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PECULIARITIES OF LIGHT-INDUCED MEMORY IN NLCs

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We report on the observation and investigation of the light-induced director reorientation due to the change in the orienting properties of the boundary surfaces of the homeotropically aligned NLCs in the samples containing pure (nondoped) nematic matrices and in the samples doped with the conformationally active azo and stilbene dyes, as well as the conformationally stable anthraquinone dyes. The specific features of the light-induced memory are established, among which an effect of light-initiated director self-reorientation—the continuation of director reorientation upon switching off the illumination—is the most interesting one.

Keywords: photoalignment; nematic liquid crystal; dye; light-induced reorientation; optical memory

INTRODUCTION

The light-induced director reorientation in nematic liquid crystals (NLCs) under the polarized light that persists upon switching off the illumination belongs to the optical phenomena of practical significance.

The light-induced memory was first observed in NLCs of planar orientation doped with azodyes [1–6][1].

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[1]No consideration is given here to the orientational phenomena in the cells with photosensitive layers on the substrates [7,8].

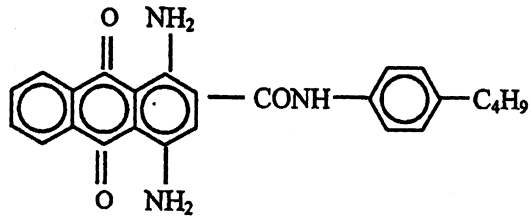
In Zolot'ko and Kitaeva [9] the effect of the light-induced memory was observed in the smectic phase of 8CB doped with the azocompound methyl red (MR). Here the homeotropic texture was transformed to the stable (the memory effect) focal-conic texture with the preferred domain orientation perpendicular to the electric field of the light wave.

Below we report on the effect of orientational memory in a rich variety of homeotropically aligned NLCs embracing both the pure nematic matrices and the samples doped with anthraquinone, azo, and stilbene dyes. The very first observation of the orientational effect in homeotropicaly aligned NLCs was reported earlier in Barnik et al. [10].

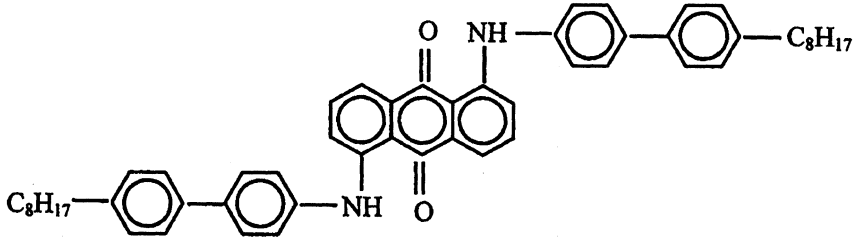
NLC SAMPLES AND EXPERIMENTAL CONDITIONS

The liquid-crystalline materials under study, ZhKM-1277 and ZhKM-1282, are multicomponent mixtures based on biphenyls and esters; E63 is a mixture of biphenyls and phenycyclohexanes [11].

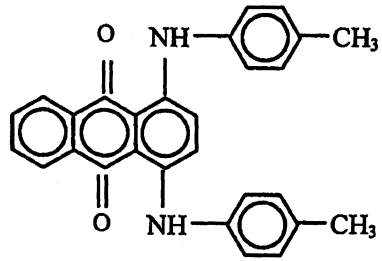
The dopants used were the conformationally stable anthraquinone dyes KD-4, KR-19, and D4; conformationally active monoazodyes DEANAB, MR, and KR-22; conformationally active diazodyes KD-1 and KD-184; dye KD-10, containing both the anthraquinone fragment and the azobridge; and the conformationally active stilbene dye DEANS. The structural formulas of the doping dyes ($\sim$0.05–0.3 wt%) are



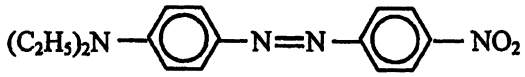
(KD-4)



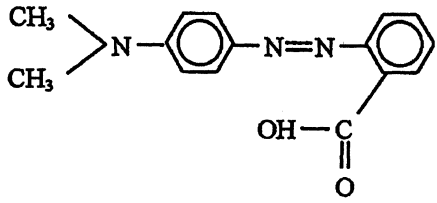
(KR-19)



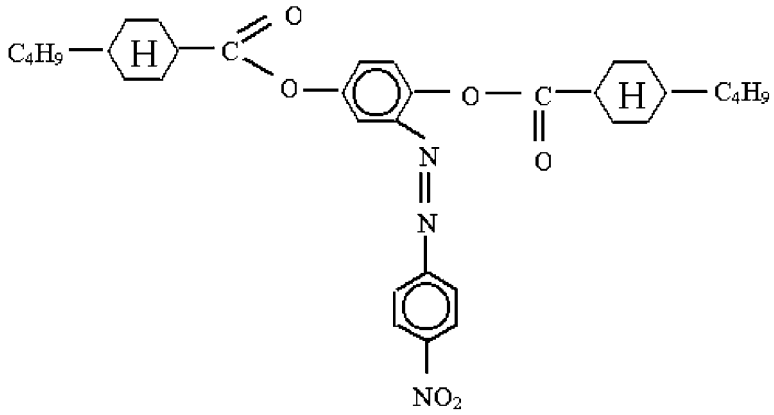
(D4)



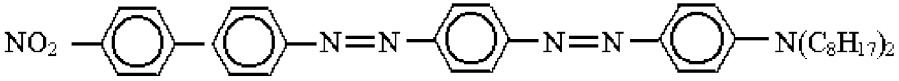
(DEANAB)



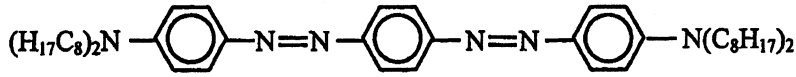
(MR)



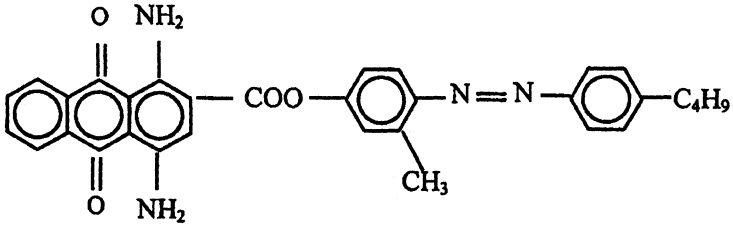
(KR-22)



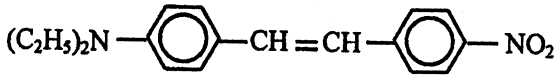
(KD-1)



(KD-184)



(KD-10)



(DEANS)

The maxima of the absorption bands of the dyes are $\lambda_m = 450$ (KR-22), 490 (DEANAB), 500 (MR), 510 (KD-1), 530 (KR-19 and KD-184), 600 (KD-4 and DEANS), and 650 nm (D4 and KD-10).

The samples under study included ZhKM-1282 doped with KD-4, KR-19, DEANAB, KR-22, KD-1, KD-184, and KD-10; E63 doped with D4; and ZhKM-1277 doped with MR, KD-184, KD-10, and DEANS.

The interior sides of the glass plates of the liquid crystal cells were coated with the transparent conducting SnO_2 layers, which makes it possible to apply an electric field to the cells. The homeotropic alignment of the majority of the samples was produced by means of the chromium stearyl chloride. In some instances, buffing of the glasses by Polirit was used for this purpose.

A light beam from argon, argon-krypton, or diode-pumped solid-state lasers ($\lambda = 458$, 515, 532, and 647 nm) with horizontal polarization plane was focused into a NLC (in so doing the extraordinary wave was excited in the crystal). The beam waist radius (determined by decreasing the intensity by a factor of e^{-2} against the maximum value) was $\sim$40–80 μm. An aberrational pattern, which allows us to study the light-induced director reorientation [12], was observed on a screen placed in the path of the light beam behind the NLC.

Consider this in more detail. A light beam, when passing through the crystal, produces a director reorientation[2] that is inhomogeneous over the

[2]This reorientation can be due to both the torques applied to each point of NLC bulk and to the change in orienting properties of the substrates.

beam cross-section, which results in the change in refractive index; to put it differently, a nonlinear lens is formed in the crystal. The latter exerts a backward action on the light beam (that is, the self-action of the light beam takes place). If the nonlinear lens is positive (this case corresponds to an increase in the refractive index due to director rotation to the light field), the self-action manifests itself as a self-focusing; if the nonlinear lens is negative (the refractive index decreases due to director rotation away from the light field), the self-defocusing shows up. The change in the refractive index being sufficiently large, the far-field divergence of the beam increases drastically and a system of rings (aberrational pattern) is formed in the beam cross-section [13,14]. The number of rings N is related in a simple way to the change in the refractive index averaged over the crystal thickness, Δn,

$$N = \frac{\Delta n\, L}{\lambda} \tag{1}$$

where L is the crystal thickness.

As shown in Kitaeva et al. [12], the sign of the refractive-index change (that is, the sense of director rotation) can be determined from the character of the transformation of the aberrational pattern under small (of the order of beam waist) and quick crystal displacement transversely to the light beam. If the crystal is shifted upward, the intensity in the upper part of the aberrational pattern increases while that in the lower part decreases; the opposite intensity redistribution corresponds to self-defocusing (this effect of the intensity redistribution in the aberrational pattern is somewhat similar to the deflection of a light ray passing through the lens center under its upper displacement: for the positive lens the ray deflects upward; for the negative one, downward). Thus, the observation of the aberrational pattern of the orientational self-action of the light beam makes it possible to study the sense and value of the director rotation.

Upon switching off the illumination the changes in the crystals were examined with a polarizing microscope.

The principal results were obtained on the samples with the thickness L ranging from 60 to 100 μm. The angle of the light beam incidence on NLC, α, was in the range 30–60°. The light beam power varied from several mW to several tens of mW, depending on the sample.

RESULTS

The distortion of the director field memorized by the crystal is produced under action of light. Two partially overlapping spots (from each of the NLC boundary surfaces) are observed therewith under microscope (Fig. 1), their

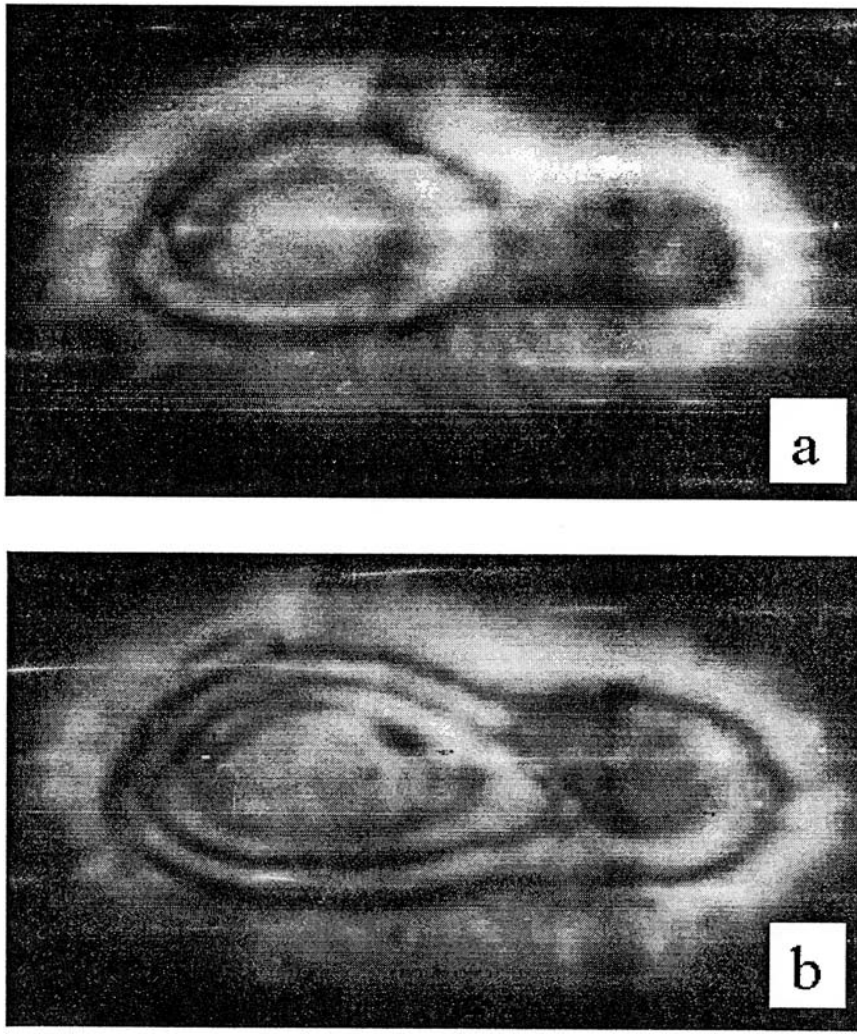


FIGURE 1 The distortions of the director field observed with a microscope between crossed polaroids in the sample ZhKM-1282 + 0.2 wt% KR-19 in (a) 20 min and (b) 20 h upon switching off the illumination. The polarizer and analyzer are directed at an angle of 45° to the polarization plane of the light beam illuminating the crystal.

centers being shifted relative to each other by the distance $R = Ltg\gamma$ (γ is the angle of refraction of the incident extraordinary wave).[3] The dark background corresponds to the unperturbed homeotropic alignment. An appearance of the ring (or, more precisely, oval) structure is due to the spatial inhomogeneity of the phase delay between the extraordinary and ordinary waves resulting from the director rotation in the plane of light beam polarization (transmission maxima correspond to the phase delay values $\Phi = (2m+1)\pi (m = 1,2\ldots)$; transmission minima correspond to $\Phi = 2m\pi$). The typical spot size (along the horizontal extent) is $\sim$140 μm (ZhKM-1282+0.2 wt% KR-19, $\lambda = 647$ nm, $\alpha = 34^\circ$, $P \sim 20$ mW, and $N = 3$).

The distortions of the director field are memorized for a long time (years). However, their appearance is time-dependent. The changes with the characteristic times of tens of minutes or hours (Fig. 1) are largely due to the effect of light-initiated director self-reorientation (see below). The changes of a longer timescale are affected by the closeness of the other light-induced spots and the defects of various types encountered in the crystals. If NLC is heated to the isotropic phase and then cooled, the spots persist at the same place.

The following specific features of the memory were established:

1. The manifestation of the memory depends on the sample composition. The memory was observed in the following samples:
   a. Pure (nondoped) nematic matrices ZhKM-1282 and E63;
   b. Nematic matrix ZhKM-1282 doped with anthraquinone dyes KD-4 and KR-19; azodyes DEANAB, KR-22, KD-1, and KD-184; and dye KD-10, containing both the anthraquinone fragment and the azobridge;
   c. Nematic matrix E63 doped with anthraquinone dye D4;
   d. Nematic matrix ZhKM-1277 doped with azodye MR, dye KD-10 containing both the anthraquinone fragment and the azobridge, and stilbene dye DEANS.

   We fail to observe the memory in pure nematic matrix ZhKM-1277 and ZhKM-1277 doped with azodye KD-184.

   The memory was observed in the samples aligned by both the chromium stearyl chloride and the substrate polishing.
2. The memory depends on the light wavelength and dye concentration.
   a. Within the entire spectral range studied ($\lambda = 458$–647 nm), the memory was only observed in ZhKM-1282 doped with KR-19 and

[3] An external electric field can "take off" the aberrational pattern on the screen and very strongly weaken the spots observed with a microscope (only a small-sized trace is left). The pattern on the screen and the spots recover completely upon removing the field.

KD-10, E63 doped with D4, and ZhKM-1277 doped with MR and KD-10.

b. All the other samples (pure matrices ZhKM-1282 and E63; ZhKM-1282 doped with KD-4, DEANAB, KR-22, KD-1, and KD-184; and ZhKM-1277 doped with DEANS) exhibited the memory at the wavelength $\lambda = 458$ nm alone, independently of its closeness to the absorption band of crystal.

c. Decrease in the doping-dye concentration can affect the spectral range in which the memory effect is observed. Thus in the samples doped with MR this range was 458–647 nm and 458–515 nm for the dye concentrations 0.3 and 0.1 wt%, respectively.

3. The sign of the light-beam self action manifested during the memory formation depends on the light wavelength.

a. $\lambda = 458$ nm. For all the samples studied the memory development is accompanied by the self-defocusing of the light beam. The self-defocusing is usually preceded by either short (of the length of seconds: ZhKM-1282 doped with KD-4, KD-1, and KD-10 and E63 doped with D4) or long (of the length of minutes: pure ZhKM-1282 and E63), self-focusing. The one exception is ZhKM-1277 + 0.3 wt% MR, where the memory formation is associated with the changeover from the self-defocusing to the self-focusing: the late stage of the memory development accompanied by self-focusing is preceded by long (of several tens of minutes) self-defocusing.

In the sample ZhKM-1277 + 0.1 wt% MR, the memory is only developed upon rather long illumination ($\sim$30–60 min, $P \sim 3$–8 mW, $\alpha = 50°$, $N \sim 5$–8) under the stable self-defocusing, which manifests itself immediately (≤ 3 s) after starting the illumination; no change in sign is observed in this case.

b. $\lambda = 647$ nm. At this wavelength the sign of the light-beam self-action changes in the course of the illumination of the samples E63 doped with D4 and ZhKM-1277 doped with 0.3 wt% MR. For E63 doped with D4 the long self-defocusing is followed by the self-focusing. Conversely, for ZhKM-1277 + 0.3 wt% MR the long self-focusing is substituted by the self-defocusing.

4. The development of the memory can be associated with the effect of light-initiated director self-reorientation.

The process of the light-induced director reorientation in the dye-doped NLCs can proceed even upon switching off the illumination, provided that the director is already substantially rotated away from the initial homeotropic orientation. This effect was observed with ZhKM-1277 doped with KD-10 (Fig. 2) and ZhKM-1282 doped with KR-19 (Fig. 1). However,

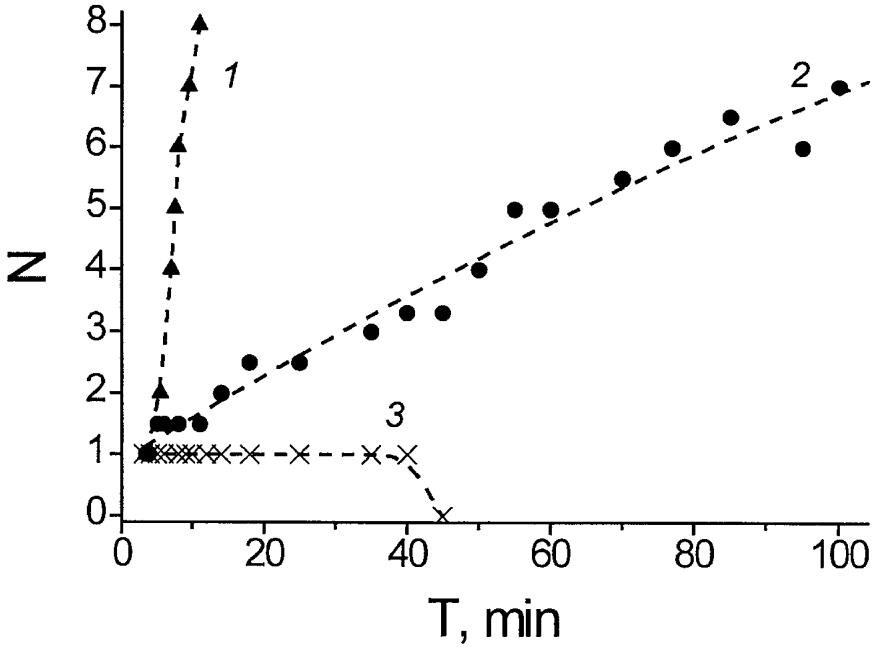


FIGURE 2 The temporal dependences of the number of the self-focusing rings N in ZhKM-1277 + 0.05 wt% KD-10 (beam power P = 7 mW, light wavelength $\lambda = 458$ nm, and angle of incidence $\alpha = 52°$): (*1*) continuos illumination, (*2*) the illumination was switched off in 5 min (N = 1.5), and (*3*) the illumination was switched off in 3 min (N = 1). The data upon illumination were obtained using a weak probe beam.

as is clearly seen from Figure 2, the characteristic time of reorientation increases substantially.

The following conclusions can be immediately drawn from the above experimental data:

a. The memory can be observed both in the NLCs doped with various dyes and in pure nematic matrices.
b. An important role in the memory development is played by the short-wave light radiation. Thus in all the samples exhibiting the memory effect the latter is necessarily observed at the wavelength $\lambda = 458$ nm. In pure nematic matrices the memory manifests itself at nothing but this wavelength. The spectral range, in which the memory is manifested, depends on the dye concentration.
c. The sign of the light-beam self-action can change in the course of the memory development.

d. The absorption coefficient plays no important part in the development of memory. Thus the memory was observed in the weakly absorbing matrices ZhKM-1282 and E63. The presence of the dyes can produce the memory both in their absorption maximum and far away from this maximum.
e. The director reorientation in the dye-doped NLCs in the course of the memory development can proceed even upon switching off the illumination; that is, the effect of light-initiated director self-reorientation does show up.

DISCUSSION

The memorizing of the light-induced director field deformation testifies that the orienting properties of the NLC surfaces are changed. Indeed, if this were not the case the director field would regain its initial homogeneous homeotropic orientation in a characteristic time of the orientational relaxation ($\sim$10 s) upon switching off the illumination. In addition, the light-induced change in the orienting properties of the boundary surfaces is supported by restoring of the director distortions upon removing the electric field and after successively heating and cooling the crystals.

Because the memory in ZhKM-1282 doped with KD-4, KD-22, DEANAB, KD-1, and KD-184 was only observed at the same wavelength $\lambda = 458$ nm, as in the pure nematic matrix ZhKM-1282, the question of whether these dyes themselves can induce the memory effect calls for further investigation. However, a number of conformationally active dyes (azodye MR, dye KD-10 containing both the azobridge and anthraquinone fragment, and stilbene dye DEANS) induce the memory effect in nematic matrix ZhKM-1277, in which the memory is not observed in the absence of doping. Conformationally stable anthraquinone dyes KR-19 and D4 substantially extend the spectral range of the memory manifestation in nematic matrices ZhKM-1282 and E63, respectively.

Temporal change in the self-action sign observed in some cases (ZhKM-1277 doped with MR and E63 doped with D4) is due to the competition between the light-induced orientational effects of two different types. The effect of the first type (surface-induced reorientation) is associated with the change of the orienting properties of the crystal boundary surfaces (the anchoring direction at the surface and the anchoring energy). Here the change in the orientation in the boundary layer is transmitted into the crystal. The effect of the second type (bulk-induced reorientation) is associated with the torques applied to each point of the crystal bulk and stemming either from the orienting action of the light electric field on

the dipoles induced by the same field [15,16] or from the change in the intermolecular forces due to the absorption of light quanta by dye molecules [17,18].

By way of illustration let us consider in detail the development of memory in ZhKM-1277 + 0.3 wt % MR. At the wavelength $\lambda = 458$ nm the light-beam self-defocusing is first observed. This means that the refractive index of the extraordinary wave decreases; that is, the director rotates away from the direction of the light electric field (the rotation is maximum at the crystal center and small close to the boundaries). The reason for this rotation can only be the light-induced change in the intermolecular forces (the torque on the induced dipoles alone would rotate the director to the light field and, hence, lead to the beam self-focusing). Further, due to NLC illumination, the orienting properties of the boundary surfaces are changed with characteristic time of $\sim$10 min and, as a consequence, director rotates away from the boundary normal (homeotropic alignment) to the direction of the light field, thus increasing the refractive index of the extraordinary wave. With time the surface-induced reorientation starts to prevail over the bulk-induced one, which results in the change in the self-action sign. At the wavelength $\lambda = 647$ nm the self-focusing manifests itself immediately following switching on the illumination; that is, the director rotates to the light field. Since the wavelength is far apart from the MR absorption maximum, this rotation is most likely due to the torque produced by the light-induced orientation of the induced dipoles. Then the self-focusing is followed by the self-defocusing; that is, the director rotates away from the light field under the effect of the surfaces.

It is therefore concluded that the sense of the surface-induced (memorized) director reorientation in NLC doped with MR varies with the light wavelength. Notice that similar change was previously observed for the bulk-induced reorientation [12,19,20].

Now we turn to the question on the reason for the light-induced change in the orienting properties of the NLC boundaries. In Zolot'ko and Kitaeva [9] this was related to the reorientation of the MR molecules, deposited at the NLC surface, produced by their photoconformational *trans-cis* transformations. However, in the present study the orienting properties of the boundary surfaces vary even in the absence of the conformationally active molecules. In Francescangeli [6], Komitov and Ichimura [21], and Ouskova et al. [22] the change in the properties of the boundary surfaces were explained by the light-induced absorption and desorption of the molecules at the NLC boundaries. In our experiments, however, the director reorientation can proceed even upon switching off the illumination (Fig. 2). This result rather indicates that the light field only initiates the processes of the self-assembly of dye molecules at the NLC substrates.

CONCLUSIONS

In summary, we studied the light-induced memorized director reorientation due to the change in the orienting properties of the boundary surfaces of the homeotropically aligned NLCs. The following specific features of this reorientation are established: its independence from the conformational activity, the change in the sign of the lightbeam self-action in the course of the memory development, the change in the sense of the director reorientation with the light wavelength, high efficiency of the short-wave radiation, the absence of substantial influence of the absorption coefficient, and the effect of light-initiated director self-reorientation—the continuation of the director reorientation even upon stopping the illumination.

The results obtained indicate a need for further theoretical studies of the mechanisms of the light-induced memory.

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