] in this high-temperature region. Dependence (5) is fulfilled in a range of S^2 maximally wide for nematics, which is twice wider than for 4-n-alkyl-4'-cyanobiphenyls (nCB) [1] and 4-methoxybenzylidene-4'-butylaniline (MBBA) [4]. This shows that the absence of terms with higher degrees of S in (5) is caused by the symmetry of the nematic phase [4] rather than by small values of S.

The coefficients Γ_0 of the functions $\Delta\gamma(S)$ and $\bar{\gamma}(S)$ correspond to equilibrium values of $\Delta\gamma_i$ and $\bar{\gamma}_i$ in the isotropic phase. In the nematic phase, the dependences of the quantities $\xi_1 = \Delta\gamma - \Delta\gamma_i$ and $\xi_2 = \bar{\gamma} - \bar{\gamma}_1$ on S have the form [4]

$$\xi_1 = S^2\frac{\chi_1(\eta_1 - \eta_2\chi_2/\chi_m)}{1 - \chi_1\chi_2/\chi_m^2},$$
$$\xi_2 = S^2\frac{\chi_2(\eta_2 - \eta_1\chi_1/\chi_m)}{1 - \chi_1\chi_2/\chi_m^2}. \qquad (6)$$

Here, the constant coefficients satisfy the inequalities $\eta_{1,2} > 0$, $\chi_{1,2,m} > 0$, and $\chi_m/\chi_1 > \chi_2/\chi_m$ [4], which determine possible combinations of the signs $\xi_{1,2}$ in the nematic phase. The forbidden variants are those with $\xi_{1,2} \leq 0$ in which none of the functions $\xi_{1,2}(S)$ are increasing. In addition to the known variants $\xi_{1,2} > 0$ (nCB [1], MBBA [4]), $\xi_1 > 0$ and $\xi_2 \approx 0$ (heptyl cinnamic acid cyanophenyl ester [1]) and $\xi_1 < 0$ and $\xi_2 > 0$ (4-nitrophenyl-4'-octyloxybenzoate [1]), for the nematic phase of EEBM, a new admissible variant with $\xi_1 \approx 0$ and $\xi_2 > 0$ is observed. The last possible variant with $\xi_1 > 0$ and $\xi_2 < 0$ has not been found yet.

The N–SmA phase transition in EEBM with no change in S at $T = T_{NA}$ and a noticeable additional increase in S in the smectic phase practically does not affect dependence (5) for γ_t and manifests itself as kinks at $T = T_{NA}$ in the linear dependences $\Gamma(S^2)$ for γ_l, $\Delta\gamma$, and $\bar{\gamma}$. For the smectic phase of EEBM, formula (5) takes the form

$$G = G_0 + G_2 S^2 \qquad (7)$$

Dependences of (1) γ_l, (2) $\Delta\gamma$, (3) $\bar{\gamma}$, and (4) γ_t on S^2 in the nematic and smectic A phases of EEBM at $\lambda = 0.5893$ μm. Curve 1 (4) is displaced downward (upward) by 20 (10) Å³. Solid and dashed lines represent dependences (5) and (7) in the nematic and smectic phases. The arrow marks the value $S(T_{NA})$.

with the coefficients presented in Table 2. The coefficients of formulas (5) and (7) are connected by the relation $G_0 = \Gamma_0 + (\Gamma_2 - G_2)S_{NA}^2$, $S_{NA} = S(T_{NA})$. The difference between dependence (7) in the smectic and dependence (5) in the nematic is caused by the influence of the smectic density wave $\psi = |\psi|\exp(i\varphi)$ on the parameters $\bar{\gamma}$, $\gamma_{l,t}$, and $\Delta\gamma$ due to the layered structure of the smectic and the additional increase in S induced by the layered structure [3, 5]. Let us obtain formula (7) for the quantity $G = \bar{\gamma}$. As an invariant of the tensor γ, the quantity $\bar{\gamma}(I_1, I_2)$ in the smectic phase is a function of the invariants $I_1 = \mathrm{Sp}(S^2) \propto S^2$ and $I_2 = |\psi|^2$. In the lowest approximation with respect to the moduli of S and $|\psi|$, the function $G = \bar{\gamma}$ has the form

$$G = \Gamma_0 + \Gamma_2 S_N^2 + \kappa|\psi|^2, \qquad (8)$$

where $S_N(\Delta T)$ is the analytic continuation of the dependence $S(\Delta T)$ from the nematic phase to the smectic one without regard for the influence of the

Table 2. Coefficients (Å³) of dependences (5) and (7) for the given values of Γ and G at $\lambda = 0.5893$ μm

Γ, G	Γ_0	Γ_2	G_0	G_2
γ_l	79.75	5.44	90.71	−11.35
γ_t	27.10	5.83	27.00	5.51
$\Delta\gamma$	52.65	−0.36	63.71	−16.86
$\bar{\gamma}$	44.65	5.68	48.23	−0.10

of a molecular ensemble are still the ensemble-averaged quantities $Q_k = \langle \cos^2 \varphi_k \rangle$, on which the measured values of $F_{n\pi}(Q_k)$, $F_{\pi\pi}(Q_k)$, and $\gamma_l(Q_k)$ depend. The variation of the parameters Q_k in the nematic and smectic phases from to their values Q_{ki} in the isotropic phase according to the dependence [1, 16]

$$Q_k = Q_{ki} + p_k S^2 + q_k |\psi|^2 \qquad (14)$$

causes similar dependences $F_{n\pi}(S, |\psi|)$ and $F_{\pi\pi}(S, |\psi|)$ [1, 14], which make a contribution to (5) and (7) for γ_l, $\Delta\gamma$, and $\bar{\gamma}$. A specific feature of EEBM molecules is that, due to the electron-accepting properties of the fragment C(O)O, a decrease of the angle φ_1 increases the angle φ_2 [14], which leads to an additional coupling $Q_2 = Q_2^{(0)} + \mu Q_1$, where $Q_2^{(0)} = Q_2(Q_1 = 0)$ and $\mu = (dQ_2/dQ_1)_{Q_1 = 0} < 0$. As a result, a positive variation in the quantities γ_l, $\Delta\gamma$, and $\bar{\gamma}$ with an increase in Q_1 in LC is accompanied by a negative variation in these quantities due to the reduction in Q_2. The balance of these contributions determines the values of Γ_2 and G_2.

In the nematic phase of EEBM, the balance of the contributions of Q_k to $\Gamma_2(\bar{\gamma})$ is positive and the value $\Gamma_2/\Gamma_0 = 0.127$ coincides with the same value for the nematic phase of MBBA [4], as expected due to the similarity of the chemical and electron structures of these molecules. It is worth noting the proximity of the values $\Gamma_2(\bar{\gamma})$ and $\Gamma_2(\gamma_t)$, caused by different reasons. The transition of EEBM into the smectic phase with an additional increase in Q_1 due to the increase in the packing density of molecules in layers is accompanied by a negative balance of the contributions of Q_k to $g_2(\bar{\gamma})$ and by the mutual compensation of these contributions to $G_2(\bar{\gamma}) \approx 0$.

For $\Gamma_2(\gamma_l) = 3\Gamma_2(\bar{\gamma}) - 2\Gamma_2(\gamma_t)$ in the nematic phase, the positive contribution of Q_k from the term $\Gamma_2(\bar{\gamma})$ is partly compensated by the negative contribution from the dipole−dipole intermolecular interactions from the term $\Gamma_2(\gamma_t)$, and the value of $\Gamma_2(\gamma_l)$ is close to the same value for γ_t and $\bar{\gamma}$. In the smectic phase, since $G_2(\bar{\gamma}) \approx 0$, the quantity $G_2(\gamma_l) = 3G_2(\bar{\gamma}) - 2G_2(\gamma_t)$ is almost completely determined by the double negative contribution of the intermolecular interactions from the terms $G_2(\gamma_t)$.

For $\Gamma_2(\Delta\gamma) = 3[\Gamma_2(\bar{\gamma}) - \Gamma_2(\gamma_t)]$ in the nematic phase, the positive contribution of Q_k from the term $\Gamma_2(\bar{\gamma})$ is compensated by the negative contribution of the dipole−dipole intermolecular interactions from the term $\Gamma_2(\gamma_t)$, as a result of which $\Gamma_2(\Delta\gamma) \approx 0$. In the smectic phase, since $G_2(\bar{\gamma}) \approx 0$, the quantity $G_2(\Delta\gamma) = 3[G_2(\bar{\gamma}) - G_2(\gamma_t)]$ is almost completely determined by

the triple negative contribution of $G_2(\gamma_t)$ from the dipole−dipole intermolecular interactions.

3. CONCLUSIONS

The experimental data, presented in this work, on the change in the quantities $\gamma_{l,t}$, $\Delta\gamma$, and $\bar{\gamma}$ in the nematic and smectic A phases of EEBM are free from a priori assumptions and model conceptions about unobserved properties of molecules or tensors $\mathbf{L}$ and $\mathbf{f}$. Dependences (5) and (7) for the quantities $\gamma_{l,t}$, $\Delta\gamma$, and $\bar{\gamma}$ in the nematic and smectic phases are caused by the symmetry of these phases and the corresponding order parameters. For EEBM, dependence (5) is fulfilled in a range of S maximally wide for the known LC. The character of variation of the quantities $\Delta\gamma$ and $\bar{\gamma}$ in the nematic phase of EEBM corresponds to the new variant of variation of these quantities, which coincides with one of the possible variants predicted earlier [4]. Dependence (7), originally obtained experimentally and theoretically in this work, ensues from the interaction of the nematic ($\mathbf{S}$) and smectic (ψ) order parameters and is valid for the $N-SmA$ second-order phase transitions and weak first-order phase transitions. The intersection of dependences (5) and (7) for EEBM at the point T_{NA} of the $N-SmA$ transition results from the continuous variation of S at this point.

In formulas (5) and (7) for $\gamma_{l,t}$, $\Delta\gamma$, and $\bar{\gamma}$, the quantities Γ_2 and G_2 are determined by the balance of the opposite-sign contributions from the dipole−dipole induction intermolecular interactions and from the change in the parameters $Q_{1,2}$ of the conformation state of molecules. For $\gamma_t(\bar{\gamma})$, the quantities $\Gamma_2 \approx G_2$ ($\Gamma_2 \neq G_2$) are determined by the first (second) of these factors. The influence of the smectic ordering of molecules on the coefficient $G_2 \approx 0$ for $\bar{\gamma}$ may be related to the interaction—specific for the EEBM molecule—of the conformation degrees of freedom, which leads to a decreasing dependence $Q_2(Q_1)$. The quantities G_2 for γ_l and $\Delta\gamma$ are completely caused by the contribution of the dipole−dipole induction intermolecular interactions. Dependence (7) introduces the tensor γ as a new molecular characteristic that self-consistently changes with variation of the order parameter $|\psi|$. This extends the capabilities of experimental study of specific features of this transition.

REFERENCES

1. E. M. Aver'yanov, *Local Field Effects in Optics of Liquid Crystals* (Nauka, Novosibirsk, 1999) [in Russian].

2. E. M. Aver'yanov, JETP **108** (1), 176 (2009).

3. P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1974; Mir, Moscow, 1977).

4. E. M. Aver'yanov, Phys. Solid State **55** (10), 2136 (2013).

5. S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1977; Mir, Moscow, 1980).

6. E. M. Aver'yanov, JETP **110** (4), 622 (2010).

7. G. Pelzl and H. Sackmann, Symp. Faraday Soc. **5**, 68 (1971).

8. A. Hauser, G. Pelzl, C. Selbmann, D. Demus, S. Grande, and A. Petrov, Mol. Cryst. Liq. Cryst. **91**, 97 (1983).

9. K.-C. Lim and J. T. Ho, Phys. Rev. Lett. **40**, 944 (1978).

10. E. M. Aver'yanov, Russ. J. Phys. Chem. A **86** (5), 720 (2012).

11. E. M. Aver'yanov, Sov. Phys. JETP **70** (3), 479 (1990).

12. H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules* (Academic, New York, 1967).

13. E. M. Aver'yanov and V. F. Shabanov, Sov. Phys. Crystallogr. **26** (1), 96 (1981).

14. E. M. Aver'yanov, *Steric Effects of Substituents and Mesomorphism* (Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2004) [in Russian].

15. M. Mizuno and T. Shinoda, Mol. Cryst. Liq. Cryst. **69**, 103 (1981).

16. E. M. Aver'yanov, Sov. Phys. Solid State **24** (9), 1609 (1982).

Translated by E. Chernokozhin