Thermal, orientational, and photo-orientational nonlinearities of azoxy liquid crystals

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We have observed a strong aberrational self-interaction of a light beam in a planar azoxy liquid crystal. We have found that, depending on the conditions of the experiment, three optical nonlinearities are manifested to a varying degree—thermal, and orientational, and photo-orientational. We give an explanation for the properties of the thermal nonlinearity in an azoxy liquid crystal. Using a simple model we calculate the magnitude of the photo-orientational nonlinearity of the nematic phase and estimate the reorientation threshold of the director. Good agreement is obtained with experiment. We show that the light wave reflected from the lower boundary of the crystal carries information about the reorientation of the director and makes it possible to separate the orientational nonlinearity from the photo-orientational. © *1994 American Institute of Physics.*

1. INTRODUCTION

The high susceptibility of azo and azoxy molecules to the action of light[1,2] causes a number of interesting physical phenomena to be observed in substances consisting of such molecules or containing them as a dopant.

Thus, in strongly viscous solutions of azo compounds in glycerol a reversible orientational photodichroism was observed at low temperatures.[3] Light-induced anisotropy has been observed in polymer films of polyvinyl alcohol doped with an azo compound[4] and in liquid-crystal comb-shaped polymers[5,6] containing azofragments.

In the interaction of light with liquid-crystal (LC) phases containing azo and azoxy compounds the following effects have been observed: a lowering of the smectic-nematic and nematic-isotropic liquid phase transition points,[7–9] variation of the refractive index,[10,11] and variation of the step of the cholesteric spiral[9,12] leading to the formation of periodic structures.[9]

It is of special interest to observe orientational effects due to the collective nature of the response of the LC molecules to an external stimulus in liquid crystals containing azo and azoxy compounds. At present, there are a number of publications on this theme. Reference 13 reports that the director has been observed to undergo reorientation in response to the electric field of a light wave. References 14–18 report the observation of reorientation of the director associated with light-induced variation of the orienting properties of the surface. In Ref. 19 the self-diffraction method was used to record a purely bulk orientational effect due to photoconversion of the molecules in an azo-doped nematic liquid crystal.

In the present paper we report the results of experiments and theoretical studies of strong nonlinear optical effects associated with thermal and orientational nonlinearities, and also with molecular photoexcitation, manifested in a crystal made up of conformationally active azoxy molecules.

2. EXPERIMENTAL CONDITIONS

A diagram of the experimental setup is shown in Fig. 1. An argon laser beam [Karl Zeiss, ILA-120, $\lambda=458$ nm ($P=1$–10 mW), $\lambda=488$ nm ($P=10$–50 mW), $\lambda=515$ nm ($P=10$–100 mW)] is focused by a lens ($f=180$ mm) in a planar nematic liquid crystal (NLC) of thickness $L=40$ μm or $L=100$ μm. Variations originating with the light beam were observed on screens S_1 and S_2 located perpendicular to the beam that has passed through the crystal and the beam reflected from it, respectively. The angle of incidence α of the light wave on the crystal could be varied by rotating the crystal about the vertical axis. The director $\mathbf{n}$ was located in the horizontal plane (the plane of the figure). The incident radiation was polarized either in the plane of the figure (the *e* wave) or in the plane perpendicular to it (the *o* wave). The polarization plane was rotated with the help of a Fresnel double rhombus.

The investigated nematic liquid crystal (mixture *A*) consisted of two azoxy compounds: 2/3 BMAOB plus 1/3 BHAOB.[1),20] Absorption by mixture *A* in the visible range decreases abruptly with increasing wavelength.[20,9] The absorption coefficient of one of the components of the mixture, BMAOB, was measured in Ref. 21. It is equal to $\beta=2$ cm^{-1} at $\lambda=515$ nm and 0.2 cm^{-1} at $\lambda=633$ nm. The elastic constants of mixture *A* at 25 °C are[20] $K_1=8.5\cdot10^{-7}$ dyn, $K_2=7.2\cdot10^{-7}$ dyn, $K_3=10.6\cdot10^{-7}$ dyn. The temperature interval over which the nematic phase of mixture *A* exists is $0\,^\circ\mathrm{C}<t<70\,^\circ\mathrm{C}$. The experiments were carried out at room temperature.

The neck radius of the light beam (by the e^{-2} criterion), calculated from the laser cavity parameters and other parameters of the optical scheme was $w=35$ μm ($\lambda=515$ nm).

This value was also obtained experimentally[22] from the dependence of w on the threshold power P_{th} of the Fréedericksz transition in the homeotropically oriented nematic liquid crystal OCBP. We obtained the value $P_{\mathrm{th}}=75$ mW in a

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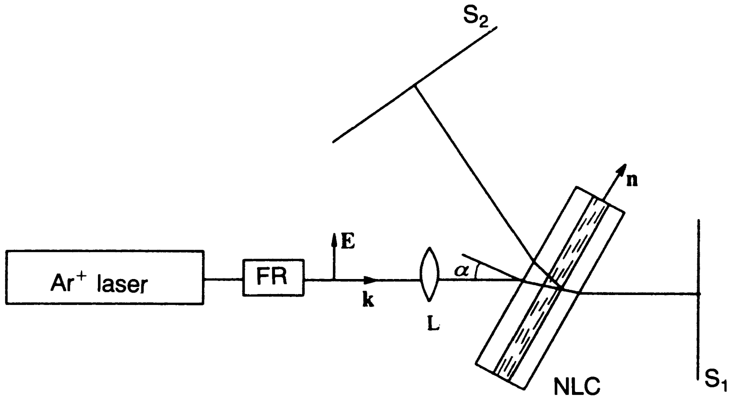

FIG. 1. Diagram of the experimental setup. Ar$^+$—cw argon laser, FR—Fresnel double-rhombus, L—lens, focusing the laser radiation onto the crystal, NLC—nematic liquid crystal, S$_1$ and S$_2$—screens for observing the transmitted (S$_1$) and reflected (S$_2$) light beams.

crystal of thickness $L=120$ μm at $t=37$ °C, which corresponds to $w=35$ μm.

3. EXPERIMENTAL RESULTS

3.1. $\alpha=0$, the *e* wave

1. For normal incidence of the *e* wave, immediately after illumination of the crystal has begun, the beam in the liquid crystal broadens, and at high enough power P a system of distinct circular immobile aberration rings appears almost instantaneously on the screen behind the crystal, with the outer ring being the most intense. The higher the power P and the smaller the wavelength, the larger is the number of these rings N_0 ($\lambda=515$ nm: $P=40$ mW, $N_0=1$; $P=65$ mW, $N_0=3$; $\lambda=458$ nm: $P=7$ mW, $N_0=2$).

2. If the power is less than some threshold value P_{th} which depends on the wavelength λ, then the number of rings increases with time T and after some set-up time T_{est} it arrives at its steady-state value N_{st}. A graph of N_{st} as a function of P for various wavelengths λ is shown in Fig. 2. T_{est} is of the order of ten minutes (e.g., for $\lambda=515$ nm at $P=40$ mW, $T_{\text{est}}=13$ min). The shape of the rings evolves during the transient period, namely, they stretch in the direction perpendicular to the electric field vector of the light wave **E**.

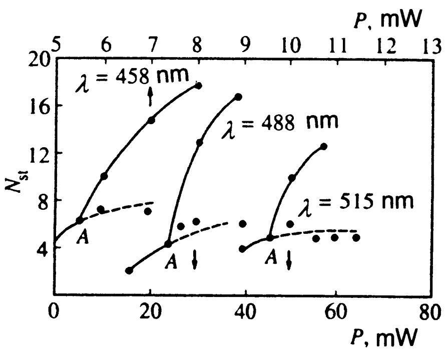

FIG. 2. Graph of the number of rings of the aberration pattern as a function of beam power for different wavelengths λ (the lower scale corresponds to $\lambda=515$ nm and $\lambda=488$ nm, the upper scale corresponds to $\lambda=458$ nm). The solid curves plot the dependence of N_{st} on the beam power P, the point A corresponds to the threshold powers $P_{\text{th}}(\lambda)$ (the abrupt change in slope of these curves). The dashed curves plot the dependence of the number of aberration rings observed before the pattern "fuzzes out" at $P>P_{\text{th}}$.

If the power of the light beam is decreased rapidly (over a time ~0.1 s) the aberration pattern contracts to the center (its divergence and the number of rings decrease with equal or greater rapidity, i.e., its relaxation time is $T_{\text{R}}\leqslant 0.1$ s.$^{2)}$

If, however, the beam power is rapidly brought back up to its original value immediately after this relaxation, the aberration pattern is equally abruptly regained. This enhanced susceptibility to the action of light is preserved in the memory of the crystal for several minutes after the initial stimulus.

3. For values of the power exceeding the threshold value, immediately after the start of illumination, as for the case $P<P_{\text{th}}$, an aberration pattern is observed with greatest intensity in the outer ring (Fig. 3a,b). Afterwards, however, a qualitatively new phenomenon arises: after a time T_{del} the aberration pattern "fuzzes out" (as if it were covered by a veil): the rings become indistinct (Fig. 3c).

The threshold power P_{th} rapidly decreases with decreasing wavelength ($\lambda=515$ nm: $P_{\text{th}}=55$ mW; $\lambda=488$ nm: $P_{\text{th}}=25$ mW; $\lambda=458$ nm: $P_{\text{th}}=5.5$ mW).

The time T_{del} that elapses between the start of illumination and the "fuzzing out" of the pattern depends on P and λ.

A graph of T_{del} as a function of P for various λ is shown in Fig. 4. From Fig. 4 it follows that for all the wavelengths the time T_{del} grows rapidly as the power approaches its threshold value $P_{\text{th}}(\lambda)$.

The washed-out pattern is not stable. After a few seconds two new ring patterns form on top of it. The first consists of distinct rings whose number and brightness increases with time. The second is made up of pale, wide rings, which also vary with time and become finer and more distinct, and, finally, after several minutes only one system of rings is observed (Fig. 3d), whose intensity falls off from the center toward the outer edge of the pattern. This pattern "jitters" somewhat. Its number of rings grows with time and after a time T'_{est} it arrives at its steady-state value N_{st}, which depends on P (see Fig. 2).

The behavior of the pattern when the power P ($P>P_{\text{th}}$) is decreased rapidly (~0.1 s) to some value $P'<P$ depends on the value decreased to (P') and differs markedly from

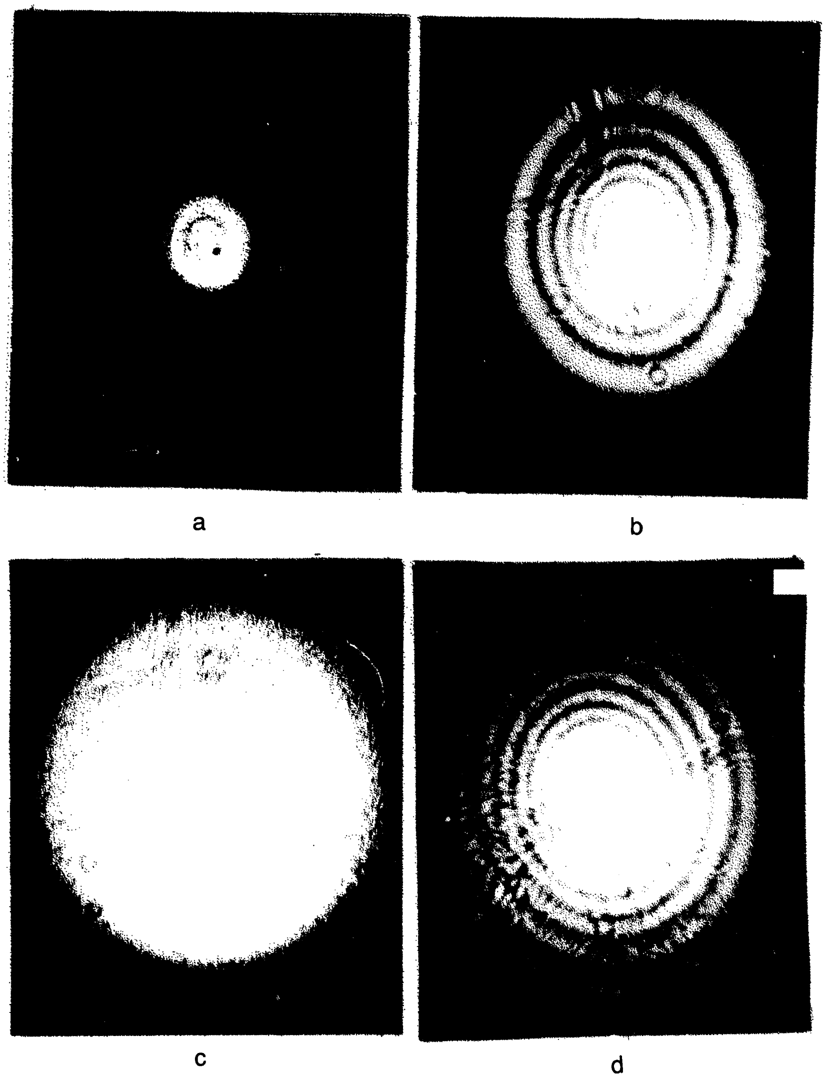

FIG. 3. Dynamics of the aberration pattern observed on the screen S_1 for the *e* wave and normal incidence of the light beam on the crystal for $P>P_{\mathrm{th}}$ ($\lambda=488$ nm, $P=30$ mW): a) $T=2$ s, b) $T<T_{\mathrm{del}}=30$ s, c) $T\approx T_{\mathrm{del}}$, d) $T>T_{\mathrm{del}}$.

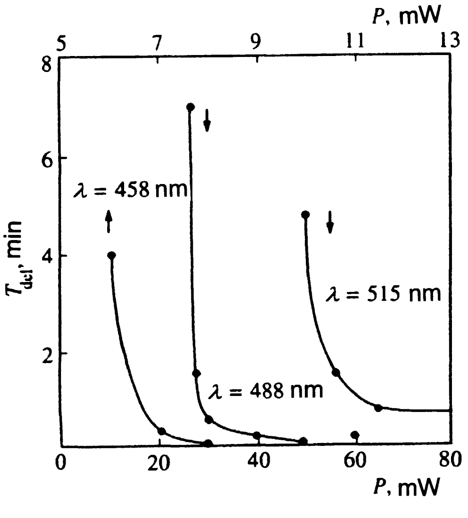

FIG. 4. Dependence of the time T_{del} on the beam power P for different wavelengths λ (the lower scale corresponds to $\lambda=515$ nm and $\lambda=488$ nm, and the upper scale, to $\lambda=458$ nm).

that described in Paragraph 2. For $P'>P_{\mathrm{th}}$ the aberration pattern noticeably contracts during a time on the order of a few seconds and recovers during roughly the same time after the power has been rapidly jacked back up to its original value. For $P'<P_{\mathrm{th}}$ the pattern returns after 10–15 s to the system of immobile rings described in Paragraph 2.

3.2. $\alpha>0°$, *e* wave

Immediately after illumination of the crystal has commenced, the transmitted light beam (the beam observed on screen S_1) broadens, like in the case $\alpha=0°$.

For $\lambda=458$ nm or $\lambda=488$ nm the pattern "fuzzes out" after a few seconds, the rings begin to "jitter," and their number grows with time and reaches its steady-state value. In this case the ratio of intensities of the aberration rings varies. To start with, the outer ring is the most intense (Fig. 5a), then the outer rings become less bright than the central rings (Fig. 5b). The higher the power of the light beam, the higher the growth rate of the number of rings and their steady-state value. The time it takes the pattern to contract if the power is suddenly decreased is a few seconds.

For $\lambda=515$ nm the transition from one pattern to another takes place more slowly.

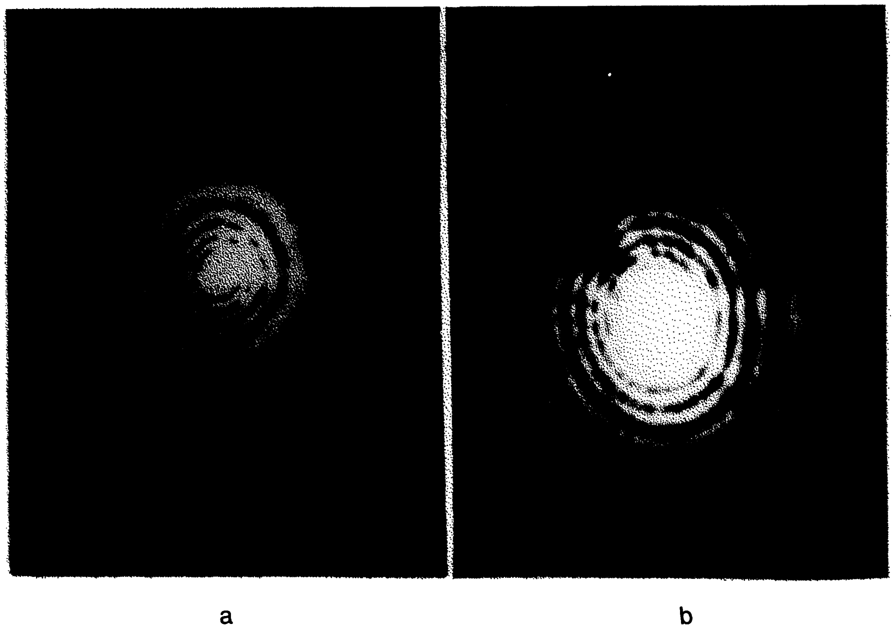

FIG. 5. Dynamics of the aberration pattern observed on the screen S_1 for the *e* wave for oblique incidence of the light beam on the crystal for $\alpha=10°$, $\lambda=458$ nm, $P=8$ mW: a) pattern before fuzzing out, b) after.

In the reflected light beam (the beam observed on screen S_2) a pattern is observed that substantially differs from the pattern in the transmitted beam (the beam observed on screen S_1). (The main experiments with the reflected beam were done with $\lambda=515$ nm.)

For small values of the light beam power for which "fuzzing out" of the aberrational rings is still not observed, two ring systems are observed on screen S_2. One is completely identical with the one observed on screen S_1 while the form of the other depends substantially on α.

For small α (a few degrees) this is the ordinary ring pattern, but with significantly greater divergence. For $\alpha\cong25°-30°$ it consists of semicircles, all to one side of the pattern, and for still larger values of α, circular segments.

The semicircles and segments are located to the left or the right of the vertical to the plane of Fig. 1 (at the point of intersection of the reflected beam and the screen), depending on whether the light beam is incident on the crystal from the left or the right. The divergence of the segment-shaped ring system is more than double that of the pattern on screen S_1.

Figure 6 presents photographs of patterns observed on screen S_2 for two values of α. The pattern seen in Fig. 6 was observed at a beam power $P<P_1$. When P becomes greater than P_1, the ring patterns observed on both screens become fuzzy and the segment-shaped pattern on screen S_2 simply disappears.

The experiments with the reflected beam were carried out with a crystal of thickness $L=100$ μm. No significant differences from the crystal of thickness $L=40$ μm were noted on screen S_1.

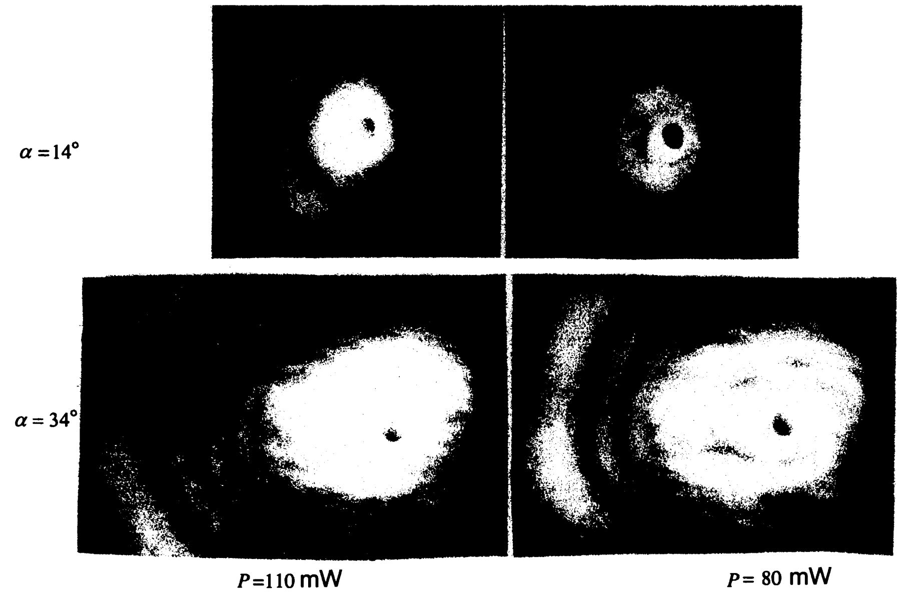

FIG. 6. Aberration pattern observed on screen S_2.

3.3. The *o* wave

The interaction of the nematic liquid crystal with the *o* wave is enormously less efficient than with the *e* wave. For example, for the *o* wave at $\alpha=0°$, $\lambda=488$ nm and $P=30$ mW the aberration rings do not appear. For the *e* wave for this same power there are 13 of them.

4. DISCUSSION OF EXPERIMENTAL RESULTS

It follows from the experimental results presented that a light beam undergoes aberrational self-action in a planar-oriented azoxy nematic liquid crystal.

The efficiency of this self-action grows as the wavelength decreases. For the *e* wave it is significantly greater than for the *o* wave. The characteristic relaxation time T_R of the aberration pattern for fixed wavelength λ depends on the beam power. It is either very low ($T_R \leqslant 0.1$ s) or a few seconds or tens of seconds.

This strong aberrational self-action is indicative of a large light-induced change in the refractive index of the liquid crystal. It can be due to a change in the order parameter or reorientation of the director. A change in the order parameter can be due to thermal[23] or conformational[24] nonlinearities with different relaxation times. The relaxation time of the director for nonlinearities associated with its reorientation obviously should not depend on the specific kind of nonlinearity. Let us calculate order-of-magnitude estimate all these times and compare them with the experimental values.

a) The thermal nonlinearity. The thermal nonlinearity is due to variation in the refractive index as a result of heating of the crystal brought about by absorption of light. Therefore the relaxation time of the thermal nonlinearity is determined by the cooling time of the crystal.

We will assume that a Gaussian light beam creates a steady Gaussian temperature profile:

$$\Delta t = \Delta t_m \exp(-\rho^2/u^2), \tag{1}$$

where Δt_m is the temperature variation of the crystal along the beam axis, ρ is the transverse coordinate, u is the halfwidth of the temperature profile. The solution of the heat conduction equation with initial condition (1), which describes the temporal variation of the temperature on the beam axis after the heat source is turned off, has the form

$$\Delta t(T) = \frac{\Delta t_m}{1+T/T_t}. \tag{2}$$

Here $T_t=u^2/2a^2$ is the characteristic temperature relaxation time, $a^2=\chi M/c\rho_0$, χ is the thermal conductivity coefficient, c_p is the molar specific heat, ρ_0 is the density of the crystal, and M is the molecular weight. The parameters χ and c_p for mixture A, so far as we know, do not appear in the literature. Therefore, to estimate the time T_t we used the parameters for the nematic liquid crystal MBBA at room temperature: $c_p=500$ J/mol/K (Ref. 25), $\chi=4\cdot 10^{-4}$ cal·cm·s/K, $\rho_0=1.1$ g/cm^3 (Ref. 26), $M=267$ g/mol.[3)] Setting u equal to the neck radius $w\approx 35$ μm of the light beam we find the relaxation time $T_t \sim 10^{-2}$ s.

b) The conformational nonlinearity. The conformational nonlinearity is due to the variation of the refractive index as a result of the appearance in the crystal subject to the action of light, of a "dopant" of excited molecules differing in their shape (conformation) from the unexcited molecules.

The relaxation time T_C of the conformational nonlinearity is determined by the smaller of two times—the lifetime T^* of the molecules in the excited state and the diffusion time of the molecules from the region illuminated by the laser beam.[27] The lifetime T^* in the excited state for molecules of mixture A, as follows from the results of Refs. 10 and 28, is not less than a few minutes. The diffusion time T_d of the molecules can be estimated in analogy with the estimate of the temperature relaxation time. It is equal to $u^2/2D$, where D is the diffusion coefficient. For a crystal of MBBA the latter is $D=2\cdot 10^{-7}$ cm^2·s^{-1} (Ref. 27) and, setting $u=w=35$ μm, we have $T_d=30$ s. Thus, the relaxation time of the photo-conformational nonlinearity is $T_C \sim 1$ min.

c) Nonlinearities associated with reorientation of the director. The relaxation time of these nonlinearities (i.e., the recovery time of the unperturbed orientation of the director) T_{OR} is determined by the elastic and viscous properties of the nematic liquid crystal. For a planar oriented sample[26]

$$T_{OR} = \gamma_1 L^2/\pi^2 K_1, \tag{3}$$

where K_1 is the Frank elastic constant and γ_1 is the rotational viscosity. For mixture A at room temperature $K_1=9\cdot 10^{-7}$ dyn. The rotational viscosity γ_1 for mixture A is equal to 1 poise.[26] From formula (3) we have $T_{OR} \sim 2$ s.

Let us now consider what nonlinearities are manifested in the above experiments.

4.1. Normal incidence ($\alpha=0°$)

a) $P<P_{th}$. In this case the experimentally observed relaxation time was very small ($T_R<0.1$ s), and consequently the main contribution to the variation of the refractive index should come from the thermal nonlinearity.

Growth of the nonlinearity of the crystal during illumination can be explained in this case by light-induced conformational transitions of the molecules of mixture A from the trans to the *cis* state. Since the light absorption coefficient for the cis-isomers can be larger than for the *trans*-isomers,[2] the *trans–cis* transition leads to an increase of the thermal nonlinearity. The conformational transition can also explain the experimentally observed large relaxation time of the crystal's memory. Indeed, the relaxation time of the crystal's memory is determined by transitions of the molecules from the excited to the ground state and by diffusion of the excited molecules out of the illuminated region. The corresponding characteristic times have already been estimated. They are on the order of minutes, like the experimentally determined relaxation time of the memory of the crystal.

It is natural to connect the increase in the efficiency of the thermal self-action of the light beam that accompanies decrease of the wavelength with an increase in the absorption coefficient of the crystal.

The significantly larger efficiency of the self-action for the *e* wave in comparison with the *o* wave is due, on the one hand, to the larger absorption coefficient and, on the other, to the larger value of the temperature derivative of the refractive index.

From the number of rings in the aberration pattern it is possible to determine the light-induced change in the refractive index. According to Ref. 29

$$N=\frac{S}{2\pi}, \tag{4}$$

where S is the nonlinear phase shift along the beam axis. Obviously,

$$S=\frac{2\pi\Delta nL}{\lambda}, \tag{5}$$

where Δn is the light-induced change in the refractive index averaged over the thickness of the crystal. From Eqs. (4) and (5) we obtain the simple relation

$$\Delta n=\frac{\lambda N}{L}. \tag{6}$$

From Eq. (6) it follows that for the e wave ($\alpha=0°$, $\lambda=488$ nm) for $P\leqslant P_{\text{th}}=24$ mW the light-induced change in the refractive index is $\Delta n_e\leqslant 0.05$. This value is significantly smaller than the difference between the refractive indices of the e and o waves, $n_e-n_o=0.34$ (Ref. 20). Since n_o varies more slowly with temperature than n_e, we can conclude that for $P\sim P_{\text{th}}$ the temperature of the crystal, heated by the light beam, remains significantly lower than the transition point to the isotropic phase.

b) $P>P_{th}$. In this case the characteristic relaxation time of the optical nonlinearity is on the order of a few seconds. Such a time is characteristic of the relaxation of the director. However, for normal incidence of the e wave onto a planar-oriented nematic liquid crystal the usual light-induced Fréedericksz transition (reorientation of the director by the electric field of the light wave) is impossible.[30] One can assume that the reason for reorientation of the director is orientationally selective excitation of the molecules of mixture A and the appearance, as a consequence, of a torque rotating the director toward the direction perpendicular to the direction of the electric field of the light wave. The possibility of such a mechanism for interaction between the light and the nematic liquid crystal was pointed out in Ref. 31 and this mechanism was used in Ref. 32 to explain the reorientation of the director of a planar-oriented dyed nematic liquid crystal.

In the present paper the validity of this new mechanism of reorientation of the director of the nematic liquid crystal is confirmed by calculations of the magnitude of the torque associated with orientationally selective molecular excitation, to which we will return below.[4)]

First of all, we will determine the angular distribution function of the excited molecules. We characterize the orientation of an individual molecule by the unit vector **m**, parallel to its long axis. In the Cartesian coordinate system xyz, whose y axis is parallel to the director **n**, and whose xy plane contains the electric field vector **E** of the light wave, the vector **m** can be characterized by the polar angle ϑ and the azimuthal angle φ:

$$m_x=\sin\vartheta\cos\varphi,\quad m_y=\cos\vartheta,\quad m_z=\sin\vartheta\sin\varphi. \tag{7}$$

We assume that the absorption oscillator of the molecule is aligned with the axis of the molecule and the polarization vector of the light field $\mathbf{e}=\mathbf{E}/|\mathbf{E}|$ forms the angle Ω with the director **n** ($e_x=\sin\Omega$, $e_y=\cos\Omega$, $e_z=0$). Then, obviously, the dependence of the light absorption coefficient β on the angle Ω is described by the expression

$$\beta=B\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta f(\vartheta,\varphi)(\mathbf{me})^2, \tag{8}$$

where B is a coefficient independent of Ω, $f(\vartheta,\varphi)$ is the angular distribution function of the molecules, normalized to unity, for which we will use the approximation

$$f(\vartheta,\varphi)=\frac{1}{4\pi}[1+5SP_2(\cos\vartheta)]. \tag{9}$$

Here $P_2(x)$ is the second-order Legendre polynomial and S is the order parameter of the nematic liquid crystal, equal to[34]

$$S=\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\,\sin\vartheta f(\vartheta,\varphi)P_2(\cos\vartheta). \tag{10}$$

We will express β in terms of the absorption coefficients $\beta_\perp=\beta(\Omega=90°)$ and $\beta_\parallel=\beta(\Omega=0°)$ of the ordinary ($\mathbf{n}\perp\mathbf{E}$) and extraordinary ($\mathbf{n}\parallel\mathbf{E}$) waves. From Eqs. (9) and (10) we obtain

$$\beta=(\beta_\parallel+2\beta_\perp)[1+2SP_2(\cos\Omega)]/3. \tag{11}$$

The distribution function of the excited molecules has the form

$$f^*(\vartheta,\varphi)=3[1+2SP_2(\cos\Omega)]^{-1}f(\vartheta,\varphi)(\mathbf{me})^2. \tag{12}$$

However, this angular distribution is valid only for molecules whose life time in the excited state T^* is shorter than the Debye relaxation time T_{D}.[26] If $T^*>T_{\text{D}}$, then at any given time T_0 only those molecules that were excited by the light during the time interval $T_0-T_{\text{D}}<T<T_0$ will have distribution (12). But it is just these molecules that create the torque acting on the director. Therefore in what follows we will use relation (12) for the angular distribution function also in the case $T^*>T_{\text{D}}$.

The concentration of excited molecules n^* participating in the creation of the torque acting on the director is obviously equal to

$$n^*=\frac{\beta S_{\text{P}}T_{\text{D}}}{\hbar\omega}, \tag{13}$$

where

$$S_{\text{P}}=\frac{cn_{\text{r}}|\mathbf{E}|^2}{8\pi} \tag{14}$$

is the magnitude of the Poynting vector, c is the speed of light, n_{r} is the crystal refractive index, **E** is the complex amplitude of the light field (in accordance with what has been said above, for $T^*<T_{\text{D}}$ we must replace T_{D} by T^* in this formula).

The interaction energy of a chosen molecule with all of its neighboring molecules (this interaction energy is responsible for the nematic ordering), according to the Maier–Saupe theory,[35,26] has the form

$$W=-4.5k_{\rm B}t_{\rm NI}S(1-1.5\sin^2\vartheta), \tag{15}$$

where $t_{\rm NI}$ is the absolute temperature of the nematic-isotropic liquid phase transition, and $k_{\rm B}$ is the Boltzmann constant. This molecule creates the torque $\mathbf{M}$ acting on the remaining molecules of the liquid crystal:

$$\mathbf{M}=-\frac{\partial W}{\partial\vartheta}\mathbf{h}, \tag{16}$$

where $\mathbf{h}=-\mathbf{i}\sin\varphi+\mathbf{k}\cos\varphi$, and $\mathbf{i}$ and $\mathbf{k}$ are the unit basis vectors of the x and z axes. Substituting relation (15) into Eq. (16), we find

$$\mathbf{M}=-13.5k_{\rm B}t_{\rm NI}S\sin\vartheta\cos\vartheta\mathbf{h}. \tag{17}$$

In the transition of the molecule to the excited state its interaction energy with its environment (15) and the torque (17) vary, and this variation can be very significant (e.g., it weakens substantially during the transition from the *trans*- to the *cis*-state, in which the molecules change their shape and generally cease to be nematogenic[36]). For an excited molecule the energy W and the torque $\mathbf{M}$ vary:

$$W^*=(1+\eta)W, \tag{18}$$

$$\mathbf{M}^*=(1+\eta)\mathbf{M}. \tag{19}$$

Here η is a factor which determines the change in the interaction energy (the interaction is enhanced if $\eta>0$ and weakened if $\eta<0$).

To determine the torque $\mathfrak{M}$ we need to average the quantity $\mathbf{M}^*-\mathbf{M}$ over the angular distribution function (12) and multiply it by the concentration of the excited molecules (13). We then have

$$\mathfrak{M}=\frac{(\beta_\parallel+2\beta_\perp)S_{\rm p}T_{\rm D}}{\hbar\omega}\int_0^{2\pi}d\varphi\int_0^{\pi}d\vartheta\sin\vartheta(\mathbf{M}^*-\mathbf{M})f(\vartheta,\varphi)(\mathbf{me})^2. \tag{20}$$

Substituting Eqs. (7) and (9) into Eqs. (19) and (20), we find

$$\mathfrak{M}_x=0,\quad \mathfrak{M}_y=0,\quad \mathfrak{M}_z=-\frac{9\eta k_{\rm B}(\beta_\parallel+2\beta_\perp)t_{\rm NI}t_{\rm D}}{5\hbar\omega}\times\left(1+\frac{5}{7}S\right)SS_{\rm p}\sin\Omega\cos\Omega. \tag{21}$$

Comparison of the torque $\mathfrak{M}$ associated with the orientationally selective molecular excitation and the ordinary orienting torque $\mathfrak{E}$ acting on the director of the nematic liquid crystal due to the electric field of the light wave

$$\mathfrak{E}_x=0,\quad \mathfrak{E}_y=0,\quad \mathfrak{E}_z=-\frac{\Delta\varepsilon S_{\rm p}}{cn_{\rm r}}\sin\Omega\cos\Omega, \tag{22}$$

shows that the dependence of $\mathfrak{M}$ and $\mathfrak{E}$ on the magnitude of the electric field of the light wave and on the angle Ω is identical.[5] Therefore we can assume that the director of the nematic liquid crystal is reoriented under the action of the torque $\mathfrak{M}$ in a way analogous to ordinary reorientation in an electric field, but the nematic liquid crystal in this case is characterized not by the ordinary anisotropy of the dielectric constant $\Delta\varepsilon$, but, as follows from comparison of Eqs. (21) and (22), by some effective quantity $\Delta\varepsilon_{\rm eff}$:

$$\Delta\varepsilon_{\rm eff}=\frac{9}{5}\eta n_{\rm r}(\beta_\parallel+2\beta_\perp)cT_{\rm D}\left(1+\frac{5}{7}S\right)S\frac{k_{\rm B}t_{\rm NI}}{\hbar\omega} \tag{23}$$

which, if expressed in terms of the wavelength of the light wave and the Debye frequency $\omega_{\rm D}=2\pi/T_{\rm D}$, has the form

$$\Delta\varepsilon_{\rm eff}=\frac{9}{5}\eta n_{\rm r}(\beta_\parallel+2\beta_\perp)\lambda\left(1+\frac{5}{7}S\right)S\frac{k_{\rm B}t_{\rm NI}}{\hbar\omega_{\rm D}}. \tag{24}$$

In contrast to the ordinary anisotropy of the dielectric constant $\Delta\varepsilon$, which is always positive at optical frequencies, the quantity $\Delta\varepsilon_{\rm eff}$ can have either sign. It is positive if excitation causes the energy of its interaction between the molecule and its environment to grow, and negative if this energy decreases. In the latter case for normal incidence of the light wave threshold reorientation of the director should take place. This is just what has been experimentally observed.

We will call the optical nonlinearity associated with orientationally selective excitation of the molecules "photo-orientational" in contrast with the ordinary orientational nonlinearity.

Let us estimate the magnitude of $\Delta\varepsilon_{\rm eff}$ for the nematic liquid crystal under study, mixture A. According to Ref. 20, $t_{\rm NI}=348$ °K. The absorption coefficients $\beta_\parallel$ and $\beta_\perp$ for mixture A are unknown to us. Therefore, in order to estimate $\Delta\varepsilon_{\rm eff}$ we will use the value $\beta=(\beta_\parallel+2\beta_\perp)/3$ ($\beta=2$ cm^{-1} ($\lambda=515$ nm) for the compound BMAOB). The Debye relaxation time $T_{\rm D}$ for mixture A is also unknown. We will take it to be equal to 10^{-8} s, which is a typical value for the nematic phase.[26] We will set the order parameter S equal to 0.4, which is somewhat smaller than actual values for the nematic phase far from the transition point to the isotropic liquid, but is the largest possible value for the model function (9) of the angular distribution which we have adopted. If we set the refractive index $n_{\rm r}$ equal to the refractive index for the extraordinary wave $n_{\rm r}=1.8$ ($\lambda=589$ nm),[20] then to order of magnitude we have $\Delta\varepsilon_{\rm eff}\approx 40\eta$. Hence it follows that even for very insignificant changes in the energy W of the interaction between an excited molecule and its environment (e.g., for $\eta=0.03$) we have $\Delta\varepsilon_{\rm eff}\approx 1$, i.e., it is comparable in absolute value with the ordinary anisotropy $\Delta\varepsilon\approx 1$ of the dielectric constant. For very large variation of the energy ($W^*=0$, $\eta=1$, i.e., when the orienting influence of the environment on the excited molecule generally disappears) we have $\Delta\varepsilon_{\rm eff}\approx -40$, which already exceeds $\Delta\varepsilon$ in absolute value by one order of magnitude. Therefore the reorientation of the director associated with orientationally selective excitation of the molecules can be significantly more efficient than reorientation by the light field (correspondingly, the photo-orientational nonlinearity is greater than the orientational nonlinearity).

Let us now determine the value of $\Delta\varepsilon_{\rm eff}$ on the basis of the measured value of the reorientation threshold $P_{\rm th}$. To this end, in the expression for the threshold of the Fréedericksz transition in a quasi-steady state electric field[26]

$$E_{\rm th}=\frac{\pi}{L}\left[\frac{4\pi K_1}{-\Delta\varepsilon}\right]^{1/2} \tag{25}$$

we replace the quantity $\Delta\varepsilon$ by the sum $\Delta\varepsilon+\Delta\varepsilon_{\rm eff}$. In addition, we multiply expression (25) by a factor which allows

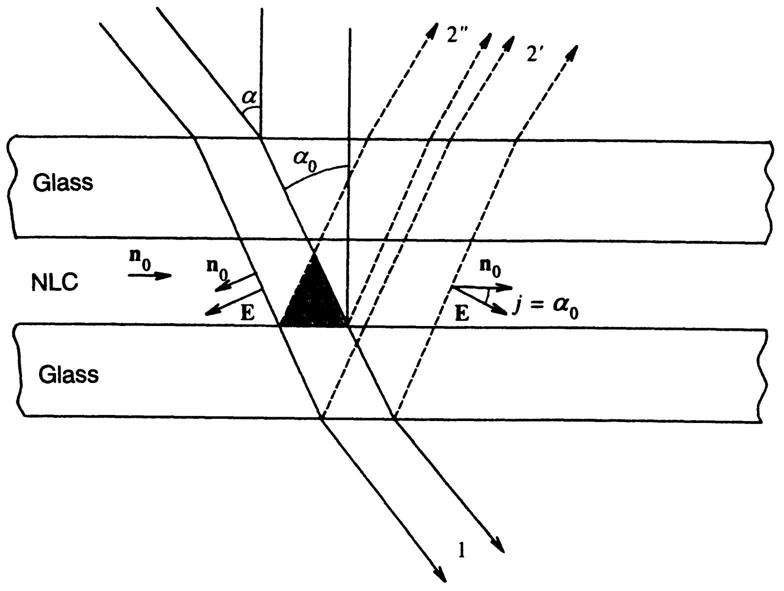

FIG. 7. Diagram of the light beams inside the nematic liquid crystal.

for the spatial boundedness of the light beam and the temporal oscillations of the light field.[29] Then for the threshold field along the axis of a Gaussian beam $E=E_0\exp(-\rho^2/w^2)$ we find

$$E_{0,\mathrm{th}}=\frac{\pi}{L}\left[\frac{8\pi K_1}{-\Delta\varepsilon-\Delta\varepsilon_{\mathrm{eff}}}\right]^{1/2}\left(1+\frac{2^{1/2}L}{\pi w}\right), \tag{26}$$

and for the threshold power of the light beam P_{th}, taking account of Eqs. (14) and (26), we obtain the relation

$$P_{\mathrm{th}}=\frac{\pi^3 c n_r w^2 K_1}{2L^2(-\Delta\varepsilon-\Delta\varepsilon_{\mathrm{eff}})}\left(1+\frac{2^{1/2}L}{\pi w}\right)^2. \tag{27}$$

For $\lambda=515$ nm experiment gives $P_{\mathrm{th}}=55$ mW. In this case, from formula (27), taking account of the fact that $\Delta\varepsilon\approx1$ (Ref. 20), we obtain $\Delta\varepsilon_{\mathrm{eff}}\approx-3$, i.e., it is entirely possible to explain the measured reorientation threshold quantitatively in terms of the photo-orientational mechanism. It is interesting to note that the value $\Delta\varepsilon_{\mathrm{eff}}\approx-3$ is already reached for a comparatively small ($\eta=-0.08$) decrease in the energy of the interaction between an excited molecule and its environment.

We can estimate the concentration n^* of the excited molecules participating in the formation of the torque $\mathfrak{M}$. With the help of Eqs. (13) and (14) we find

$$n^*=\frac{2\beta P T_{\mathrm{D}}}{\pi\hbar\omega w^2}\exp(-2\rho^2/w^2). \tag{28}$$

Setting $\beta=2\ \mathrm{cm}^{-1}$ (Ref. 20), $P\approx55$ mW, $w\approx35\ \mu$m, $T_{\mathrm{D}}=10^{-8}$ s, $\lambda=515$ nm ($\omega=3.7\cdot10^{15}\ \mathrm{s}^{-1}$), from Eq. (28) we find $n^*=1.5\cdot10^{14}\ \mathrm{cm}^{-3}$. We can compare this quantity with the total concentration $n=N_{\mathrm{A}}\rho_0/M$ of the molecules (N_{A} is Avogadro's number, M is the molecular weight). For "mixture A" the molecular weight is $M=288$ g/mol and we find $n=2\cdot10^{21}\ \mathrm{cm}^{-3}$. Thus, the density satisfies $n^*/n\sim10^{-7}$, i.e., an extremely insignificant fraction of the molecules of the liquid crystal participate in the formation of the torque rotating the director.

Now let us discuss possible reasons for variation in the energy W of the interaction between the molecules and their environment. In our view, it can vary as a result of conformational *trans–cis* transitions, and also as a result of comparatively long-lived electronic excitations of the *cis*-molecules.

As a result of the conformational transition, as was already pointed out above, the energy W decreases. However, in order for the director-rotating torque to arise it is also necessary that the lifetime of the molecules in the *cis* state be greater than the Debye relaxation time T_{D}, and that the transition time from the *trans* to the *cis* state after absorption of a photon be less than T_{D}. The lifetime in the *cis* state for molecules of mixture A, as was noted above, is on the order of minutes. The conformational transition time after absorption of a photon for molecules of mixture A is unknown. However, based on measurements of the conformational *cis–trans* transition time for 1-phenyl-azo-2-hydroxynaphthalene, in which it is $\sim10^{-10}$–10^{-11} s (Ref. 37), it is natural to assume that for molecules of mixture A it is less than or comparable with the Debye relaxation time $T_{\mathrm{D}}=10^{-8}$ s. Thus, it is entirely possible that the conformational *trans–cis* transition is the reason for reorientation of the director.

A second possible reason for variation of the energy W is the long-lived electronic excitations of the *cis*-molecules (an accumulation of such molecules, as was noted earlier, is indicated by the slow increase of the divergence of the light beam, preceding reorientation of the director).

4.2. Oblique incidence of the light beam ($\alpha\neq0°$)

First of all, let us consider the reasons for the appearance of the pattern in the reflected beam at $\lambda=515$ nm (Fig. 6). Obviously, it is created by the interference of light beams *2′* and *2″* (Fig. 7). Light beam *2′* is reflected from the glass-air boundary, after which it passes through a region of the crystal free of the influence of the transmitted beam. Therefore the pattern formed by light beam *2′* on screen S_2 is similar to the pattern created by the transmitted beam on screen S_1. Light beam *2″*, reflected from the nematic-glass boundary intercepts the region subjected to the influence of the direct beam (the hatched region in Fig. 7). This reflected beam forms the segment-shaped pattern. Let us dwell on this in more detail.

The electric field of the light beam in the case of oblique incidence can cause reorientation of the director. In this case the refractive index n_e of the extraordinary wave, which depends on the angle γ between the director n and the electric field of the light wave E according to the formula

$$n_e=\frac{(\varepsilon_\perp\varepsilon_\parallel)^{1/2}}{(\varepsilon_\perp\cos^2\gamma+\varepsilon_\parallel\sin^2\gamma)^{1/2}} \tag{29}$$

will be different. Let us estimate the change in n_e for the transmitted beam *1* and the reflected beam *2″*, assuming that the director tends to align itself with the electric field of the light wave. For undistorted planar orientation of the director we have $\gamma=2\alpha_0$ for both beams (α_0 is the refraction angle inside the crystal, see Fig. 7). If the director is oriented precisely parallel to the electric field of the light wave of the incident beam, then for it $\gamma=0°$ holds and for the reflected beam (*2″*) $\gamma=2\alpha_0$. Using formula (29), we find the change in the refractive index for the incident beam

$$(\delta n_e)_1=\frac{\Delta\varepsilon\varepsilon_\parallel^{1/2}\sin^2\alpha_0}{2\varepsilon_\perp} \tag{30}$$

and for the reflected beam

$$(\delta n_e)_2=\frac{3\Delta\varepsilon\varepsilon_\parallel^{1/2}\sin_0^2\alpha}{2\varepsilon_\perp}. \tag{31}$$

It follows from Eqs. (30) and (31) that the change in the refractive index for the reflected beam is greater than the change for the incident beam. This is why the divergence of beam *2″*, which has passed through the crystal twice, is more than twice that of beam *1*. If photo-orientation takes place (tilting of the director away from the field), then the divergence of beam *2′* cannot be double that of beam *1*. From the above considerations it thus follows that examination of the reflected light makes it possible to determine the direction of reorientation of the director.

The segmented shape of the aberration pattern is an obvious consequence of the asymmetry of the distortion of the director field, created by the incident beam, relative to the axis of the reflected beam.

For large values of the beam power $P>P_1$, after the pattern has "fuzzed out," the influence of the photo-orientational nonlinearity, as in the case of normal incidence, begins to manifest itself (the segment-shaped pattern on the screen disappears). The existence of the characteristic power P_1 (less than P_{th}) is not associated with the threshold character of the reorientation of the director since the director is not aligned with the field. It is due, apparently, to the need to accumulate enough *cis*-molecules in the region illuminated by the beam whose electronically excited states contribute to the formation of the torque.

For $\lambda=458$ nm or $\lambda=488$ nm the observed patterns are very similar to the patterns for normal incidence. We can therefore conclude that in this case thermal and photo-orientational nonlinearities play the main role.

4.3. Interaction of the crystal with the *o* wave

The significantly smaller value of the response of the nematic liquid crystal to the action of the *o* wave can be explained by the low efficiency of all of the above-considered optical nonlinearities. Indeed, the director cannot be reoriented by the electric field of an *o* wave in a planar crystal because the wave propagates adiabatically.[30] The torque associated with the orientationally selective molecular excitation tends to orient the director perpendicular to the electric field of the light wave, as is always the case for the *o* wave. Thermal and conformational nonlinearities are inefficient for the *o* wave because the absorption coefficient is smaller than for the *e* wave.

Thus, efficient aberrational self-action of a light beam takes place in a planar azoxy liquid crystal. We have found that for such liquid crystals, depending on the experimental conditions, three different optical nonlinearities are manifested:

1) The thermal optical nonlinearity (associated with variation of the refractive index due to heating of the crystal by the light beam), which is characterized by a very short relaxation time ($T_t \leqslant 0.1$ s).

2) The orientational nonlinearity (due to reorientation of the director parallel to the electric field of the light wave (the Fréedericksz transition), which is characterized by a slower relaxation (T_{OR}, of the order of a few seconds).

3) The photo-orientational nonlinearity (due to reorientation of the director perpendicular to the electric field of the light wave and associated with orientationally selective excitation of the azoxy molecules), which is also characterized by the relaxation time T_{OR}, of the order of a few seconds.

For the photo-orientational nonlinearity we have carried out a calculation, within the framework of a simple model, of the torque acting on the director and have estimated the threshold power of reorientation of the director, which is in good agreement with the experimentally determined value.

We have found that the magnitude of the thermal nonlinearity grows rapidly with increase of power of the illuminating beam. This growth is explained by variation of the absorption of the azoxy molecules as a result of the *trans–cis* transition.

We have also found that when the crystal interacts with an obliquely incident light wave under conditions in which the orientational nonlinearity plays the main role, the divergence of the weak beam reflected from the lower boundary of the crystal more than doubles. In this case the aberration pattern has a complicated segmented shape.

Examination of the reflected beam allows one to determine the direction of reorientation of the director.

In conclusion, the authors express their gratitude to M. I. Barnik and V. G. Rumyantsev for helpful discussions and providing a quantity of the liquid crystal MNPO NIOPIK and to M. P. Ermilova for preparing the oriented samples.

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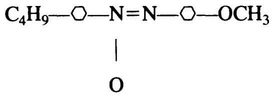
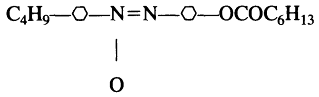
[1)] BMAOB stands for *n*-butyl-*n*′-methoxyazoxybenzene; its chemical formula is



$$C_4H_9\text{—O—}\underset{\underset{O}{|}}{N}\text{=N—O—}OCH_3$$

BHAOB stands for *n*-butyl-*n*′-heptanoyloxyazoxybenzene; its chemical formula is



$$C_4H_9\text{—O—}\underset{\underset{O}{|}}{N}\text{=N—O—}OCOC_6H_{13}$$

[2)] Note that extended, continuous work with the crystal causes the number of rings observed for a fixed power and illumination time, and also the characteristic times of the light-induced processes, to decrease. The crystal recovers, however, after several days.

[3)] Far from the phase transitions these parameters are similar for different nematic liquid crystals.

[4)] After acceptance of the present paper for publication the authors became aware of the publication of Ref. 33, in which a theory of reorientation of the director as a result of orientationally selective molecular excitation was constructed on the basis of a more complex and rigorous model, allowing numerical calculation of the torque.

[5)] Expression (22) was obtained on the basis of the expression given in Ref. 34 for the orienting torque acting on the director due to a quasisteady-state wave.

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