

Orientalional Order and Polarizability of Molecules in a Nematic Liquid Crystal

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Abstract—The influence of the orientational order of molecules in a nematic liquid crystal on the mean value $\bar{\gamma}$ and anisotropy $\Delta\gamma$ of the molecular polarizability has been studied in the framework of the molecular statistical approach with allowance for the perturbation of the electronic structure of molecules due to the change in the conformation of their aromatic core and intermolecular interactions. Experimental dependences of $\bar{\gamma}$ and $\Delta\gamma$ on the molecular orientational order parameter S have been derived, and their specific features for the known objects have been explained. The possibility of separating the contributions of opposite signs to the dependence $\Delta\gamma(S)$ due to the change in the conformation of molecules and intermolecular interactions has been shown using nematic MBBA as an example.

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1. INTRODUCTION

The self-organization of uniaxial molecules into a uniaxial liquid crystal (LC) is accompanied by the appearance of local anisotropy of the coordination environment of molecules and long-range orientational order of the longitudinal molecular axes \mathbf{l} with respect to the director \mathbf{n} . The anisotropic close packing steric effects and the short- and long-range order dispersion intermolecular interactions in LC cause the change in the conformation, polarization, and electronic structure of molecules and the molecular properties depending on them [1]. This mostly affects the components γ_{ij} of the polarizability tensor of molecules having a chain of π -electron conjugation of molecular fragments along the axis \mathbf{l} and low barriers for variation in the angles φ_k of internal rotation between these fragments. For typical molecules in thermotropic nematics, the barriers of relative rotation of fragments of the molecular core about single chemical bonds are comparable with the intermolecular interaction energies [1]. As a result, while the molecular order in a nematic has a statistical character, in a separate molecule with the center of mass at a point \mathbf{r} , the values $\varphi_k(\mathbf{r}, \theta)$ fluctuate with the angle $\theta(\mathbf{r})$ between the molecular axis $\mathbf{l}(\mathbf{r})$ and the director \mathbf{n} . Fluctuations of $\varphi_k(\mathbf{r}, \theta)$ cause fluctuations in the degree of electron conjugation of molecular fragments and the polarizability components $\gamma_{ij}(\mathbf{r}, \theta, \varphi_k)$.

The correlation in the variations of the angles θ and φ_k for nematic molecules leads to the absence of the factorization, $f(\theta, \varphi_k) \neq f(\theta)f(\varphi_k)$, for a single-particle distribution function $f(\theta, \varphi_k)$ of the nematic. This

causes the dependence of the quantities $\langle A(\theta) \rangle$ averaged with the distribution function $f(\theta, \varphi_k)$ on the conformational order of molecules and the dependence of the quantities $\langle B(\varphi_k) \rangle$ on the orientational order of molecules [1]. The polarizability components $\gamma_j = \langle \gamma_{ij}(\theta, \varphi_k) \rangle$ measured with the polarization of the light wave parallel ($j = \parallel$) and perpendicularly ($j = \perp$) to the director \mathbf{n} depend on the orientational and conformational order of molecules and intermolecular interactions. The joint influence of these factors determines the character of experimental dependences of the mean value $\bar{\gamma} = (\gamma_{\parallel} + 2\gamma_{\perp})/3$ and anisotropy of polarizability $\Delta\gamma = (\gamma_{\parallel} - \gamma_{\perp})/S$ on the parameter of orientational order of molecules, $S = \langle 3 \cos^2 \theta - 1 \rangle / 2$, and the ratio of these contributions determines the amplitude of the variation in $\bar{\gamma}(S)$ and $\Delta\gamma(S)$.

In [2], for the nematic of 4-methoxybenzylidene-4-butyraniline (MBBA), the general dependence

$$\Gamma(\lambda, S) = \Gamma_0(\lambda) + \Gamma_2(\lambda)S^2 \quad (1)$$

for the functions $\bar{\gamma}(\lambda, S)$ and $\Delta\gamma(\lambda, S)$ at different optical wavelengths λ was established experimentally. This dependence also follows from the phenomenological theory [2] in the lowest-order approximation with respect to S with allowance for the symmetry of the nematic phase. The values of $\Gamma_2(\lambda)$ are determined by two opposite-sign contributions, whose ratio depends on the chemical structure of molecules [2]. Questions remaining unanswered concern the possibility of separating these contributions, their relation with the orientational and conformational order of molecules and

intermolecular interactions, and the dependences of the ratios Γ_2/Γ_0 for $\Delta\gamma$ and $\bar{\gamma}$ and $\Gamma_2(\Delta\gamma)/\Gamma_2(\bar{\gamma})$ on the chemical and electronic structure of molecules [2]. The present work is devoted to the molecular statistical analysis of the functions $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ and clarifying these questions for MBBA and other known LC.

2. GENERAL FORM OF THE DEPENDENCES $\bar{\gamma}(S)$ AND $\Delta\gamma(S)$

Let us consider a uniaxial nonpolar nematic consisting of rod-shaped molecules with the free rotation about their longitudinal axes \mathbf{l} . Assume that the aromatic core of the molecule has two plane fragments connected by the electron conjugation along a single chemical bond parallel to the axis \mathbf{l} . The hindered relative rotation of these fragments is characterized by a dihedral angle φ . In the system of the director $\mathbf{n} \parallel \mathbf{Z}$, the orientation of the molecule is defined by the polar angle θ between \mathbf{l} and \mathbf{n} and the azimuth angle ϕ , fixing the projection of \mathbf{l} onto the plane XY . In the LC transparency region, the polarizability component γ_j can be represented in the following form:

$$\gamma_j(\lambda) = D \left\langle \sum_q \Phi_q(\lambda) F_q(\theta, \varphi, S) d_{qj}^2(\theta, \beta_q) \right\rangle, \quad (2)$$

where $D = e^2/(4\pi^2 c^2 m)$, e and m are the electron charge and mass, c is the speed of light in vacuum, $\Phi_q(\lambda) = \lambda^2 \lambda_q^2 / (\lambda^2 - \lambda_q^2)$, λ_q and F_q are the wavelength and the oscillator strength of the molecular transition from the ground state to the q th excited state. The quantities d_{qj}^2 have the form

$$\begin{aligned} d_{qj}^2 &= [1 + C_j S_{\beta_q} P_2(\cos\theta)]/3, \\ C_{\parallel} &= 2, \quad C_{\perp} = -1, \end{aligned} \quad (3)$$

where $S_{\beta_q} = (3 \cos^2 \beta_q - 1)/2$, β_q is the angle between the basis vector \mathbf{d}_q of the transition dipole moment and the axis \mathbf{l} ; $P_2(\cos\theta)$ is the Legendre polynomial; and $\langle P_2 \rangle = S$. Formula (2) takes into account the averaging with respect to the isotropic distribution of the angles ϕ in the plane XY (uniaxiality of LC) and with respect to the rotation of \mathbf{d}_q about the axis \mathbf{l} . The averaging $\langle \dots \rangle$ is performed with the distribution function $f(\theta, \varphi)$, taking into account the correlation of the variation in the angles θ and φ . In accordance with the theory [3] and experiment [4], formula (2) disregards the weak dependences $\lambda_q(\theta, \varphi, S)$ and $\beta_q(\theta, \varphi, S)$ against the background of the strong dependence $F_q(\theta, \varphi, S)$.

Let us consider the general properties of the function $F_q(\theta, \varphi, S)$ with allowance for the symmetry of the nematic phase and molecules, not restricting the consideration to a particular type of intermolecular interactions. The symmetry conditions $F_q(\theta, \varphi) = F_q(-\theta,$

$\varphi) = F_q(\pi \pm \theta, \varphi) = F_q(\theta, -\varphi) = F_q(\theta, \pi \pm \varphi)$ correspond to the following general representation

$$F_q(\theta, \varphi, S) = \sum_{n,k} F_{nk}^{(q)}(S) P_n(\cos\theta) \cos^k \varphi, \quad (4)$$

where the summation is performed with respect to even values of n , $k \geq 0$. A good approximation for molecular transitions is the restriction $k \leq 2$ [5]. For finding out quantitative consequences of functions (4), it suffices to take into account the values $n \leq 2$. As a result, we have

$$\begin{aligned} F_q(\theta, \varphi, S) &= F_{00}^{(q)} + F_{02}^{(q)} \cos^2 \varphi + F_{20}^{(q)}(S) P_2(\cos\theta) \\ &+ F_{22}^{(q)}(S) P_2(\cos\theta) \cos^2 \varphi. \end{aligned} \quad (5)$$

Here, the first two terms on the right-hand side give the dependence $F_q(\varphi)$ for a molecule in an anisotropic coordination environment of its nearest neighbors. The form of these terms does not depend on the phase state of the medium, so that the possible weak dependence of the coefficients $F_{00}^{(q)}$ and $F_{02}^{(q)}$ on S can be neglected. The two next terms characterize the perturbation of molecular transitions by anisotropic intermolecular interactions of the short- and long-range orders. In this case, the third term is independent of the conformation of the molecule and electron conjugation of its fragments. For a molecule with a given value θ , this term depends on S and determines the degree of perturbation of the electronic structure of the molecule due to its anisotropic environment in the scales corresponding to the formation of the long-range orientational order of molecules. At a given S , this term characterizes the dependence of the electronic structure of a molecule on its orientation with respect to \mathbf{n} . The last term on the right-hand side of (5) describes the perturbation of the electronic structure of the molecule due to its interaction with the environment at a certain orientation of the molecule with respect to \mathbf{n} and conformation of molecular fragments.

The substitution of expressions (3) and (5) into formula (2) yields

$$\begin{aligned} \bar{\gamma} &= (D/3) \sum_q \Phi_q(\lambda) [F_{00}^{(q)} + F_{02}^{(q)} Q_2 + F_{20}^{(q)}(S) S \\ &+ F_{22}^{(q)}(S) \langle P_2 \cos^2 \varphi \rangle], \end{aligned} \quad (6)$$

$$\begin{aligned} \gamma_{\parallel} - \gamma_{\perp} &= D \sum_q \Phi_q(\lambda) S_{\beta_q} [F_{00}^{(q)} S + F_{02}^{(q)} \langle P_2 \cos^2 \varphi \rangle \\ &+ F_{20}^{(q)}(S) \langle P_2^2 \rangle + F_{22}^{(q)}(S) \langle P_2^2 \cos^2 \varphi \rangle]. \end{aligned} \quad (7)$$

Hereinafter, we will omit for brevity the argument in the functions $P_2(\cos\theta)$ and $P_2^2(\cos\theta)$. The value $Q_2 = \langle \cos^2 \varphi \rangle$ for LC in formula (6) differs from the value $Q_{2i} = \langle \cos^2 \varphi \rangle_i$, which corresponds to the isotropic

phase or the factorization $f(\theta, \varphi) = f(\theta)f(\varphi)$ in LC. In the lowest order with respect to S , the molecular statistical [1, 5] and phenomenological [6] theories imply the dependence

$$Q_2 = Q_{2i} + \eta S^2, \quad (8)$$

which is valid for any scalar quantity $\langle B(\varphi) \rangle$. Below, in formula (7), we will perform the expansion $P_2^2 = 1/5 + (2/7)P_2 + (18/35)P_4$. With allowance for the relation $\gamma_{\parallel} - \gamma_{\perp} = \Delta\gamma S$ and coefficients $K_n = \langle P_n \cos^2 \varphi \rangle / [\langle P_n \rangle Q_2]$, formulas (6) and (7) take the form

$$\bar{\gamma} = (D/3) \sum_q \Phi_q(\lambda) [F_{00}^{(q)} + F_{02}^{(q)} Q_2 + F_{20}^{(q)}(S)S + F_{22}^{(q)}(S)K_2 S Q_2], \quad (9)$$

$$\Delta\gamma = D \sum_q \Phi_q(\lambda) S_{\beta q} \{ F_{00}^{(q)} + F_{02}^{(q)} K_2 Q_2 + [F_{20}^{(q)}(S)/S][1/5 + (2/7)S + (18/35)\langle P_4 \rangle] + [F_{22}^{(q)}(S)/S][Q_2/5 + (2/7)K_2 S Q_2 + (18/35)K_4 \langle P_4 \rangle Q_2] \}. \quad (10)$$

For $S = 0$, the coefficients $F_{n0}^{(q)}(S)$ and $F_{n2}^{(q)}(S)$ should be equal to zero and we can set $F_{n0}^{(q)}(S) = F_{n0}^{(q)} S^\mu$ and $F_{n2}^{(q)}(S) = F_{n2}^{(q)} S^\nu$. In order that formula (10) correspond to dependence (1) in the lowest approximation with respect to S , one should set $\mu = \nu = 3$. Substituting (8) into (9) yields

$$\bar{\gamma} = (D/3) \sum_q \Phi_q(\lambda) [F_{00}^{(q)} + F_{02}^{(q)} Q_{2i} + S^2 \eta F_{02}^{(q)} + S^4 (F_{20}^{(q)} + F_{22}^{(q)} K_2 Q_{2i}) + S^6 \eta K_2 F_{22}^{(q)}]. \quad (11)$$

The inequality $Q_{2i} \gg \eta S^2$ [1, 6] makes it possible to neglect the term $\propto S^6$ as compared with the term $\propto S^4$. If experimental dependence (1) for the function $\bar{\gamma}(S)$ is satisfied up to the ultimately large values $S \approx 0.8$ in the nematic phase [7], the correction term $\propto S^4$ is small. As a result, the dependence $\bar{\gamma}(S)$ has form (1) with the coefficients

$$\Gamma_0(\bar{\gamma}) = (D/3) \sum_q \Phi_q(\lambda) (F_{00}^{(q)} + F_{02}^{(q)} Q_{2i}), \quad (12)$$

$$\Gamma_2(\bar{\gamma}) = (D\eta/3) \sum_q \Phi_q(\lambda) F_{02}^{(q)}. \quad (13)$$

The value of $\Gamma_2(\bar{\gamma})$ is determined by variation (8) in the parameter Q_2 of the conformational state of molecules

in LC. The molecular transitions in which the oscillator strengths are insensitive to the variation in the conformation and electron conjugation of molecular fragments ($F_{02}^{(q)} = 0$) do not contribute into $\Gamma_2(\bar{\gamma})$.

Taking into account (8) and the explicit form of the functions $F_{n0}^{(q)}(S)$ and $F_{n2}^{(q)}(S)$ in expression (10), we obtain

$$\Delta\gamma = D \sum_q \Phi_q(\lambda) S_{\beta q} \{ F_{00}^{(q)} + F_{02}^{(q)} K_2 Q_{2i} + S^2 [\eta K_2 F_{02}^{(q)} + (F_{20}^{(q)} + F_{22}^{(q)} Q_{2i})/5] + (2/7)S^3 (F_{20}^{(q)} + F_{22}^{(q)} K_2 Q_{2i}) + (18/35)S^2 \langle P_4 \rangle (F_{20}^{(q)} + F_{22}^{(q)} K_4 Q_{2i}) \}. \quad (14)$$

The maximum experimental values $\langle P_4 \rangle$ [8], S being given, satisfy the Maier–Saupe theory [9], in which the relations $\langle P_4 \rangle \approx (5/7)S^2$ are well satisfied for $S \leq 0.85$ [10]. Taking into account this fact and the equality $K_{2,4} \approx 1$ [1, 5], we can neglect in formula (14) the term $\propto S^2 \langle P_4 \rangle$ as compared to the term $\propto S^2$. For the values $S(T_{NI}) > 2/7$, typical for real nematics (T_{NI} is the nematic–isotropic liquid transition temperature), we have $2S^3/7 < S^4$ and, for the entire nematic interval, we can neglect the term $\propto S^3$ as compared to the term $\propto S^2$ in formula (14). As a result, expression (14) reduces to formula (1), in which the coefficient

$$\Gamma_0(\Delta\gamma) = D \sum_q \Phi_q(\lambda) S_{\beta q} (F_{00}^{(q)} + F_{02}^{(q)} K_2 Q_{2i}) \quad (15)$$

differs insignificantly from the anisotropy of the polarizability of the molecule in the isotropic phase,

$$\Delta\gamma_i = D \sum_q \Phi_q(\lambda) S_{\beta q} (F_{00}^{(q)} + F_{02}^{(q)} Q_{2i}), \quad (16)$$

because $K_2 \approx 1$. The coefficient $\Gamma_2 = \Gamma_2^{(1)} + \Gamma_2^{(2)}$ involves the terms

$$\Gamma_2^{(1)}(\Delta\gamma) = D\eta K_2 \sum_q \Phi_q(\lambda) S_{\beta q} F_{02}^{(q)}, \quad (17)$$

$$\Gamma_2^{(2)}(\Delta\gamma) = (D/5) \sum_q \Phi_q(\lambda) S_{\beta q} (F_{20}^{(q)} + F_{22}^{(q)} Q_{2i}).$$

The quantity $\Gamma_2^{(1)}(\Delta\gamma)$ depends on variation (8) in the parameter Q_2 , whereas the quantity $\Gamma_2^{(2)}(\Delta\gamma)$ is caused by the variation in the quantities F_q due to intermolecular interactions.

If the spectral dispersion of the quantities $\bar{\gamma}$ and $\Delta\gamma$ and their coefficients $\Gamma_{0,2}$ in the visible region is determined by a set of m close long-wavelength electron transitions with the values $S_{\beta q} = S_\beta$, the dependences

of $\bar{\gamma}$, $\Delta\gamma$, and $\Gamma_{0,2}$ on λ in this region can be approximated by the function [2]

$$y = y_b + P\lambda^2/(\lambda^2 - \lambda_r^2). \quad (18)$$

The coefficient y_b give the background values $\bar{\gamma}_b$, $\Delta\gamma_b$, and $\Gamma_{0,2}^{(b)}$ caused by the short-wavelength transitions with $q > m$. The comparison of formulas (12) and (15) for $K_2 = 1$ with (18) yields the relation

$$\Gamma_0(\Delta\gamma) - \Gamma_0^{(b)}(\Delta\gamma) = 3S_\beta[\Gamma_0(\bar{\gamma}) - \Gamma_0^{(b)}(\bar{\gamma})], \quad (19)$$

which can be used for determining the quantity S_β or the angle β [2]. Separating out the background contributions into the quantities $\Gamma_2(\bar{\gamma})$ and $\Gamma_2(\Delta\gamma)$ in formulas (13) and (17) leads to the following relations

$$\Gamma_2(\bar{\gamma}) = \Gamma_2^{(b)}(\bar{\gamma}) + (D\eta/3) \sum_{q=1}^m \Phi_q(\lambda) F_{02}^{(q)}, \quad (20)$$

$$\Gamma_2(\Delta\gamma) = \Gamma_2^{(b)}(\Delta\gamma) + \delta_1 + \delta_2, \quad (21)$$

$$\delta_1 = 3S_\beta K_2 [\Gamma_2(\bar{\gamma}) - \Gamma_2^{(b)}(\bar{\gamma})], \quad (22)$$

$$\delta_2 = (DS_\beta/5) \sum_{q=1}^m \Phi_q(\lambda) (F_{20}^{(q)} + F_{22}^{(q)} Q_{2i}). \quad (23)$$

Using the quantities Γ_2 and $\Gamma_2^{(b)}$ for $\Delta\gamma$ and longitudinal components of polarizability $\gamma_l = \bar{\gamma} + 2\Delta\gamma/3$, which are most sensitive to the conjugation of molecular fragments and intermolecular interaction, we obtain from formulas (20)–(22)

$$\delta_2 = (1 + 2S_\beta K_2) [\Gamma_2(\Delta\gamma) - \Gamma_2^{(b)}(\Delta\gamma)] - 3S_\beta K_2 [\Gamma_2(\gamma_l) - \Gamma_2^{(b)}(\gamma_l)]. \quad (24)$$

Relations (19), (21), (22), and (24) enable one to find the quantities $\delta_{1,2}$.

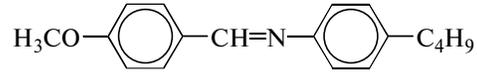
3. COMPARISON WITH THE EXPERIMENT AND DISCUSSION

For testing the relations obtained, we will use the coefficients $\Gamma_{0,2}(\lambda)$ of dependence (1) for the polarizability parameters $\bar{\gamma}$, $\Delta\gamma$, and γ_l in the nematic phase of MBBA [2] (see the table). For $\lambda = \infty$, the coefficients $\Gamma_{0,2}$ correspond to the quantities $\bar{\gamma}_\infty$, $\Delta\gamma_\infty$, and $\gamma_l^{(\infty)}$ obtained from the approximation of the dependences $\bar{\gamma}(\lambda)$, $\Delta\gamma(\lambda)$, and $\gamma_l(\lambda)$ by function (18) at different nematic phase temperatures. Formula (12) gives the polarizability of molecules in the isotropic phase, $\bar{\gamma}_i$. This fact is confirmed by the comparison of $\Gamma_0(\bar{\gamma})$ with the values

$$\bar{\gamma}_i = 3M(n_i^2 - 1)/[4\pi N_A \rho_i (n_i^2 + 2)], \quad (25)$$

calculated from the known refractive indices $n_i(\lambda)$ [11] and density $\rho_i = 1.0252 \text{ g/cm}^3$ [12] of the isotropic phase of MBBA at the temperature $T = T_{NI} + 1^\circ\text{C}$. Here, M and N_A are the molecular weight and the Avogadro constant. The limiting value $\bar{\gamma}_i^{(\infty)}$, following from the approximation of the dependence $\bar{\gamma}_i(\lambda)$ by function (18), also agrees with the value $\Gamma_0(\bar{\gamma}_\infty)$.

As was established earlier [2] using approximation (18), in the isotropic and nematic phases of MBBA with the molecular structure



the dispersion of the quantities $\bar{\gamma}_i$, $\bar{\gamma}$, $\Delta\gamma$, and γ_l and their coefficients $\Gamma_{0,2}$ in the visible region is determined by two long-wavelength electron transitions $n-\pi^*$ and $\pi-\pi^*$ with the maxima of the corresponding absorption bands $\lambda_{n\pi} = 0.285 \mu\text{m}$ and $\lambda_{\pi\pi} = 0.325 \mu\text{m}$ [13, 14] and polarization along the N–phenyl bond [15]. The value $\cos^2\beta = 0.962$ [2], obtained from three expressions like (19) for the coefficients $\Gamma_0(\lambda)$ and $\Gamma_0^{(b)}$ of the quantities $\bar{\gamma}$, $\Delta\gamma$, and γ_l and averaged over tabulated values of λ , can be used in formulas (22) and (24). The approximation of tabulated dependences $\Gamma_2(\lambda)$ for $\bar{\gamma}$, $\Delta\gamma$, and γ_l by function (18) without regard for the fluctuations of Γ_2 ($\lambda = 0.5893 \mu\text{m}$) yields the values $\Gamma_2^{(b)}(\bar{\gamma}) = -0.77$, $\Gamma_2^{(b)}(\Delta\gamma) = -1.18$, and $\Gamma_2^{(b)}(\gamma_l) = -1.56 \text{ \AA}^3$. For MBBA, the experimental values $K_2 > 1$ are close to unity and weakly depend on S [5]. The table presents the values of $\delta_{1,2}$ calculated at $K_2 = 1$ by formulas (21) and (24), using the tabulated and above mentioned parameters. The calculation by formulas (21) and (22) gives the values of $\delta_{1,2}$ differing from the tabulated ones by no more than 1%.

For MBBA, the values of δ_1 and δ_2 have opposite signs. The value $\Gamma_2^{(b)}(\Delta\gamma) < 0$, small as compared to $|\delta_{1,2}|$, shows that $\Gamma_2^{(2)}(\Delta\gamma) < 0$ in the entire range of λ . The partial mutual compensation of the terms δ_1 and δ_2 in formula (21) explains the small values of $\Gamma_2(\Delta\gamma)$ and the ratio $\kappa_1 = \Gamma_2(\Delta\gamma)/\Gamma_0(\Delta\gamma) \approx 0.1$ for MBBA as compared to $\kappa_1 \approx 0.5$ for homologues 5CB and 7CB of the 4-*n*-alkyl-4'-cyanobiphenyl (*n*CB) series [8]. In contrast to the nematic phase of MBBA, which is formed by separate molecules, the nematic phase of homologues *n*CB consists of molecular dimer associates and has a local quasi-smectic structure [9]. The ratio of the parameters κ_1 for MBBA and homologues *n*CB shows that, for the latter, the inequality $\delta_1 \gg |\delta_2|$

Polarizability $\tilde{\gamma}_i$ of MBBA molecules in the isotropic phase, coefficients $\Gamma_{0,2}$ of dependence (1) for the indicated quantities in the nematic phase, and parameters $\delta_{1,2}$ (all in \AA^3) for different wavelengths λ (μm)

λ	$\tilde{\gamma}_i$	$\Gamma_0(\tilde{\gamma})$	$\Gamma_2(\tilde{\gamma})$	$\Gamma_0(\Delta\gamma)$	$\Gamma_2(\Delta\gamma)$	$\Gamma_2(\gamma_l)$	δ_1	$-\delta_2$
0.4678	37.94	37.87	5.60	44.31	5.21	9.04	17.94	11.55
0.4800	37.52	37.60	5.29	43.69	4.22	8.10	17.14	11.74
0.5086	36.88	36.99	5.08	41.58	4.41	7.98	16.45	10.86
0.5893	35.89	35.94	4.60	37.95	5.77	8.45	15.21	8.26
0.6438	35.47	35.63	4.12	37.40	3.02	6.15	13.89	9.69
∞	34.23	34.14	3.00	32.74	2.06	4.02	9.68	6.44

takes place. Indeed, in the visible region, the value of $\delta_1/\Gamma_0(\Delta\gamma) \approx 0.40$ for MBBA is comparable with the value of κ_1 for *n*CB and the ratio $\delta_1/\Gamma_2(\tilde{\gamma}) \approx 3.27$ is close to the corresponding value for *n*CB [8].

This agreement is caused by the presence of electron conjugation of fragments of the aromatic core of MBBA and *n*CB molecules. The electronic structure of MBBA is sensitive to the angle φ_N between the plane bridge fragment CH=N and the aniline phenyl ring [15]. In the MBBA molecule, the first two terms in formula (5) for the $n-\pi^*$ and $\pi-\pi^*$ transition oscillator strengths correspond to the dependences $F_{n\pi}(\varphi_N) \propto \sin^2 \varphi_N$ and $F_{\pi\pi}(\varphi_N) \propto \cos^2 \varphi_N$ [1, 15]. In the nematic phase of MBBA, the variation in the parameter $Q_2 = \langle \cos^2 \varphi_N \rangle$ in formula (8) with $\eta > 0$ [6] determines the contribution $\propto (1 - Q_2)$ to the average quantity $F_{n\pi} = \langle F_{n\pi}(\varphi_N) \rangle$ and the contribution $\propto Q_2$ to the quantity $F_{\pi\pi} = \langle F_{\pi\pi}(\varphi_N) \rangle$. The sum of these contributions causes the positive values of $\Gamma_2(\tilde{\gamma})$, $\Gamma_2^{(1)}(\Delta\gamma)$, and δ_1 . For *n*CB molecules, the values of $\Gamma_2(\tilde{\gamma})$ and $\Gamma_2^{(1)}(\Delta\gamma)$ are determined by the dependence $F_{\pi\pi}(\varphi) \propto \cos^2 \varphi$ of the oscillator strength of the long-wavelength electron transition $\pi-\pi^*$ on the angle φ between the phenyl rings of the biphenyl fragment [3] and the variation in $Q_2 = \langle \cos^2 \varphi \rangle$ in the nematic phase according to (8) with $\eta > 0$ [6]. This causes the proximity of the values of $\kappa_2 = \Gamma_2(\tilde{\gamma})/\Gamma_0(\tilde{\gamma})$ for MBBA [2] and *n*CB [1, 8] in the visible spectral region.

In the ratio of the terms $\Gamma_2^{(1)}$ and $\Gamma_2^{(2)}$, the nematic phase of MBBA has an intermediate position between homologues of the *n*CB series and ethyl-*p*-(4-ethoxybenzylideneamino)- α -methyl cinnamate (EEBM) [7]. The cores of the MBBA and EEBM molecules are identical. For EEBM, the relation $\Gamma_2(\Delta\gamma) \approx 0$ [7] takes

place, which corresponds to the equality $|\Gamma_2^{(2)}| \approx \Gamma_2^{(1)}$. Negative values of $\Gamma_2^{(2)}$ and δ_2 increase the coefficient

$$\Gamma_2(\gamma_t) = \Gamma_2^{(b)}(\gamma_t) + (1 - S_\beta K_2)[\Gamma_2(\tilde{\gamma}) - \Gamma_2^{(b)}(\tilde{\gamma})] - \delta_2/3 \quad (26)$$

for the transverse component of polarizability $\gamma_t = \tilde{\gamma} - \Delta\gamma/3$ and reduce the coefficient

$$\Gamma_2(\gamma_l) = \Gamma_2^{(b)}(\gamma_l) + (1 + 2S_\beta K_2)[\Gamma_2(\tilde{\gamma}) - \Gamma_2^{(b)}(\tilde{\gamma})] + 2\delta_2/3 \quad (27)$$

for the longitudinal component γ_l . Due to the smallness of the parameter $\Gamma_2^{(b)}(\gamma_t) = \Gamma_2^{(b)}(\tilde{\gamma}) - \Gamma_2^{(b)}(\Delta\gamma)/3 = -0.38 \text{\AA}^3$ and the relation $S_\beta K_2 \approx 1$ for MBBA, the experimental values $\Gamma_2(\gamma_t)$ [2] reproduced by formula (26) practically equal $-\delta_2/3$, i.e., the quadratic dependence $\gamma_t(S)$ for MBBA and EEBM is completely caused by the influence of intermolecular interactions on the long-wavelength electron transition oscillator strengths.

In the absence of the conjugation of fragments of the aromatic cores of the molecule and the long-wavelength absorption bands, which are sensitive to variations in the conformation of the core, the inequalities $|\Gamma_2^{(2)}| > \Gamma_2^{(1)}$ and $\Gamma_2(\Delta\gamma) < 0$ take place. It is typical for molecules of 4-nitrophenyl-4'-octyloxybenzoate (NP8OB), in the nematic phase of which the dependences of $\tilde{\gamma}$, $\gamma_{l,t}$, and $\Delta\gamma$ on S in the visible region [8, 16] correspond to negative (positive) values of Γ_2 for $\Delta\gamma$ and $\gamma_t(\tilde{\gamma}, \gamma_t)$. The specific features of the influence of intermolecular interactions on the parameters $\gamma_{l,t}$ and $\Delta\gamma$ for MBBA, EEBM, and NP8OB agree with the earlier-predicted features [17] for the induction dipole-dipole interaction of orientationally ordered molecules.

For high values of S , the first correcting terms for the quadratic dependences $\tilde{\gamma}(S)$ and $\Delta\gamma(S)$ in formulas (11) and (14) are caused by the intermolecular interactions and are negative. This fact qualitatively corre-

sponds to the vanishing of the positive coefficient $\Gamma_2(\bar{\gamma})$ and the variation in the coefficient Γ_2 for $\gamma_i(\Delta\gamma)$ from positive (close to zero) to negative on the transition from the nematic phase to the smectic *A* phase of EEBM with the values $S > 0.8$ [7]. For the analysis of the variation in $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ in the smectic phase, expansion (5) must be complemented with terms reflecting the positional ordering of molecules along the director \mathbf{n} and its connection with the orientational and conformational ordering of molecules.

4. CONCLUSIONS

In this work, we have presented the molecular statistical approach to the analysis of mutually consistent dependences $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ in the nematic phase with allowance for the symmetry of this phase and the electronic structure of molecules in the presence of a correlation between the orientational degree of freedom of molecules with respect to the director and the conformational degree of freedom of the internal rotation of molecular fragments. It has been shown that, in the visible LC transparency region, the dependences $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ are caused by the perturbation of the molecular long-wavelength electron transition oscillator strengths due to the variation in the conformation of the aromatic molecular core and intermolecular interactions. The functions $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ have the form of power series with respect to S , starting from terms $\propto S^2$. The coefficients Γ_0 of function (1) for $\bar{\gamma}$ and $\Delta\gamma$ correspond to the values $\bar{\gamma}_i$ and $\Delta\gamma_i$ in the LC isotropic phase, which is confirmed by the comparison of the values $\Gamma_0(\bar{\gamma}, \lambda)$ and $\bar{\gamma}_i(\lambda)$ for MBBA. The relation between the coefficients of the power series for $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ with the variation in the conformation of molecules and intermolecular interactions has been elucidated.

The explicit form of the dispersion relations derived for $\Gamma_2(\lambda)$ for $\bar{\gamma}$ and $\Delta\gamma$ made it possible to develop a method of separating contributions of different nature to $\Gamma_2(\Delta\gamma) = \Gamma_2^{(1)} + \Gamma_2^{(2)}$. As well as the coefficient $\Gamma_2(\bar{\gamma})$, the quantity $\Gamma_2^{(1)}$ depends on the variation in the long-wavelength electron transition oscillator strengths due to the variation in the conformation and electron conjugation of fragments of the molecular core, and the quantity $\Gamma_2^{(2)}$ is caused by the perturbation of these transition oscillator strengths by the intermolecular interactions. The application of this method to MBBA has shown that $\Gamma_2^{(1)} > 0$ and $\Gamma_2^{(2)} <$

0 and the terms $\Gamma_2^{(1)} > |\Gamma_2^{(2)}|$ have comparative values.

The ratio of the terms $\Gamma_2^{(1)}$ and $\Gamma_2^{(2)}$, which depends on the chemical and electronic structure of molecules, determines the value and sign of the coefficient $\Gamma_2(\Delta\gamma)$ and the ratios Γ_2/Γ_0 for $\Delta\gamma$ and $\bar{\gamma}$ and $\Gamma_2(\Delta\gamma)/\Gamma_2(\bar{\gamma})$. With allowance for the chemical structure of molecules for known nematics, this made it possible to explain the observed dependences of the quantities $\bar{\gamma}$, $\gamma_{l,t}$, and $\Delta\gamma$ on S , which correspond to the relations $\Gamma_2^{(1)} \gg |\Gamma_2^{(2)}|$ (nCB), $\Gamma_2^{(1)} > |\Gamma_2^{(2)}|$ (MBBA), $\Gamma_2^{(1)} \approx |\Gamma_2^{(2)}|$ (EEBM), and $\Gamma_2^{(1)} < |\Gamma_2^{(2)}|$ (NP8OB). The character of the influence of intermolecular interactions on the parameters $\gamma_{l,t}$ and $\Delta\gamma$ for these LC corresponds to the induction dipole–dipole interaction of orientation-ordered molecules.

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