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Change in the Polarizability of MBBA Molecules
upon the Nematic–Isotropic Liquid Transition
and Physical Consequences

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Abstract—The Lorentz tensor components L_j and the polarizability tensor components γ_j of 4-methoxybenzylidene-4'-butylaniline (MBBA) liquid crystal molecules in nematic and isotropic phases have been determined experimentally. The quadratic dependences of the mean value $\bar{\gamma}(S)$ and anisotropy $\Delta\gamma(S)$ of the polarizability in the nematic phase on the orientational order parameter S of molecules have been established. Within the phenomenological approach, the dependences $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ have been derived, and their features for MBBA and other known objects have been interpreted. The relation of the dependences $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ to the features of the nematic–isotropic liquid phase transition has been found.

1. INTRODUCTION

Liquid crystals (LCs) represent the general model of self-organized anisotropic molecular media. This causes interest in LC self-organization manifestations in properties of molecules, features of LC structural ordering, and phase transitions [1]. The properties of molecules are characterized by molecular susceptibilities of various ranks, among which the molecule polarizability γ is most important [2, 3]. The components γ_{ij} depending on the electronic structure and conformation of molecular fragments control the anisotropic intermolecular interactions and mesophase stability [1, 4]. At the same time, as a result of electronic structure perturbations and changes in the conformation of molecular fragments in LCs due to short- and long-range-order intermolecular interactions, the components γ_{ij} themselves depend on the nature and degree of ordering of LC molecules [1], i.e., the polarizability and structural ordering of LC molecules vary mutually consistently. To clarify the consequences of these factors with respect to the phase transitions in LCs, it is necessary to determine the dependence of the components γ_{ij} on LC order parameters.

Currently, this problem can be experimentally solved only for thermotropic uniaxial LCs, which is caused by two circumstances. First, to determine the components γ_j averaged over molecule orientations in the system of LC refraction ellipsoid axes, the difference of the local field $E_j^{(\text{loc})}(\omega)$ of the light wave polarizing the molecule from the macroscopic field $E_j(\omega)$ of the light wave in a medium should be considered [5].

These fields are related as $E_j^{(\text{loc})} = f_j E_j$. The components $f_j = 1 + L_j(\varepsilon_j - 1)$ of the local field tensor diagonal in this coordinate system are related to the components L_j of diagonal Lorentz tensor ($\text{Sp}\,L = 1$) and the permittivity ε_j. The method for determining L_j from experimental data [6], free of a priori assumptions about unobservable properties of molecules, is still developed for uniaxial molecular media. Second, in uniaxial LCs, during free rotation of molecules about their longitudinal axes I (effective uniaxiality of the tensor γ), two measured values of γ_j are sufficient for determining the longitudinal (γ_l) and transverse (γ_t) components of the tensor γ with the availability of magnitudes of the molecule orientational order parameter S determined by independent methods. This dictated the choice of 4-methoxybenzylidene-4'-butylaniline (MBBA) nematic LC with the molecular formula

$$H_3CO—⟨○⟩—CH{=}N—⟨○⟩—C_4H_9$$
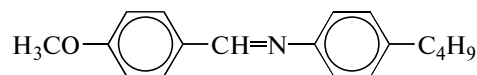
as an object of the present study.

The objectives of this work are the study of the experimental dependences $L_j(T)$, $\gamma_{l,t}(\lambda, S)$ on the temperature of the MBBA nematic phase, the light wavelength, and order parameter S; the interpretation of the dependences $\gamma_{l,t}(S)$ within the phenomenological approach with clarification of their effect on the nematic–isotropic liquid (N–I) phase transition.

2. DETERMINATION OF THE COMPONENTS L_j

For a uniaxial LC with N uniaxial molecules per unit volume, the tensor γ is characterized by the parameters $\bar{\gamma} = (\gamma_l + 2\gamma_t)/3$, $\Delta\gamma = \gamma_l - \gamma_t$. In the coordinate system of the director $\mathbf{n}$ in the visible transparency region, we have $\varepsilon_j = n_j^2$, where n_j are the LC refractive indices for light waves polarized along ($j = \parallel$) and normally to $\mathbf{n}$ ($j = \perp$). We introduce the parameters $\bar{\varepsilon} = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$, $Q = (\varepsilon_\parallel - \varepsilon_\perp)/(\bar{\varepsilon} - 1)$ and the quantities

$$r_0 = 1 - \frac{2Q^2(\bar{\varepsilon} - 1)}{3(3 + Q)(\bar{\varepsilon} + 2)}, \quad b = \frac{3(\bar{\varepsilon} - 1)}{4\pi N\bar{\gamma}(\bar{\varepsilon} + 2)} - r_0,$$

$$b_1 = \frac{2r_0 Q^2}{(3 - Q)(3 + 2Q)}, \quad b_2 = b_1[(6 + Q)/Q]^2. \tag{1}$$

The desired component $L_\perp$ ($L_\parallel = 1 - 2L_\perp$) is related to these quantities as [7]

$$L_\perp = L_{\perp k} - \frac{(\bar{\varepsilon} + 2)}{12(\bar{\varepsilon} - 1)} \tag{2}$$

$$\times [(b_1 b_2)^{1/2} - b - [(b_1 - b)(b_2 - b)]^{1/2}],$$

where $L_{\perp k} = (3 + 2Q)/[3(3 + Q)]$. The function $b(\lambda, T)$ depends on the unknown function $\bar{\gamma}(\lambda, T)$ and the signs of b and $\Delta f = f_\parallel - f_\perp$ are identical [7]. The equality $L_\perp = L_{\perp k}$ corresponds to the condition $\Delta f = b = 0$. Without a priori assumptions about the function $\bar{\gamma}(\lambda, T)$ at a given LC temperature, the unknowns $L_\perp(T)$ and $b(\lambda, T)$ are determined as follows [6]. At known values of $n_j(\lambda_i, T)$, for a discrete set of λ_i ($i = 1 - p$) in the visible region, the function $b(\lambda, T)$ in the range $\lambda_1 - \lambda_p$ is approximated by the polynomial

$$b(\lambda, T) = a_0(T) + a_1(T)\lambda + \ldots + a_m(T)\lambda^m. \tag{3}$$

The parameter $L_\perp(T)$ is independent of λ; at temperature T of the nematic phase, there are $m + 2$ unknowns $\{L_\perp^{(m)}, a_0 - a_m\}$. They are determined from the system of $m + 2 = p$ equations (2) each corresponding to one of values of λ_i. The higher approximation in polynomial (3) requires a higher accuracy of $n_j(\lambda, T)$, otherwise, the system of equations for $\{L_\perp^{(m)}, a_0 - a_m\}$ can have no physical solutions. The criterion of adequacy of the used approximation in (3) is the agreement of the values of $L_\perp^{(m)}$ with the values of $\langle L_\perp^{(m-1)} \rangle$ averaged over the values of $L_\perp^{(m-1)}$ which correspond to all possible combinations of $p - 1$ references λ_i from the set $\lambda_1 - \lambda_p$ [6].

The dependences $n_j(\lambda, \Delta T)$ for the nematic and isotropic phases of MBBA are tabulated in [8] at $\lambda_1 = 0.4678$, $\lambda_2 = 0.48$, $\lambda_3 = 0.5086$, $\lambda_4 = 0.5893$, and $\lambda_5 = 0.6438\ \mu m$. Here, $\Delta T = T_{NI} - T$, T_{NI} is the N−I tran-
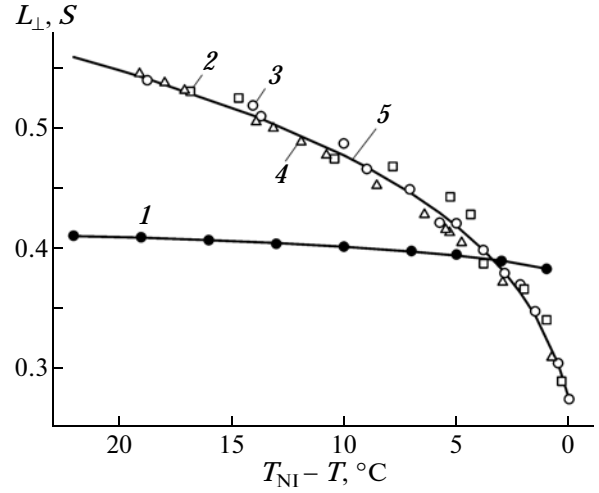

Fig. 1. Temperature dependences of (*1*) the component $L_\perp$ and (*2–4*) the orientational order parameter S of molecules in the MBBA nematic phase according to (*2*) ^{13}C NMR data [9], (*3*) ^{2}H NMR data [10, 11], and (*4*) [12]. Solid curves *1* and *5* are dependence (4) at $\lambda = 0.5893\ \mu m$ and dependence (7), respectively, with the parameters given in the text.

sition temperature. The degrees $m \geq 1$ of polynomial (3) are inadequate to the accuracy of the values of $n_j(\lambda, T)$ [8], since the dependences $L_\perp^{(3)}(\Delta T)$ and $\langle L_\perp^{(2)}(\Delta T) \rangle$ are irregular and differ between each other; at some values of ΔT and combinations of λ_i, physical solutions for $L_\perp^{(1, 2)}$ are absent. For $L_\perp^{(0)}(\Delta T)$, physical solutions to the system of equations (2) exist for all values of ΔT and all pairs $\lambda_{k, n}$ of the set λ_i. Standard deviations of $L_\perp^{(0)}(\Delta T)$ from averages $\langle L_\perp^{(0)}(\Delta T) \rangle$ do not exceed 0.005. Within the accuracy of $\langle L_\perp^{(1)}(\Delta T) \rangle$ and $\langle L_\perp^{(2)}(\Delta T) \rangle$, they are in agreement with the dependence $\langle L_\perp^{(0)}(\Delta T) \rangle$ in the entire nematic phase and at $\Delta T \geq 16°$, respectively. Thus, it should be accepted that $L_\perp(\Delta T) = \langle L_\perp^{(0)}(\Delta T) \rangle$; this dependence is shown in Fig. 1.

There is correlation between the dependences $L_\perp(\Delta T)$ and $L_{\perp k}(\Delta T, \lambda)$,

$$L_\perp(\Delta T) = A(\lambda)L_{\perp k}(\Delta T, \lambda) + B(\lambda), \tag{4}$$

whose parameters are related as $B \approx (1 - A)/3$. At $\lambda = \lambda_4$, dependence (4) with the parameters $A = 1.631$ and $B = -0.203$ is shown in Fig. 1. From relation (4), it follows that

$$A = (L_\perp - 1/3)/(L_{\perp k} - 1/3) \approx \text{const.} \tag{5}$$

Taking into account the smallness $Q \ll 3$, we have $(L_{\perp k} - 1/3) \propto Q$. At the same time, $Q \propto S$ [5] is valid in

Coefficients $\Gamma_{0,2}$ (Å^3) of dependence (8) for the quantities Γ, correlation coefficients R, and parameters $\kappa = \Gamma_2/\Gamma_0$ at indicated values of λ, μm

Γ	λ	Γ_0	Γ_2	R	κ
$\bar{\gamma}$	0.4678	37.87	5.60	0.9893	0.1479
	0.4800	37.60	5.29	0.9978	0.1407
	0.5086	36.99	5.08	0.9979	0.1373
	0.5893	35.94	4.60	0.9956	0.1280
	0.6438	35.63	4.12	0.9949	0.1156
	∞	34.14	3.00	0.9230	0.0879
γ_l	0.4678	67.42	9.04	0.8797	0.1341
	0.4800	66.72	8.10	0.9349	0.1214
	0.5086	64.71	7.98	0.9373	0.1233
	0.5893	61.24	8.45	0.9698	0.1380
	0.6438	60.55	6.15	0.9296	0.1016
	∞	56.00	4.02	0.8321	0.0718
γ_t	0.4678	23.11	3.86	0.9451	0.1670
	0.4800	23.03	3.88	0.9626	0.1685
	0.5086	23.13	3.61	0.9441	0.1561
	0.5893	23.29	2.68	0.9549	0.1151
	0.6438	23.16	3.12	0.9684	0.1347
	∞	23.36	2.06	0.9109	0.0882
$\Delta\gamma$	0.4678	44.31	5.21	0.6060	0.1176
	0.4800	43.69	4.22	0.6818	0.0966
	0.5086	41.58	4.41	0.6998	0.1061
	0.5893	37.95	5.77	0.8944	0.1520
	0.6438	37.40	3.02	0.6526	0.0807
	∞	32.74	2.06	0.6891	0.0629

the approximation linear in S, and, from (5), we obtain $(L_\perp - 1/3) \propto S$.

3. DEPENDENCES $\bar{\gamma}(S)$ AND $\Delta\gamma(S)$ IN THE NEMATIC PHASE

For the uniaxial LC, components ε_j, γ_j, and L_j are related as [5]

$$\varepsilon_j = 1 + 4\pi N\gamma_j[1 + L_j(\varepsilon_j - 1)] \quad (j = \|, \perp), \quad (6)$$

from which the parameters $\bar{\gamma} = (\gamma_\| + 2\gamma_\perp)/3$, $\Delta\gamma = (\gamma_\| - \gamma_\perp)/S$, $\gamma_l = \bar{\gamma} + 2\Delta\gamma/3$, $\gamma_t = \bar{\gamma} - \Delta\gamma/3$ are determined. Here, $S = \langle 3\cos^2\theta - 1\rangle/2$, θ is the angle between the $\mathbf{l}$ molecular axis and $\mathbf{n}$, and angle brackets $\langle...\rangle$ mean averaging over molecular ensemble. On the ΔT scale, the quantities $n_j(\Delta T)$, $S(\Delta T)$, and the density $\rho(\Delta T)$ for various samples is low-sensitive to the difference of T_{NI} due to the presence of impurities. In this study, these values for various MBBA samples are combined at the same ΔT. The magnitudes of S for MBBA, determined by ^{13}C [9] and ^{2}H [10–12] NMR methods

are shown in Fig. 1. They were approximated by the function [13]

$$S = S_0(1 - T/T_H)^{\beta_H} \quad (7)$$

with $T_{NI} = 317.16$ K [8], $S_0 = 0.978 \pm 0.028$, $T_H - T_{NI} = 0.78 \pm 0.17°$C, and $\beta_H = 0.211 \pm 0.009$. The values of $L_\perp(\Delta T)$ in Fig. 1, S (7), and $\rho(\Delta T)$ [14] were used in (6) to determine $\gamma_j(\Delta T, \lambda)$ and $\gamma_{l,t}(\Delta T, \lambda)$ from the refractive indices $n_j(\Delta T, \lambda)$ [8].

In the MBBA nematic phase, the thermal change in the parameters $\bar{\gamma}$, $\gamma_{l,t}$, and $\Delta\gamma$ at all λ_{1-5} is best approximated by the function

$$\Gamma(\lambda, S) = \Gamma_0(\lambda) + \Gamma_2(\lambda)S^2 \quad (8)$$

with the coefficients given in the table. Figure 2 shows the typical dependences of $\bar{\gamma}$ and γ_t on S^2 at $\lambda = \lambda_{1,5}$. The values of Γ_0 correspond to the values of the parameters $\bar{\gamma}$, $\Delta\gamma$, $\gamma_{l,t}$ at $S = 0$. This is confirmed by good agreement of the values of $\Gamma_0(\bar{\gamma}, \lambda)$ with the values of $\bar{\gamma}_i(\lambda)$ in the isotropic MBBA phase at all λ_{1-5}. The dependences $\Gamma_{0,2}(\lambda)$ for $\bar{\gamma}$, γ_l, $\Delta\gamma$ have normal dispersion in the range λ_{1-5}. To determine the electronic transitions responsible for this dispersion, the dependences of $\bar{\gamma}$, γ_l, $\Delta\gamma$, and $\Gamma_{0,2}$ on λ in the range λ_{1-5} were approximated by the function

$$y = y_b + P\lambda^2/(\lambda^2 - \lambda_r^2). \quad (9)$$

The use of this procedure for the nematic phase for each value of ΔT yielded the values $\lambda_r(\bar{\gamma}) = 0.298 \pm 0.015$, $\lambda_r(\gamma_l) = 0.301 \pm 0.011$, and $\lambda_r(\Delta\gamma) = 0.305 \pm 0.011$ μm having no regular temperature behavior. They are localized between the maxima $\lambda_{n\pi} = 0.285$ μm and $\lambda_{\pi\pi} = 0.325$ μm of long-wavelength MBBA electronic absorption bands [15, 16] related to the $n-\pi*$ and $\pi-\pi*$ transitions with polarization along the $N-$phenyl bond of the MBBA molecule [17]. These transitions control the dispersion variance of $\bar{\gamma}(\lambda)$, $\gamma_l(\lambda)$, and $\Delta\gamma(\lambda)$ in the visible region. The coefficient y_b in (9) yields background values of $\bar{\gamma}_b$, $\gamma_{l,t}^{(b)}$, and $\Delta\gamma_b$ caused by shorter-wavelength transitions. In the nematic phase, thermal changes in $\bar{\gamma}_b$, $\gamma_{l,t}^{(b)}$, and $\Delta\gamma_b$ is absent. The thermal change in the parameters $\bar{\gamma}_\infty$, $\gamma_{l,t}^{(\infty)}$, and $\Delta\gamma_\infty$ corresponding to the limit $\lambda \longrightarrow \infty$ and obtained from approximation (9) is characterized by function (8) with the coefficients given in the table.

Approximation of the values of $\Gamma_0(\lambda)$ for $\bar{\gamma}$, γ_l, and $\Delta\gamma$ by function (9) yielded the values $\lambda_r(\bar{\gamma}) = 0.311$, $\lambda_r(\gamma_l) = 0.320$, and $\lambda_r(\Delta\gamma) = 0.324$ μm close to the same values for the nematic phase and experimental values [15, 16]. The values $\Gamma_0^{(\infty)} = \Gamma_0(\lambda \longrightarrow \infty)$ for $\bar{\gamma}$, γ_l, and $\Delta\gamma$ coincide with the coefficients Γ_0 of formula (8) for

the parameters $\bar{\gamma}_\infty$, $\Delta\gamma_\infty$, and $\gamma_l^{(\infty)}$. The coefficients P of function (9) are given by the expressions

$$P(\bar{\gamma}) = D/3, \quad P(\gamma_l) = D(1 + 2S_\beta)/3,$$
$$P(\Delta\gamma) = DS_\beta. \tag{10}$$

Here $D = $ const, $S_\beta = (3\cos^2\beta - 1)/2$, β is the angle between the **l** molecular axis and the direction of the dipole moment of the electronic transition responsible for the dispersion of $\Gamma_0(\lambda)$ in the range λ_{1-5}. The relations

$$w_0^{(1)} = \frac{\Gamma_0(\Delta\gamma) - \Gamma_0^{(b)}(\Delta\gamma)}{\Gamma_0(\bar{\gamma}) - \Gamma_0^{(b)}(\bar{\gamma})} = 3S_\beta,$$

$$w_0^{(2)} = \frac{\Gamma_0(\gamma_l) - \Gamma_0^{(b)}(\gamma_l)}{\Gamma_0(\Delta\gamma) - \Gamma_0^{(b)}(\Delta\gamma)} = (1 + 2S_\beta)/3S_\beta \tag{11}$$

and $w_0^{(3)} = w_0^{(1)} w_0^{(2)} = 1 + 2S_\beta$ used to determine $\cos^2\beta$ follow from formulas (9) and (10). The values of $w_0^{(1-3)}(\lambda_{1-5})$ obtained from the table data and the values $\Gamma_0^{(b)}(\bar{\gamma}) = 29.47$ Å^3, $\Gamma_0^{(b)}(\gamma_l) = 43.05$ Å^3, and $\Gamma_0^{(b)}(\Delta\gamma) = 20.23$ Å^3 yield $\cos^2\beta = 0.962 \pm 0.013$ and the angle $\beta = 11.2° \pm 2°$. It is close to the angle $\beta^* \approx 10°$ between the N-phenyl bond and the axis passing through the centers of MBBA molecule phenyl rings, accepted as the molecular **l** axis in the analysis of NMR data [9–12]. This confirms the dominant contribution of the $n-\pi^*$ and $\pi-\pi^*$ transitions polarized along the N-phenyl bond to the dispersion of the parameters $\bar{\gamma}(\lambda)$, $\gamma_l(\lambda)$, and $\Delta\gamma(\lambda)$ in the visible region. The low value of β explains the weak dispersion of $\gamma_l(\lambda)$.

Approximation of the dependences $\Gamma_2(\lambda)$ for γ_l and $\Delta\gamma$ by function (9) in the range $\lambda_{1-3,5}$ without regard to $\Gamma_2(\lambda_4)$ fluctuations yields $\lambda_r(\gamma_l) = 0.304$ µm and $\lambda_r(\Delta\gamma) = 0.327$ µm close to $\lambda_{n\pi}$ and $\lambda_{\pi\pi}$, together with values of $\Gamma_2^{(\infty)}$ coinciding with the coefficients $\Gamma_2(\gamma_l^{(\infty)})$ and $\Gamma_2(\Delta\gamma_\infty)$ of formula (8) in the table. This shows the relation of the coefficient $\Gamma_2(\lambda)$ to the change in oscillator strengths $f_{n\pi}(S)$ and $f_{\pi\pi}(S)$ of the $n-\pi^*$ and $\pi-\pi^*$ transitions, which correlates to the experimental dependence $f_{\pi\pi}(S)$ of type (8) in the MBBA nematic phase [18].

The MBBA electronic structure is sensitive to the angle φ_N between the fragment C(H)=N and the aniline ring [17]. For an isolated MBBA molecule in gas or an isotropic medium (LC isotropic phase), the expressions $f_{\pi\pi}(\varphi_N) \propto \cos^2\varphi_N$, $f_{n\pi}(\varphi_N) \propto \sin^2\varphi_N$ [1, 17] are valid. For the LC, the measured parameter of the conformational state of its molecules is the ensemble-average quantity $Q_2 = \langle\cos^2\varphi_N\rangle$ [1], on which the measured oscillator strengths $f_{\pi\pi} \propto Q_2$, $f_{n\pi} \propto (1 - Q_2)$ depends. The consequence of the change in the parameter Q_2 in the MBBA nematic phase [19]
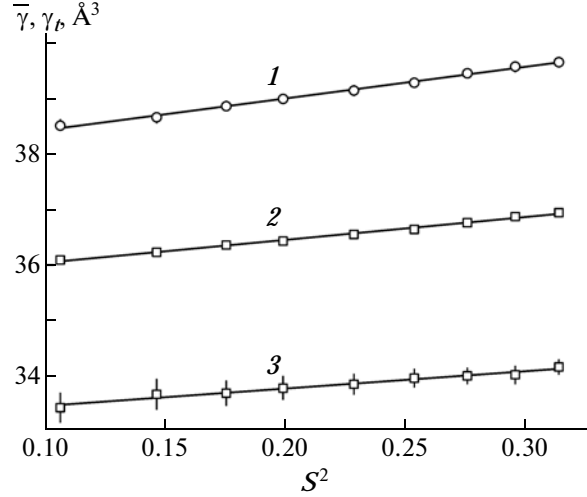
$$Q_2 = Q_{2i} + \eta S^2 \tag{12}$$

Fig. 2. Dependence of the parameters (*1, 2*) $\bar{\gamma}$ and (*3*) γ_l on S^2 in the MBBA nematic phase at $\lambda = $ (*1*) 0.4678 and (*2, 3*) 0.6438 µm. Plot *3* is shifted upward by 10 Å^3. Solid lines are dependences (8) with tabulated coefficients.

relative to its value Q_{2i} in the isotropic phase are the quadratic dependences $f_{\pi\pi}(S)$ and $f_{n\pi}(S)$ which contribute to quadratic dependences (8) for the measured polarizability parameters. A comparison of the values of $\kappa = \Gamma_2/\Gamma_0$ for the parameters $\bar{\gamma}$ and $\Delta\gamma$ in nematic MBBA phases, 4-n-alkyl-4'-cyanobiphenyls (nCB) [1, 5] and 4-nitrophenyl-4'-octyloxybenzoate (NP8OB) [20] shows that the conformational contribution (change in Q_2) to the coefficient Γ_2 is not unique. For nCB, the quantity $\Gamma_2(\Delta\gamma)$ is defined by the dependence of the oscillator strength $f_{\pi\pi}(\varphi) \propto \cos^2\varphi$ of the long-wavelength electronic $\pi-\pi^*$ transition on the angle φ between phenyl rings of the biphenyl fragment [21] and the change in $Q_2(S)$ in the nematic phase according to (12) [19]. In the visible region, the values of $\kappa(\bar{\gamma})$ for MBBA are close to those for 5CB and 7CB [1, 5], whereas the values of $\kappa(\Delta\gamma)$ for MBBA are significantly lower than $\kappa(\Delta\gamma) > 0.5$ for these homologues nCB. The ratios $\Gamma_2(\Delta\gamma)/\Gamma_2(\bar{\gamma}) > 3$ for nCB are significantly larger than those for MBBA. For the nematic NP8OB phase, positive (negative) values of Γ_2 for $\bar{\gamma}$ and $\gamma_t(\Delta\gamma, \gamma_l)$ correspond to the dependences of $\bar{\gamma}$, $\gamma_{l, t}$, and $\Delta\gamma$ on S in the visible region [20]. These facts show the existence of the negative contribution to $\Gamma_2(\Delta\gamma)$ (along with the positive conformational contribution), associated with intermolecular interactions in LCs. The determination of the general dependence (8) for polarizability parameters in nematic LCs makes it possible to turn to its interpretation and clarification of physical consequences within the phenomenological approach not limited by particular types of intermolecular interactions.

4. CONSEQUENCES OF THE DEPENDENCES $\bar{\gamma}(S)$ AND $\Delta\gamma(S)$

The molecular polarizability tensor γ averaged over molecule orientations with respect to the director $\mathbf{n}$ in an arbitrary coordinate system can be written as $\gamma = \bar{\gamma}\mathbf{E} + (2/3)\Delta\gamma\mathbf{S}$, where $\mathbf{E}$ is the unit tensor with components $E_{ik} = \delta_{ik}$, $\mathbf{S}$ is the tensor order parameter of nematic with components $S_{ik} = S(3n_i n_k - \delta_{ik})/2$, $n_{i, k}$ are components of the director $\mathbf{n}$ in this coordinate system [22]. In the system of the director $\mathbf{n} \parallel Z$, the diagonal tensor $\gamma(\gamma_\perp, \gamma_\perp, \gamma_\parallel)$ with components $\gamma_\perp = \bar{\gamma} - \Delta\gamma S/3$, $\gamma_\parallel = \bar{\gamma} + 2\Delta\gamma S/3$ corresponds to the diagonal tensor $\mathbf{S}(-S/2, -S/2, S)$ with the indicated components. The dependences $\bar{\gamma}(S)$ and $\Delta\gamma(S)$ minimize the nematic free energy density

$$\Delta F = \Delta F_S + \Delta F_\gamma + \Delta F_{S\gamma}. \quad (13)$$

The term ΔF_S caused by the orientational ordering of molecules in the absence of the relation of the tensors $\mathbf{S}$ and γ is given as [22]

$$\Delta F_S = a(T - T_0^*)S^2/2 - BS^3/3 + CS^4/4 + \ldots, \quad (14)$$

where the temperature dependence of the coefficients $B, C, \ldots$ in a narrow interval of the nematic phase is disregarded. The contribution of ΔF_γ is associated with the changes $\xi_1 = \Delta\gamma - \Delta\gamma_i$ and $\xi_2 = \bar{\gamma} - \bar{\gamma}_i$ in the parameters $\Delta\gamma$ and $\bar{\gamma}$ in the liquid crystal relative to the equilibrium parameters $\Delta\gamma_i$ and $\bar{\gamma}_i$ in the isotropic phase. Dependence (8) is satisfied in the entire range of λ variation from the visible region to $\lambda = \infty$, and the values of $\Delta\gamma(\lambda)$ and $\bar{\gamma}(\lambda)$ differ from the extrapolated values $\Delta\gamma_\infty$ and $\bar{\gamma}_\infty$ by a weakly varying proportionality factor. Therefore, we suppose that $\Delta\gamma_\infty$ and $\bar{\gamma}_\infty$ figure in formula (13). The function $\Delta F_\gamma(\xi_{1, 2})$ with a minimum at $\xi_{1, 2} = 0$ is given in the lowest approximation by the positive definite quadratic form

$$\Delta F_\gamma = \xi_1^2/2\chi_1 + \xi_1\xi_2/\chi_m + \xi_2^2/2\chi_2 \quad (15)$$

with the coefficients $\chi_{1, 2} > 0$ and $\chi_m^2 > \chi_1\chi_2$. Due to the non-critical behavior of $\xi_{1, 2}$ with respect to nematic ordering of molecules, the temperature dependence of $\chi_{1, 2, m}$ can be neglected. The term $\Delta F_{S\gamma}$ is caused by the relation of the tensors $\mathbf{S}$ and γ. In the lowest order in $S, \Delta\gamma, \bar{\gamma}$, the function $\Delta F_{S\gamma}(I_1, I_2)$ depends on the invariants $I_1 = \mathrm{Sp}(\mathbf{S}\gamma) = \Delta\gamma S^2$, $I_2 = \mathrm{Sp}(\mathbf{S}^2)\mathrm{Sp}(\gamma) = 9\bar{\gamma} S^2/2$ and has the form $\Delta F_{S\gamma} = -(\eta_1 I_1 + 2\eta_2 I_2/9)$. It consists of the two parts

$$\Delta F_{S\gamma}(\gamma_i) = -(\eta_1\Delta\gamma_i + \eta_2\bar{\gamma}_i)S^2, \quad (16)$$

$$\Delta F_{S\gamma}(\xi_{1, 2}) = -(\eta_1\xi_1 + \eta_2\xi_2)S^2. \quad (17)$$

Substitution of the term $\Delta F_{S\gamma}(\gamma_i)$ into (13) and its inclusion into ΔF_S (14) yields

$$T^* = T_0^* + (2/a)(\eta_1\Delta\gamma_i + \eta_2\bar{\gamma}_i). \quad (18)$$

The experimental difference between the temperatures T_{NI} and T^* is about one degree [4, 5, 22], and the dependence (18) is also valid for T_{NI}. At $\eta_1 > 0$, the linear increase in $T_{\mathrm{NI}}(\Delta\gamma_i)$ is consistent with that during the increase in $\Delta\gamma_i$ due to substituents in mesogenic molecules [1]. At $\eta_2 > 0$, the linear dependence $T_{\mathrm{NI}}(\bar{\gamma}_i)$ corresponds to the linear correlation between T_{NI} and molecular refraction $R_M \propto \bar{\gamma}_i$ of nematic LCs as R_M is varied due to variations of substituents in molecules [23, 24]. The dependence of the T_{NI} on $\Delta\gamma_i$ and $\bar{\gamma}_i$ explains the increase in T_{NI} for a number of LCs with a simultaneous decrease in $\Delta\gamma_i$ and an increase in $\bar{\gamma}_i$ [1], which is a stumbling block for the Maier–Saupe theory [4] in which $T_{\mathrm{NI}} \propto (\Delta\gamma_i)^2$. Thus, for known LCs, $\eta_{1, 2} > 0$ is satisfied.

Minimization of the sum $\Delta F_\gamma + \Delta F_{S\gamma}(\xi_{1, 2})$ with respect to $\xi_{1, 2}$ yields

$$\begin{aligned}
\xi_1 &= S^2\frac{\chi_1(\eta_1 - \eta_2\chi_2/\chi_m)}{1 - \chi_1\chi_2/\chi_m^2}, \\
\xi_2 &= S^2\frac{\chi_2(\eta_2 - \eta_1\chi_1/\chi_m)}{1 - \chi_1\chi_2/\chi_m^2}.
\end{aligned} \quad (19)$$

These dependences $\xi_{1, 2}(S)$ correspond to the experimental ones (8). The values $\chi_m < 0$ ($\xi_{1, 2} > 0$) exclude the feasibility $\xi_1 < 0$, $\xi_2 > 0$ observed for NP8OB and are disregarded. At $\chi_m > 0$, either $\xi_{1, 2}$ is determined by two opposite-sign contributions. The case $\eta_1 > \eta_{1c} = \eta_2\chi_2/\chi_m$, $\xi_1 > 0$ is characteristic of homologues nCB and MBBA. At $\xi_1 = 0$, due to the mutual compensation of contributions to ξ_1, we have $\xi_2 = \eta_2\chi_2 S^2$. The relations $\eta_1 < \eta_{1c}$, $\xi_1 < 0$ correspond to the nematic NP8OB phase [20] and some other LCs [5]. The case $\xi_2 = 0$ at $\eta_2 = \eta_{2c} = \eta_1\chi_1/\chi_m$ and $\xi_1 = \eta_1\chi_1 S^2$ was observed for cyan-phenyl ether of heptyl cinnamic acid [25]. For other LCs studied to date, the relations $\eta_2 > \eta_{2c}$, $\xi_2 > 0$ hold true [5, 20, 26]. Depending on $R_1 = \eta_1/\eta_{1c}$ and $R_2 = \eta_2/\eta_{2c}$, the quantity $\xi_1/\xi_2 = \Gamma_2(\Delta\gamma)/\Gamma_2(\bar{\gamma}) = \eta_2(R_1 - 1)/[\eta_1(R_2 - 1)]$ can widely vary.

Substitution of $\xi_{1, 2}$ (19) into (15) and (17) leads functional (13) to the form

$$\Delta F_S = a(T - T^*)S^2/2 - BS^3/3 + C^*S^4/4 + \ldots \quad (20)$$

with the parameter T^* (18) and coefficient $C^* = C - \Delta C$, where

$$\Delta C = \frac{2\eta_{1c}\eta_{2c}\chi_m}{1 - \chi_1\chi_2/\chi_m^2}(R_1 + R_2 - 2). \quad (21)$$

Taking into account $R_1 R_2 = \chi_m^2 / \chi_1 \chi_2 > 1$, from the inequalities $(R_1 + R_2) > 2(R_1 R_2)^{1/2} > 2$, it follows that $\Delta C > 0$ at any $R_{1,2} > 0$. The decrease in C^* and the possibility of changing the C^* sign to the negative one shows the need to consider the following terms of series (20) to adequately describe experimental dependences $S(T)$ by the theoretical dependence $S^*(T)$ minimizing functional (20). This is confirmed by the approximation of the dependences $S(T)$ for nCB and MBBA [5], 4-n-alcoxy-4'-cyanobiphenyls (nOCB) [27] and others LCs [28] by the functions $S^*(T)$ for series (20) with a term $\propto S^6$. The $\Gamma_2(\Delta\gamma)$ sign change from negative (NP8OB) to positive and the further increase in the ratio $\Gamma_2(\Delta\gamma)/\Gamma_2(\bar{\gamma})$ when going from MBBA to nCB and nOCB is accompanied by a monotonic decrease in β_H in formula (7) from 0.28 [20] till 0.17 [27]. This corresponds to the increasing effect of higher terms of series (20) at small positive or negative (MBBA) values of C^* [5, 28].

5. CONCLUSIONS

For the best known nematic MBBA, the possibility of the experimental determination of the components L_j and γ_j of the Lorentz tensor and the molecular polarizability tensor in the system of refraction ellipsoid axes without a priori assumptions about unobservable properties of molecules or their dependence on the LC phase state is shown. The experimentally determined quadratic dependences $\gamma_{l,t}(S)$, $\Delta\gamma(S)$, and $\bar{\gamma}(S)$ in the spectral region from the visible range to $\lambda = \infty$ are caused by changes in the oscillator strengths of long-wavelength electronic transitions of MBBA molecules due to the intermolecular interactions and the change in the molecular core conformation.

The derivation of the observed dependences $\Delta\gamma(S)$ and $\bar{\gamma}(S)$ in the lowest approximation of the phenomenological theory showed that the absence of a term linear in S is a consequence of the nematic phase symmetry and the absence of the invariant $\mathrm{Sp}\,\mathbf{S} = 0$ for the tensorial order parameter $\mathbf{S}$ of this phase. Either of the functions $\xi_1(S) = \Delta\gamma - \Delta\gamma_i$ and $\xi_2(S) = \bar{\gamma} - \bar{\gamma}_i$ is defined by two opposite-sign terms. Various relations between these terms lead to the features of changes in $\Delta\gamma(S)$ and $\bar{\gamma}(S)$, which correspond to those observed for MBBA and other known LCs.

A consequence of changes in $\Delta\gamma(S)$ and $\bar{\gamma}(S)$ is the linear dependence of the N−I transition temperature T_{NI} on the parameters $\Delta\gamma_i$ and $\bar{\gamma}_i$, which explains the available data on changes in T_{NI} when varying $\Delta\gamma_i$ and $\bar{\gamma}_i$ in mesogenic molecules. This makes it possible to control the nematic phase position on the temperature scale. The mutually consistent change in the parameters $\Delta\gamma$, $\bar{\gamma}$, and S manifests itself in renormalization of the ΔF_S functional coefficients and the change in the dependence $S^*(T)$ minimizing this functional. There-

fore, to approximate the experimental dependence $S(T)$ by the function $S^*(T)$, the terms to S^6 should be taken into account in the functional ΔF_S.

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