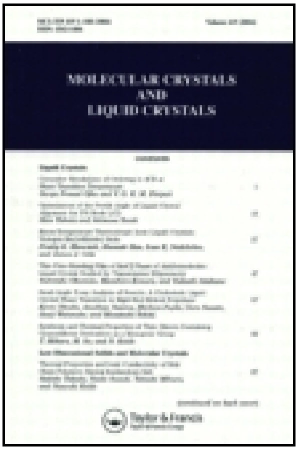

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Nanosecond Laser Pulse-Induced Refractive Index Changes in Anthraquinone-Doped Liquid Crystal

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Nanosecond Laser Pulse-Induced Refractive Index Changes in Anthraquinone-Doped Liquid Crystal

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The liquid crystal response to instantaneous strong laser pulses is related to its electronic, orientational, as well as thermal nonlinear optical properties. In this work, the transients of the refractive index variation in a pentyl-cyanobiphenyl (5CB) liquid crystal doped with an anthraquinone dye are studied with nanosecond laser pulse excitation at 532 nm. The magnitude of the response and its sign are studied as functions of the dye concentration and the ac electric field applied to a planarly or homeotropically aligned liquid crystal cell.

Keywords: liquid crystal; Mach–Zehnder interferometer; organic dye; pump-probe

INTRODUCTION

Liquid crystals (LC) are widely exploited materials in a variety of electrooptic devices and displays due to their unique optical and nonlinear optical properties [1,2]. It is commonly accepted that molecular reorientation is an important mechanism of nonlinear optical response in fluids. Optical field induces dipole moments in anisotropic molecules and aligns them due to the interaction with the electric field of light (the phenomenon is known as the optical Kerr effect)

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[3]. The reorientation and redistribution of molecules influence molecular polarizabilities that become dependent on the field strength and lead to nonlinear optical (NLO) responses described by the third-order susceptibility tensor $\chi^{(3)}$. Of course, similar phenomena were observed in nematic liquid crystals. However, they cannot be described within the simple theories of liquids. The main difference is related to the fact that calamitic molecules in LCs undergoing reorientation are constrained by elastic forces that are not present in liquids. This makes description of these phenomena more complicated. Because the light-induced birefringence $\Delta n(I) = n_{||}(I) - n_{\perp}(I)$ changes are relatively large, often called gigantic [4–6], the optical properties of LCs cannot be analyzed by a simple power series expansion of the dielectric polarization. Many studies on the influence of optical fields on a behavior of liquid crystal molecules revealed that an optical field acts in a similar way as the low-frequency electric or magnetic field changing the director orientation. The effects were studied either by the observation of self-induced effects (self-focusing) or the pump and probe methods. Both methods demonstrate the dependence of the effective refractive index n of LC on the light intensity I as $n(I) = n_0 + n_2 I$. In 1990, it was discovered [7] that the presence of a small amount, usually less than $\sim$1% by weight, of an absorbing organic dye in a nematic host enhances the orientational response by a large factor, while other physical parameters such as refractive indices and elastic constants remain almost unchanged. This effect is due to the presence of an extra torque acting on the LC director, named “dye-induced torque”. A molecular model describing the microscopic origin of this torque was proposed by Janossy [8–10] and later extended by Marucci *et al.* [11–13]. The main hypotheses put forward describe it in terms of effective molecular interactions between host molecules and excited guest molecules or their aggregates [14].

Experimental investigation of dye-nematic systems was carried out using mostly the self-action technique [15–17]. When the response time of the material for a light pulse is longer than the pulse duration, the two-beam pump-probe technique is adequate [18]. The excitation is due to short laser pulses, while a cw laser beam is used for monitoring the induced refractive index variations.

The aim of this paper is to provide an explanation of the dye enhancement effect by presenting and analyzing the results of light-induced refractive index changes in the host-guest system consisting of an anthraquinone dye dissolved in nematic liquid crystal 5CB. The dye is excited by 6-ns pulses delivered by a Nd:YAG laser at the 532-nm wavelength.

EXPERIMENTAL

The dye-liquid crystal system investigated in this work is 1,4-di(p-aminotoluene)-9,10-anthraquinone (hereafter referred to as an anthraquinone dye and abbreviated as AQ) dissolved in the 4′-pentyl-4-cyanobiphenyl (5CB characterized by the phase transition scheme K 24 N 35.3 I) liquid-crystalline matrix. Nonlinear optical properties of this system were intensively investigated and reported in [19–21]. The nematic LC was doped with AQ dye at concentrations ranging from 0.2% up to 1.6 wt %. Optical experiments were performed using a typical LC cell equipped with ITO transparent electrodes. The alignment of 5CB molecules was induced by coating glass substrates with specific orienting layers. These orienting layers provided either a normal or tangent anchoring direction for 5CB molecules and, therefore, induced a homeotropic or planar director orientation, respectively. The thickness of the LC layer amounted to 10 μm. All experiments were performed at room temperature.

The transmittance spectra of 5CB-AQ were recorded with a Perkin Elmer Lambda 35 UV-VIS-IR spectrophotometer in the spectral range 250–1100 nm. The absorption coefficients of 5CB-AQ were calculated by taking into account the absorption of a cell material and the reflection from the cell surfaces. The refractive indices of 5 CB measured at 25.1°C and at a wavelength of 633 nm are $n_e = 1.7089$ and $n_o = 1.5301$.

Optical Setup

Preliminary experiments taken in the 5CB-AQ system showed that the NLO response time is much longer (μs up to ms) than the excitation pulse duration ($\tau = 6$ ns). Therefore we could not record the instant NLO response with such self-action techniques as Z-scan or instantaneous transient grating recording. Consequently, we used the pump and probe technique with a Mach–Zehnder interferometer for the registration a light-induced phase shift accumulated by the probe light in LC cells due to the pump pulsed excitation of AQ dye molecules. A Nd^{3+}:YAG mode-locked laser Continuum Surelite II-10 doubled in frequency ($\lambda = 532$ nm) was used as an excitation source. Pulse duration was estimated to be 6 ns. The exciting beam passed through the system of mirrors and was focused on the sample resulting in the average intensity $I = 7.4$ MW/cm^2 at a 0.3 mm (FWHM) diameter spot. The sample was located in one arm of a Mach–Zehnder interferometer. The probe was delivered by a cw He-Ne laser Spectra-Physics model 127 working at the 632.8 nm wavelength. This beam was directed to the entrance prism P1 of an interferometer. The pump and probe beams were superimposed on the LC cell, and the obliquely incident pump beam has smaller diameter than the normally incident probe beam. The polarizations of both beams from Nd^{3+}:YAG and He-Ne lasers were linear with the polarization plane being horizontal. The He-Ne beam propagating in the two arms of the interferometer converged at its output prism. The interference image observed by 632.8-nm light depended on the pulsed (532 nm) light-induced phase shift in the sample.

The output beam from an interferometer, after passing through a lens, was projected on the screen. The interferometer was adjusted for the interference pattern consisted of only one bright and one dark fringe, and the pinhole was located in-between (cf. Fig. 2a). By this, we obtained the optimal sensitivity and linearity of the signal observed as a light intensity change due to the fringe movement. The phase shift measured in this way can be observed on the oscilloscope screen, and its sign can also be determined in that configuration. The interference filter was located before a photodiode to cut off the scattered pump laser emission ($\lambda = 532\,\text{nm}$). The signal due to the interference pattern shift was recorded with a fast photodiode with an internal amplifier (Thorlabs PDA55). The signal was recorded with the help of a digital oscilloscope Tektronix TDS 220 (1-GHz bandwidth) and transmitted to a PC for the further processing. The data acquisition process was synchronized electronically with pump laser pulses.

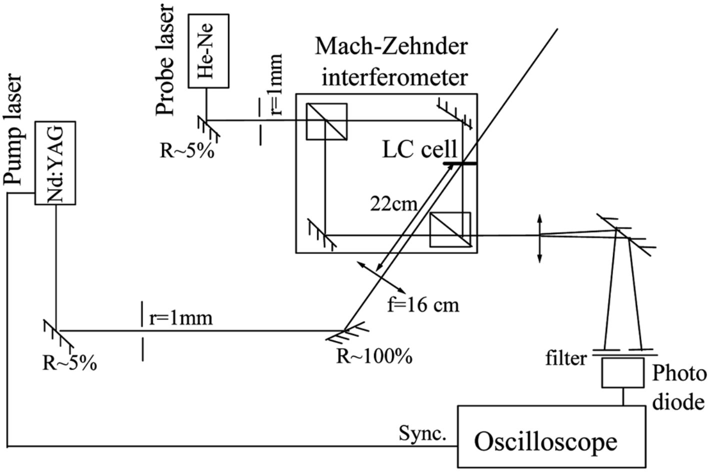


FIGURE 1 Scheme of an optical setup for measurement of light-induced refractive index changes in LC-dye system. $\lambda_{\text{exc}} = 532\,\text{nm}$, $\tau_{\text{exc}} = 6\,\text{ns}$, $\lambda_{\text{probe}} = 632.8\,\text{nm}$.

The light-induced refractive index variation of a liquid crystal readout by a linearly polarized 632.8-nm light $\Delta n(I) = n_2 \cdot I$, where I is the intensity of the 532-nm pump beam inducing the phase shift in an interferometer arm equal to $\Delta\varphi(I) = k \cdot L \cdot \Delta n(I)$, where k is the probe light propagation vector, and L is the LC layer thickness. The phase shift $\Delta\varphi(I)$ introduced by green light resulted in a shift of the interference fringes at the screen. Around the point $\Delta\varphi = 0$, the signal shows approximately a linear dependence at least for small $\Delta\varphi(I)$.

For the estimation of the absolute value of phase shift $\Delta\varphi(I)$, it was necessary to determine the range of intensity changes $2A$ seen by a photodiode for two extreme positions of the set of fringes manually by tuning the interferometer (cf. Fig. 2).

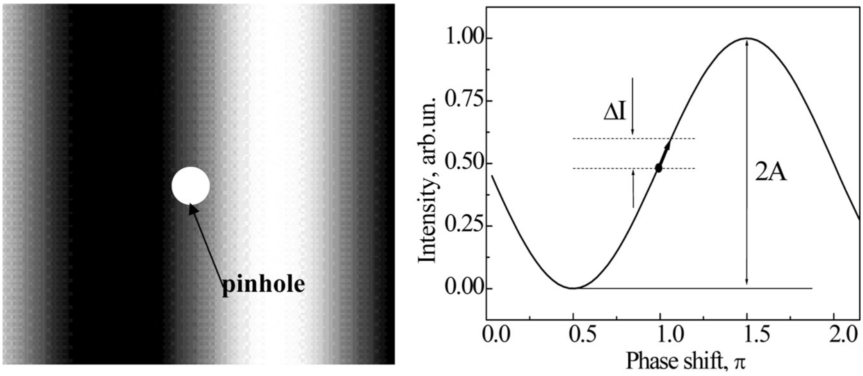
The simple relation links the signal derivative with the refractive index for a small phase distortion:

$$\frac{\Delta U}{\Delta n(I)} = (A\sin(\Delta\varphi(I))'_{\varphi=0} \approx A \cdot k \cdot L \tag{1}$$

It follows from Eq. (1) that light-induced refractive index variations can be approximated as

$$\Delta n(I) = \frac{\Delta U}{k \cdot L \cdot A}, \tag{2}$$

where $k = 2\pi/\lambda_{He-Ne}$.



(a) (b)

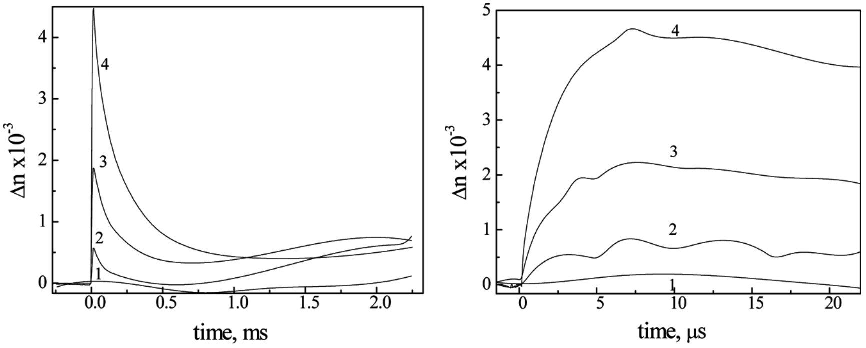
FIGURE 2 Schematic view of (a) – interference pattern with location of a pinhole, (b) – signal seen by a photodiode vs. phase shift.

RESULTS AND DISCUSSION

Absorption spectra of the guest-host system were presented in [22]. Pure 5CB is transparent in the visible range, by having only a band in the near UV with a maximum at 325 nm. The absorption spectrum of AQ dye dissolved in 5CB shows a band centered at 420 nm and a doublet with maxima at 620 and 660 nm. The absorption coefficient α increases linearly with the dye concentration at both wavelengths, 532 and 633 nm, for the AQ concentration ranging from 0 to 1.6 wt %.

The refractive index changes induced by 6-ns pulses at 532 nm in the studied LC samples were recorded by the interferometeric technique in the time range 0–25 μs and 0–10 ms with 10 ns and 5 μs resolution, respectively.

The time dependences of the light-induced refractive index variations $\Delta n(I)$ for the homeotropically aligned LC cells with an AQ dopant concentration of 0–1.4% are presented in Figure 3 for the time ranges: a) 0–2 ms and b) 0–25 μs. For pure LC 5CB, the signal was at the noise level; while, for the dye-doped LC, a positive change of the optical phase $\Delta\varphi(I)$ was observed. The signal growth was observed during 10 μs and was followed by the relaxation process lasting 1 ms. The maximum increase of $\Delta\varphi(I)$ corresponded to a refractive index change of $4.3 \cdot 10^{-3}$ for 1.4 wt % AQ in 5CB. The refractive index variation amplitude grew superlinearly with the dopant concentration. The positive sign of a refractive index change indicates that LC molecules reorient toward the direction of the electric field of incoming light.



(a) (b)

FIGURE 3 The kinetics of the light-induced refractive index changes for excitation with 6 ns, 532 nm pulses of Nd^{3+}:YAG laser. LC samples were homeotropically oriented. 5CB was doped by AQ with weight concentration: 1–0%, 2–0.2%, 3–0.6%, 4–1.4%. The time ranges: (a) 0–2 ms and (b) 0–25 μs.

The experiment was repeated for plane-oriented samples keeping all the parameters unchanged. The results of this experiment are shown in Figure 4.

The sign of the refractive index variation Δn is now negative in contrary to the positive one for the homeotropic LC orientation. The behavior of the kinetics of light-induced refractive index variations shown in Figure 4 is qualitatively similar to that shown in Figure 3 with typical growth/decay times. The signal amplitude, as well as a light-induced refractive index change, also increases with the AQ weight percentage.

The time dependences shown in Figures 3 and 4 were fitted by the exponential growth/decay functions, respectively. The time constants of these processes as functions of the AQ concentration are shown in Figure 5.

The light-induced refractive index variation amplitude grows almost linearly with the dye concentration for both planar and homeotropic orientations (Fig. 5a). The time constants of growth and decay seem to be independent of the AQ concentration in the concentration range under study. However, they depend on the LC orientation: the growth time constant is about 1.5 times less and the decay time constant is 1.5 times more than for the homeotropic orientation than for the planar one (Fig. 5b).

The influence of the action of the sinusoidal electric field with a frequency of 100 Hz on light induced refractive index variations was examined for homeotropic and planar cells with an AQ weight

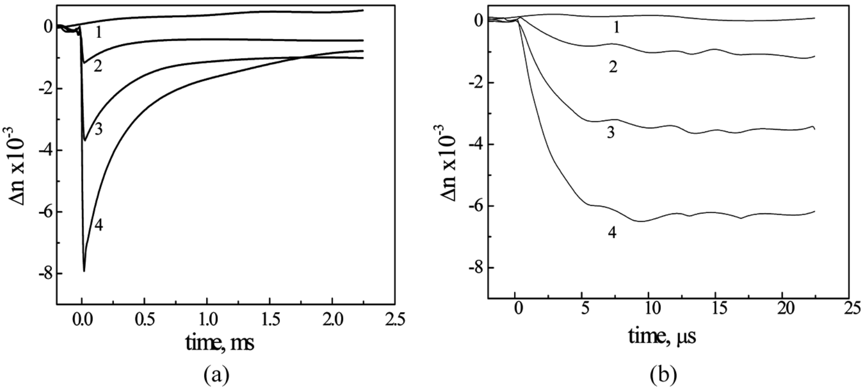


FIGURE 4 The kinetics of the light-induced refractive index changes for planarly oriented 5CB-AQ system. AQ weight concentration: 1–0%, 2–0.2%, 3–0.6%, 4–1.4%. The time ranges: (a) 0–2 ms and (b) 0–25 μs.

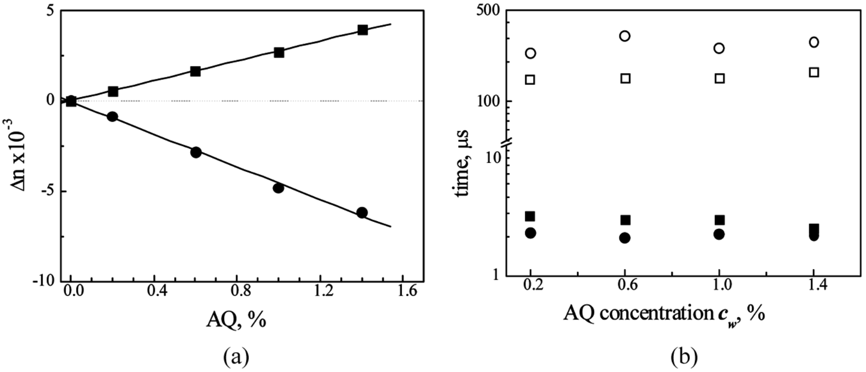


FIGURE 5 The changes in: (a) amplitude of refractive index change and (b) signal growth (closed symbols) and decay (open symbols) time constants with increasing AQ dopant percentage. Orientation of LC: squares – homeotropic, circles – planar.

concentration of 1%. As it can be predicted for a homeotropically aligned LC, we did not observe any changes between the switching-on and -off of the ac voltage. Thus the ac electric field did not change the LC orientation in that configuration.

In a plane-aligned LC with the director oriented perpendicularly to the laser polarization plane, the same transient behavior was observed. It can be explained by a fixed value (90°) of the angle between the LC director and the laser polarization plane even in the case of LC reorientation under the ac voltage action.

The planar cells with a director set parallel to the laser polarization plane displayed quite a different behavior of the temporal dependences of signals (cf. Fig. 6) due to the ns-pulse excitation. The amplitude and sign of a signal both are strongly dependent on the applied ac voltage. The shape of a signal response is changed, by depending on the voltage (increasing from 0 up to 3 V), from that characteristic of a planar LC cell to that characteristic of a homeotropically aligned LC cell. The voltage value, for which the LC response signal passes through zero-level, is above 2 V.

The photoinduced refractive index variation amplitude that was determined by the described measurements at the applied AC voltage ranging from 0 to 3.2 V is shown in Figure 7. The refraction index variation traces follow the common molecular reorientation of LC molecules due the electric field action. The signal response changes its sign from the negative to positive one at 2.6 V as for the planar and homeotropic LC alignment.

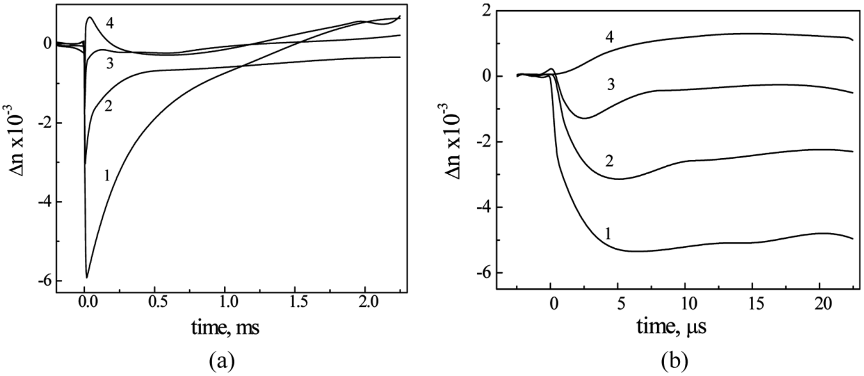


FIGURE 6 Influence of ac voltage on refractive index variation for planarly aligned LC cell with director parallel to the probe laser polarization. The values of the ac voltage: 1–0 V, 2–1 V, 3–1.7 V, 4–3.2 V.

It would be interesting to point out the main mechanisms responsible for the observed temporal signal evolution. The molecular reorientation is obvious, but its origin is related to the presence of the AQ dye. Heat dissipation due to the light absorption by a dye can be a reason for the local temperature increase and the refractive index decrease either due to a decrease in the order parameter or alternatively via temperature dependences of the refractive indices on the

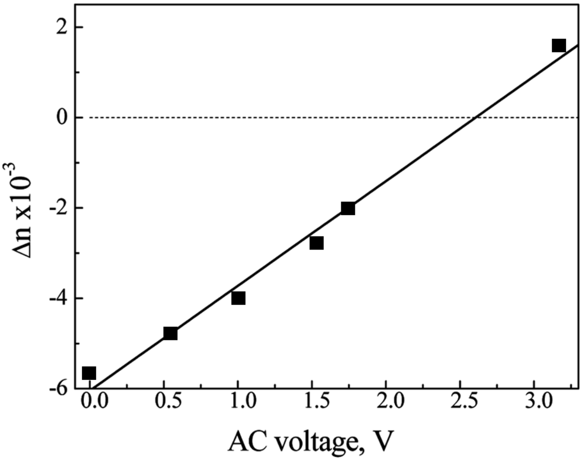


FIGURE 7 Dependence of the amplitude of the refractive index variation after pulse excitation on the ac voltage amplitude.

temperature $dn_o/dT = 10^{-3}\,\mathrm{K}$ and $dn_e/dT = -2 \cdot 10^{-3}\,\mathrm{K}$ for 5 CB at 25°C. The temperature increase of the bulk of an LC layer by 1°C degree near room temperature will produce a decrease in the refractive index of the order of $1 \cdot 10^{-3}$. The peak temperature growth due to the laser beam heating can be estimated by the relation

$$\Delta T_{peak} = \frac{(1 - e^{-\alpha d}) \cdot I \cdot \tau}{c \cdot d \cdot \rho}, \tag{3}$$

where $c \sim 2\,\mathrm{J/(g^*K)}$ is the specific heat capacity and $\rho \sim 10\ (\mathrm{g/cm^3})$ is the density. The estimation of ΔT_{peak} from (3) gives about 4 K. So, the resulting estimated refractive index variation is very close to the changes up to $5 \cdot 10^{-3}$ reported in Figure 3. The growth time of thermal expansion is determined by the sound velocity ($v \sim 10^5\,\mathrm{cm/s}$) in the LC matrix, and is about 0.3 μs for the area diameter $a = 0.3\,\mathrm{mm}$, and may be increased in our experiments (to several μs) due to the inertia of the electronic registration system. The heat dissipation time is inversely proportional to the thermal diffusion coefficient $D_T \approx 1.8 \cdot 10^{-3}\,\mathrm{cm^2\ s^{-1}}$ for 5 CB [23]. Taking the LC layer thickness $d = 10\,\mu\mathrm{m}$ into account, the decay time of this local temperature increase can be estimated from the formula

$$\tau_T = \frac{d^2}{4\pi^2 D_T} \tag{4}$$

as equal to 14 μs. This is much shorter than the time constant observed in the experiment (cf. Fig. 5b). On the other hand, one can calculate the free relaxation time for reoriented LC molecules. Assuming that the probe beam diameter is much larger than the cell thickness ($d = 10\,\mu\mathrm{m}$), the decay time of the lowest order of the orientational mode in the LC layer can be estimated from the relation [24]

$$\tau_r = \frac{\gamma \cdot d^2}{\pi^2 \cdot K_{11}}, \tag{5}$$

where γ is the rotational viscosity, and K_{11} is the elastic constant for a splay deformation of the director. For 5 CB, the parameters are as follow: $K_{11} = 4.9 \cdot 10^{-12}\,\mathrm{N}$ and $\gamma = 9.6 \cdot 10^{-3}\,\mathrm{N\ sm^{-2}}$ [25]. Then the decay time constant of a director reorientation is $\tau_\mathrm{r} \approx 20\,\mathrm{ms}$, i.e., it is much larger than actually observed decay time ones. In the presence of an ac electric field with strength E_h, this time constant is decreased according to the formula

$$\tau_r = \frac{\gamma}{\left(\frac{\pi}{d}\right)^2 \cdot K_{11} + \Delta\varepsilon_h E_h^2}, \tag{6}$$

where $\Delta\varepsilon_h$ is the dielectric anisotropy at the ac electric field frequency. The shortening of the decay time constant and the signal growth time constant which were observed and plotted in Figure 5 can be related to this mechanism.

In view of the above-presented discussion, it seems to be probable that the signal rise and the decay time constants can be also influenced by the charge carrier production mechanism for AQ dyes, as it was proposed by Rudenko and Sukhov *et al.* [25] in their paper on the photorefractive effect in an anthraquinone-doped nematic. The sudden appearance of a charge carrier on an AQ dye molecule can produce a local electric field, with assisting anisotropic LC molecules to reorient so that to compensate the additional charge. Its migration from the place of photogeneration is guided by the carrier diffusion. This process is strongly field-dependent as the charge carrier separation depends on the local electric field strength. It seems to us that both processes, i.e., the heat production and the dissipation, as well as the charge carrier photogeneration and the subsequent migration, are responsible for the observed phenomena occurring after a laser pulse. The consequence of both mechanisms and their concurrence are seen in Figure 5, where the strong electric field dependences of the signal sign and the time constant are shown.

CONCLUSIONS

With a Mach–Zehnder interferometer, we have measured optical phase changes in anthraquinone-doped nematic liquid crystal 5CB. The variations were induced by ns laser light pulses partially absorbed by the dye and followed by the nematic molecules reorientation. Experiments were performed with the varying dye content in order to show the importance of the dye for the mechanism of LC molecular reorientation. The temporal behavior of signals was measured as a function of the ac electric field strength and for two different sample configurations (homeotropic and planar ones). It has been shown that the electric filed can change the observed signal significantly either in its magnitude or sign. The discussion of possible mechanisms responsible for the effects leads us to the conclusion that, in this case, there is a mixture of molecular reorientations produced by the heat dissipation (thermal effect) and the charge carrier generation (the presence of photoconduction in the system).

REFERENCES

[1] Khoo, C. & Wu, S. T. (1993). *Optics and Nonlinear Optics of Liquid Crystals*, World Scientific: Singapore.

[2] Simoni, F. (1997). *Nonlinear Optical Properties of Liquid Crystals and PDLC*, World Scientific: Singapore.

[3] Sutherland, R. L. (2000). *Handbook of Nonlinear Optics*, Dekker: New York.

[4] Zel'dovich, B. Ya., Pilipetskii, N. F., Sukhov, A. V., & Tabiryan, N. V. (1980). *JETP Lett.*, *31*, 264.

[5] Khoo, I. C. & Zhuang, S. L. (1980). *Appl. Phys. Lett.*, *37*, 3.

[6] Durbin, S. D., Arakelian, S. M., & Shen, Y. R. (1981). *Phys. Rev. Lett.*, *47*, 1411.

[7] Janossy, I., Lloyd, A. D., & Wherret, B. S. (1990). *Mol. Cryst. Liq. Cryst.*, *179*, 1.

[8] Janossy, I., Csillag, L., & Lloyd, A. D. (1991). *Phys. Rev. A*, *44*, 8410.

[9] Janossy, I. & Kosa, T. (1992). *Opt. Lett.*, *17*, 1183.

[10] Janossy, I. (1994). *Phys. Rev. E*, *49*, 2957.

[11] Marucci, L. & Paparo, D. (1997). *Phys. Rev. E*, *56*, 1765.

[12] Marucci, L., Paparo, D., Maddalena, P., Massera, E., Prudnikova, E., & Santamato, E. (1997). *J. Chem. Phys.*, *107*, 9783.

[13] Marucci, L., Paparo, D., Vetrano, M. R., Colicchio, M., Santamato, E., & Viscardi, G. (2000). *J. Chem. Phys.*, *113*, 10361.

[14] Pergamenshchik, V., Gayvoronsky, V., Yakunin, S., Vasyuta, R., Nazarenko, V., & Lavrentovich, O. (2006). *Mol. Cryst. Liq. Cryst.*, *454*, 145.

[15] Gayvoronsky, V., Yakunin, S., Nazarenko, V., Starkov, V., & Brodyn, M. (2005). *Mol. Cryst. Liq. Cryst.*, *426*, 231.

[16] Gayvoronsky, V., Yakunin, S., Enikeeva, V., Ozheredov, I., & Shkurinov, A. (2006). *Laser Phys. Lett.*, *3*, 357.

[17] Gayvoronsky, V., Yakunin, S., Pergamenshchik, V., & Nazarenko, V. (2006). *Laser Phys. Lett.*, *3*, 531.

[18] Hsiung, H., Shi, L. P., & Shen, Y. R. (1984). *Phys. Rev. A*, *30*, 1453.

[19] Kosa, T. & Janossy, I. (1995). *Opt. Lett.*, *20*, 1230.

[20] Bartkiewicz, S., Januszko, A., Miniewicz, A., & Parka, J. (1996). *Pure Appl. Opt.*, *5*, 779.

[21] Miniewicz, A., Bartkiewicz, S., & Parka, J. (1998). *Opt. Comm.*, *149*, 89.

[22] Gayvoronsky, V., Yakunin, S., Pergamenshchik, V., Nazarenko, V., Palewska, K., Sworakowski, J., Podhorodecki, A., & Misiewicz, J. (2006). *Ukr. J. Phys. Opt.*, *7*, 116.

[23] Macdonald, R. & Eichler, H. J. (1995). *Appl. Phys. B*, *60*, 543.

[24] Sharp, K., Lagerwall, S., & Stebler, B. (1980). *Mol. Cryst. Liq. Cryst.*, *60*, 215.

[25] Rudenko, E. V. & Sukhov, A. V. (1994). *JETP Lett.*, *59*, 142.