

# Anomalous intensity dependence of optical reorientation in azo dye-doped nematic liquid crystals

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*The intensity dependence of optical nonlinearity in a nematic liquid crystal doped with an azo-dye is investigated. The reorientational part of the nonlinearity changes from self-defocusing to self-focusing character while the intensity passes through the saturation value of trans-cis photoisomerization. This observation, in accordance with previous models, indicates that the optical torque generated by the trans isomers is of opposite sign than the torque generated by the cis isomers. At very low intensities a further reorientational nonlinearity was found, which is attributed to light-induced orientational redistribution of adsorbed molecules at the surface.*

## I. Introduction

The nonlinear optical properties of dye-doped liquid crystals attracted much interest in the last decade [1]. In particular, the photo-induced enhancement of optical torque (sometimes called the Jánossy effect) was studied in detail [2, 3]. It was found that while the optical reorientation is driven entirely by the anisotropy of the director polarizability in transparent nematics, an additional ‘photo-induced’ torque is present with doped nematics. According to experiments, samples doped with *anthraquinone* dyes have a photo-induced torque with the same dependence on the angle between the director and the optical field as the optical torque. Its magnitude is determined, however, by a new dimensionless parameter,  $\zeta$ , which we will call the dopant factor [4]. The dopant factor is proportional to the dye concentration and relies strongly on the molecular structure of the dye. Depending on the dye, it can be positive or negative; in the latter case the optical field tends to orient the director perpendicularly to the electric field vector of the light beam. This effect has been successfully explained by taking into account the modification of guest-host interaction during electronic excitations of dye molecules [5–8].

The situation is more complex in the case of *azo* dopants, which are capable of light-induced conformational transitions. As first noted by Barnik et. al. [9], with azo-dye doped nematics, the dopant factor changes sign from negative to positive when the angle between the light polarization and the director is varied from  $90^\circ$  to  $0^\circ$ . A similar change of sign is also obtained at a fixed angle of incidence by superposing an ordinarily polarized beam on the reorienting extraordinary ray [10, 11]. These phenomena were shown to be a result of trans-cis photoisomerization. The trans and cis isomers independently have negative and positive contributions to the photoinduced

torques, respectively [10]. The photo-induced trans/cis ratio depends on the angle between the pump polarization and the director; in particular the fraction of the cis molecules increases when this angle is decreased and so does the impact of those isomers, thereby shifting the torque towards positive values.

An additional anomaly takes place in nematics doped with the azo dye methyl-red, where self-diffraction was observed at very low intensity levels (below  $1mW/cm^2$ ) [12]. The mechanism of this 'supranonlinear' effect has not been yet fully explained. It has been suggested that this effect is the result of a photorefractive-like behavior in the doped liquid crystal [12]. An alternative explanation involves surface realignment of the director [13].

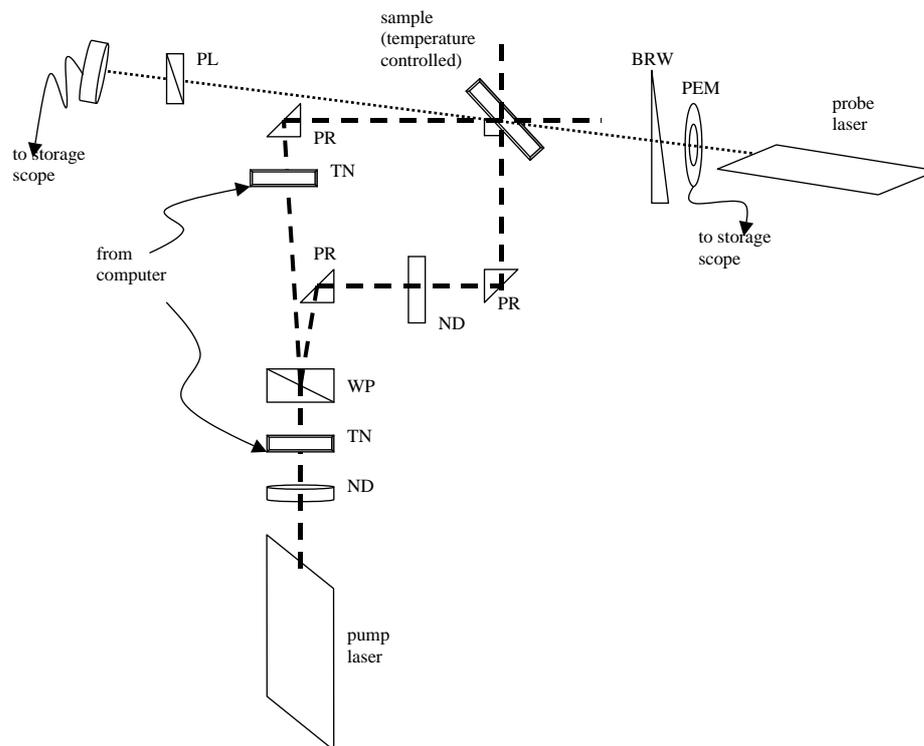
In the present paper the intensity dependence of optical reorientation is reported for an azo dye-doped nematic. In these experiments the light intensity was varied from low values, at which the dye molecules were primarily in the trans state, to high values where the cis concentration is saturated. This investigation is interesting for two reasons. First, if the interpretation of the angular dependence of the torque is correct, at low intensities, where the trans configuration is dominant, one should observe a negative torque. As the intensity is increased, the fraction of the cis component also increases, therefore the torque should become more positive and may even change its sign above a critical intensity. The observation of this effect would give strong support to the models reported earlier. Second, measurements at low intensities can reveal if there is any additional mechanism of director reorientation, similar to the supranonlinear effect reported in the case of methyl-red.

## II. Experimental

The experiments were carried out in planar cells of the nematic mixture E63, supplied by British Drug House, doped by 0.2 w/w % of Disperse Orange 3. It was shown earlier for this system that in the planar geometry the total optical torque is positive at the high-intensity limit [11]. Therefore we expect to observe sign-inversion of the optical torque when the light intensity is increased from low values to values well above the saturation intensity of photoisomerization.

As a first step, we performed pump-probe transmission measurements, which allowed us to determine the saturation intensity [14]. The pump and the probe beams were from two argon ion lasers tuned to  $\lambda = 488nm$ . The pump and probe beam diameters were 2 mm and 0.5 mm respectively. The angle of incidence of the pump beam with the normal of the sample was  $45^\circ$ , the angle between the pump and probe was approximately  $2^\circ$ .

The light-induced optical phase shift was also measured with a pump-probe setup. The probe beam was the 633 nm line from a He-Ne laser; the pump beam was the same as used in the nonlinear transmission measurements. At the probe wavelength the absorption of Disperse Orange 3 is negligible. The birefringence was measured with a photoelastic modulator (PEM) and a birefringent wedge, in a similar way as reported in [11]. In the present measurements, however, instead of translating the wedge, the AC component of the PEM signal was displayed on an oscilloscope and the shift of the zero-crossing position was monitored [15]. This technique allowed us to follow the change of the birefringence with a time resolution of about 1 sec. The



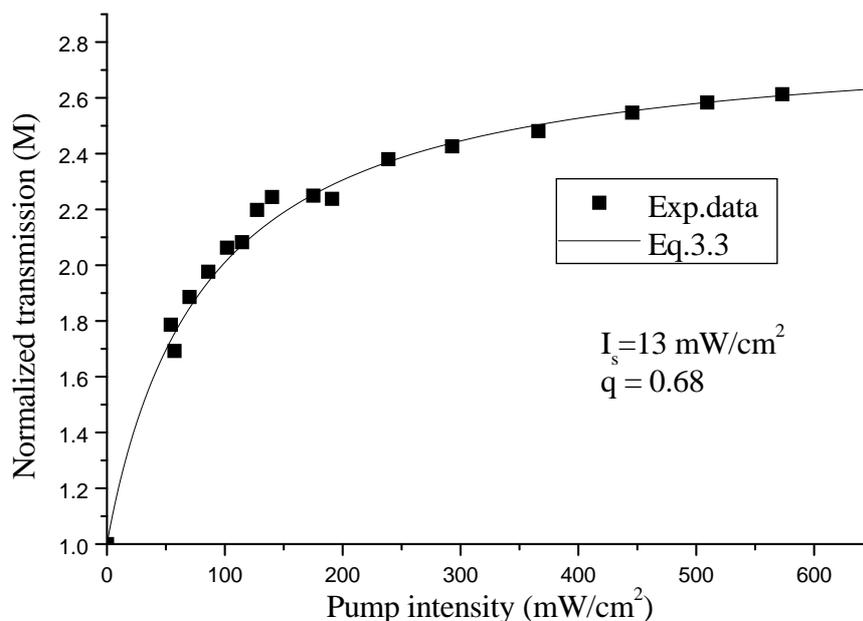
**Figure 1: Experimental set-up: PL - polarizer, PR - prism, TN - twisted nematic, BRW - birefringent wedge, PEM - photoelastic modulator, WP - Wollaston prism, ND - neutral density filter.**

temperature of the sample was stabilized at  $28^{\circ}\text{C}$ , with a precision of 0.1 degree.

In order to investigate optical reorientation, one has to distinguish between different mechanisms contributing to the induced birefringence. As it will be explained in the next section in detail, this problem was solved using the setup depicted in Fig. 1. The relative phase shift between the extraordinary ( $e$ ) and ordinary ( $o$ ) rays was measured for two pump paths. One of the paths propagated nearly parallel to the probe direction, while in the other path propagated nearly perpendicular to it. The pump was switched from one path to the other using a twisted nematic cell, which rotated the polarization of the pump, and a Wollaston prism. For the nearly parallel path, a second twisted nematic was also used to rotate the pump polarization. In this way, for both paths, the pump was p-polarized. Care was taken that the two paths overlap within the liquid crystal sample. Furthermore the two pump intensities were kept equal using a neutral density filter. The pump diameter (2 mm) was much larger than the sample thickness ( $60\ \mu\text{m}$ ). The probe beam, which had an essentially smaller beam diameter than the pump, propagated through the sample at the center of the pump paths.

### III. Results and Discussion

In Fig. 2, the probe transmission is plotted as a function of the pump intensity. The data are normalized to the linear transmission, i.e. to the probe transmission without pump. The linear transmission coefficient  $T_l$  was 3.8 .



**Figure 2: Nonlinear probe transmission normalized to the linear transmission. Squares: measured data. Continuous line: fit according to Eq. (3). The intensity values here and in subsequent figures refer to the peak intensity of the pump beam, calculated as  $I = P/\pi r^2$ , where  $P$  is the pump power and  $r$  is the pump  $1/e$  radius (1mm).**

The increase of the probe transmission with increasing pump intensity in Fig. 2 is attributed to the formation of cis isomers, which have lower absorption cross-section than the trans isomers. For a quantitative analysis, we took into account the attenuation of the pump intensity,  $I$ , along the sample normal ( $z$ ) direction) described by [14]

$$\frac{dI}{dz} = -\alpha_T \left( 1 + \frac{\alpha_C - \alpha_T}{\alpha_T} X \right) I \quad (1)$$

where  $\alpha_T$  and  $\alpha_C$  are the trans and cis absorption coefficients for the given light propagation direction and polarization, and  $X$  is the fraction of cis isomers. With the help of standard rate equations, taking into account both photoinduced and thermal trans-cis and cis-trans isomerizations,  $X$  can be expressed as

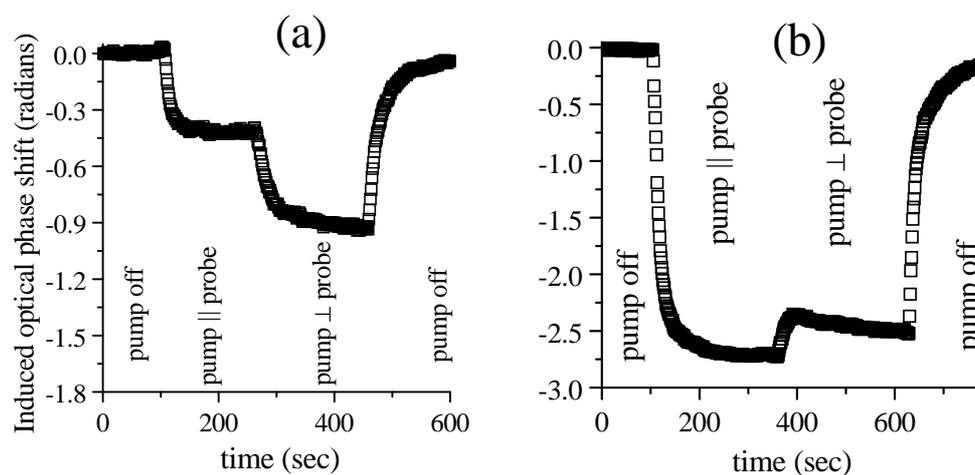
$$X = X_S \frac{I/I_S}{1 + I/I_S} \quad (2)$$

where  $I_S$  is the saturation intensity, and  $X_S$  is the saturation cis concentration of the dye, again for given light propagation direction and polarization. The transmission of the pump is determined by considering that it is attenuated in the same way as the probe. The transmission coefficient normalized to the linear transmission coefficient,  $M$ , is given by the transcendental equation [14]

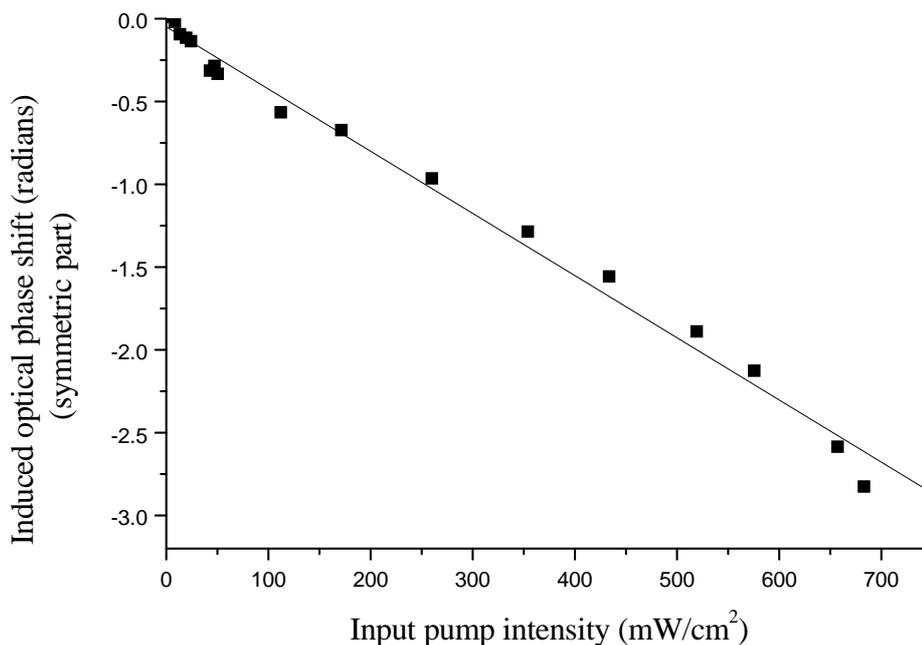
$$\ln M + (1/q - 1) \ln \frac{1 + qMT_l I_{in}/I_S}{1 + qI_{in}/I_S} = 0 \text{ with } q = 1 + \frac{\alpha_C - \alpha_T}{\alpha_T} X_S. \quad (3)$$

The line in Fig. 2 corresponds to the best fit of the data using Eq. (3), giving the parameters  $I_S = 13mW/cm^2$  and  $q = 0.68$ .

The change of the probe birefringence can originate from several sources. Some sources are related to the rate of excitations per unit volume, like thermal effects or nonlinearities caused by generation of electric charges. Others may be related to a change in the order of the liquid crystal upon trans to cis isomerization. In these cases the induced birefringence does not include a change in the direction of the optical axis of the sample. Therefore the change in the shift between the  $e$ - and  $o$ - rays of the probe would be the same as when the pump polarization is reflected into a line parallel to the sample normal. On the other hand, reorientational nonlinearity does include a rotation of the optical axis via director reorientation. In this case, the change in the shift between the  $e$ - and  $o$ - rays of the probe are reversed when the pump polarization is reflected into a line parallel to the sample normal. Using the set-up, shown in Fig. 1, the average of the optical phase shifts, measured at parallel and perpendicular pump-probe configurations gives the contribution of thermal and related mechanisms, while the difference of the birefringence in the two geometries is due to the reorientational nonlinearity.



**Figure 3: Change of the optical phase shift at pump intensity (a)  $172 mW/cm^2$  and (b)  $656 mW/cm^2$ .**

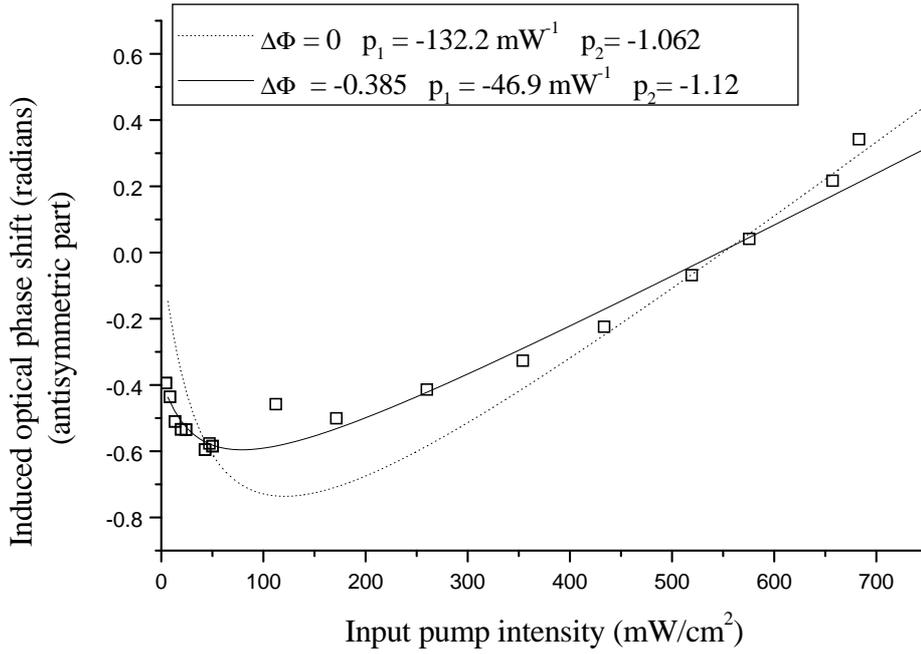


**Figure 4: Average optical phase shift as a function of the input intensity.**

In Fig. 3, the time evolution of the birefringence shift is shown for two different pump intensities. As it can be seen from the figure, the total phase shift is always negative. The change of birefringence upon switching from the parallel to the perpendicular path is, however, negative for the lower pump power and positive for the higher one. The average of the steady-state optical phase shifts as a function of the pump intensity is shown in Fig. 4. The shifts are linear with the input intensity, indicating that thermal nonlinearity probably gives the dominant contribution to this signal. Because this linearity is observed well above the saturation intensity for trans-cis isomerization where the fraction of cis isomers is relatively independent of intensity, it cannot be attributed to a decrease in order from the introduction of the cis isomers.

The difference of the phase shifts is plotted as a function of the pump intensity in Fig 5. As it can be seen from this figure, the reorientational nonlinearity shows the expected qualitative behavior: it is negative at low intensities and becomes positive when the intensity is increased above a critical value. On the other hand, at very low intensities the experimental results appear to disagree with the model, which assumes that the reorientation originates purely from the torques induced by the trans and cis components. From the model, one would expect that near zero input intensity the torque is determined alone by the trans dopant factor, hence the difference in phase shift should increase linearly with pump intensity. The data, however, tend to converge to a constant negative value, at least to the lowest non-zero intensity at which measurement was carried out ( $4.5\text{mW}/\text{cm}^2$ ).

In order to make these considerations quantitative, we first tried to fit the data with the assump-



**Figure 5: Difference in the optical phase shift as a function of input intensity. Open square: measured data. Dashed line: best fit with assuming  $\Delta\Phi_0 = 0$ . Continuous line: best fit, considering  $\Delta\Phi_0$  as a parameter.**

tion that the reorientational phase shift originates entirely from the bulk trans and cis torques. The director distribution can be calculated from the balance of elastic and optical torque. As shown by Marrucci et al [16], for non-isomerizable dyes the torque equation in the linear approximation can be written as

$$K_1 \frac{d^2\Theta}{dz^2} = -\frac{\zeta + n_e^2 - n_o^2}{2n_o^2 c} \sin 2\beta I(z). \quad (4)$$

$\Theta$  is the angle between the director and the substrate plane,  $K_1$  is the splay elastic constant,  $n_e$  and  $n_o$  are the extraordinary and ordinary refractive indices, respectively. The angle of incidence of the pump beam,  $\beta$ , is  $+45^\circ$  for the parallel and  $-45^\circ$  for the perpendicular beam path. For dyes showing photoisomerization, the dopant factor can be expressed as

$$\zeta = \zeta_T(1 - X) + \zeta_C X = \zeta_T + (\zeta_C - \zeta_T) X_S \frac{I/I_S}{1 + I/I_S}, \quad (5)$$

where  $\zeta_T$  and  $\zeta_C$  are the trans and cis dopant factors, respectively. Inserting the above relation into Eq. (4) we obtain

$$\frac{d^2\Theta}{dz^2} = -p_1 \left(1 + p_2 \frac{I/I_S}{1 + I/I_S}\right) I(z), \quad (6)$$

$$\text{with } p_1 = \frac{\zeta_T + n_e^2 - n_o^2}{2n_o^2 c K_1} \sin 2\beta, \quad (6a)$$

$$\text{and } p_2 = \frac{\zeta_C - \zeta_T}{\zeta_T + n_e^2 - n_o^2} X_S. \quad (6b)$$

The difference between the probe phase shifts in the parallel and perpendicular configurations in the linear approximation is [16]

$$\Delta\Phi = 2 \frac{2\pi(n_e^2 - n_o^2)}{\lambda_{pr} n_o^2} \sin \beta_{pr} \int_0^L \Theta(z) dz, \quad (7)$$

where  $\lambda_{pr} = 633\text{nm}$  is the probe wavelength,  $\beta_{pr} = 45^\circ$  is the probe angle of incidence.  $\Theta(z)$  is the solution of Eq. (6) for  $\beta = +45^\circ$ , with the boundary conditions  $\Theta(0) = \Theta(L) = 0$ .

As  $I(z)$  and  $I_S$  are known from the nonlinear transmission measurements, only two parameters,  $p_1$  and  $p_2$ , can be adjusted to find an agreement between the model and the experimental data. In Fig. 5, the dashed line shows the fitting corresponding to the minimal mean square deviation. Although the qualitative features of the theoretical curve are correct, the quantitative agreement is poor. As we pointed out earlier, the reason of the discrepancy is that near zero intensity the data do not follow the linear behavior predicted by the model, they converge instead to a finite negative value.

In order to improve the model, we assume that at very low pump intensities there is an additional mechanism causing light-induced director reorientation. We assume that this extra nonlinearity is saturated even at the lowest non-zero pump intensity, applied in our experiment. The phase shift is therefore

$$\Delta\Phi = \Delta\Phi_{bulk} + \Delta\Phi_0 \quad (8)$$

where  $\Delta\Phi_{bulk}$  is the phase shift originating from the bulk mechanism discussed earlier, and  $\Delta\Phi_0$  is constant in the intensity region investigated. The fit is shown in Fig. 5 by the solid line. The agreement between the theoretical curve and the measured points is now satisfactory with the mean deviation more-or-less corresponding to experimental error.

It is plausible to identify the low-intensity part of the reorientational nonlinearity with the supranonlinear effect reported earlier for methyl-red [12]. In our case, however, its source cannot be the build-up of an internal electric field due to photo-induced charge generation. Such a process would give the same contribution to the phase shift for both beam paths; hence it can modify the average of the phase shifts, but not their difference. On the other hand, photo-induced changes of the director orientation at the liquid crystal-substrate interface could explain the observed anomaly, as suggested also by Lucchetti et al. [13].

The variation of the surface director orientation may arise from the orientational redistribution of the adsorbed dye molecules at the interface. As a result of orientationally selective excitations, less adsorbed dye molecules are oriented parallel to the light polarization direction than perpendicularly to it. It is straightforward to assume that at the surface the director is reoriented towards the maximum of the dye distribution function, i.e. away from the polarization. (This mechanism is analogous with the so-called Weigert effect, observed in polymers and glasses [17, 18].) In accordance with this model,  $\Delta\Phi_0$  was found to be negative.

With the help of Eq. (8), we can estimate the magnitude of the proposed surface tilt variation,  $\delta\Theta_0$ . Assuming that the tilt is the same at both interfaces, one can replace  $\Theta(z)$  by the constant,  $\delta\Theta_0$ . With  $n_o = 1.52, n_e = 1.74$  [16],  $L = 60\mu m$  and  $\lambda = 633nm$ , for  $\Delta\Phi_0 = -0.385$ , we obtain  $\delta\Theta_0 \approx -0.1^\circ$ . This assumption could be proved by an independent measurement of the surface tilt angle e.g. by the magnetic null method [19].

From the fitted values of the  $p_1$  and  $p_2$  parameters one can get also information on the  $\zeta_T$  and  $\zeta_C$  dopant factors. With the help of Eq. (6a), inserting  $p_1 = -46.9mW^{-1}$  and  $K_1 = 0.9 \times 10^{-11}N$  [16], one obtains  $\zeta_T = -584$ . The determination of  $\zeta_C$  requires the knowledge of  $X_S$  for the given angle of pump incidence. In order to get  $X_S$ , the nonlinear transmission measurements should be carried out with different combinations of the pump and probe polarization [14]. Although in the present work we did not perform such measurements, from the data reported earlier [14] we find that  $X_S$  is around 0.5. From Eq. (6b) with  $p_2 = -1.12$ , we can estimate that  $\zeta_C$  is around +1300. As pointed out earlier [10], due to the opposite signs of the trans and cis dopant factors the two isomers compensate to a large extent each others effect; thus the overall dye-induced optical torque is relatively weak, in spite of the huge values of the individual  $\zeta$  parameters.

In conclusion, we demonstrated the peculiar intensity dependence of reorientational nonlinearity in azo-dye containing nematic liquid crystals. The bulk part of the effect can be interpreted in terms of photoinduced formation of cis isomers. The measurements indicate a negative trans and a positive cis dopant factor. This fact has been deduced earlier from the angular dependence of optical reorientation; the present experiment, however, proves it in a more direct way. The measurements at very low intensities point to the existence of another mechanism of optical reorientation, which corresponds to the supranonlinear effect, discovered few years ago [12]. We suggest that it is associated with light-induced changes of the director tilt at the liquid crystal - substrate interface. Such effects were studied in the past, mainly using the dye methyl red. A new feature of our method is that it makes possible to distinguish between birefringence changes due to reorientation, correlated to the polarization direction, and other sources of optical nonlinearities. Extension of this work to other azo dyes might give important hints about the physical process leading to the supranonlinear response.

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