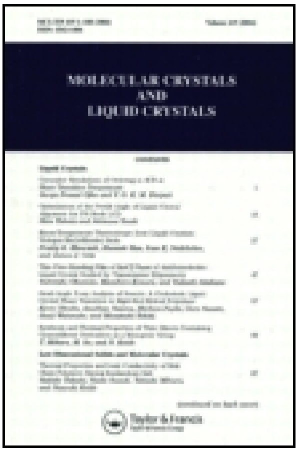

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Control of the Orientational Nonlinearity through Photoisomerization in Dye Doped Nematics

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Photoinduced reorientation in azo dye doped liquid crystals (NLCs) is investigated with consideration of photoisomerization. A model that describes photoinduced reorientation in the presence of photoisomerization [1] is verified in different experimental ways, extending previous investigations. We show that both the magnitude and the sign of the optical nonlinearity for an extraordinary beam can be controlled by an ordinarily polarized beam. Such a control of the nonlinearity provides a new functionality for optical switching and optically addressable spatial light modulators.

Keywords: Photosensitive materials; Dye doped nematics; Enhanced optical reorientation; Photoisomerization; Optical switches

INTRODUCTION

Optically induced reorientation of NLCs has been intensively studied in the last decades. It leads to a large change of the effective refractive index compared to liquids or inorganic materials at the same intensity. The NLC's sensitivity can be enhanced by doping with dichroic dyes [2, 3]. Enhancement factors of almost three orders of magnitude have been observed at dye concentrations of about 1%. Mainly anthraquinone and azo dyes have been used in investigations with the aim to identify the mechanism for the enhancement.

Light-induced anisotropy in solid matrices (polymers, glasses) doped with azo dyes is a well known phenomenon and is a consequence of angular hole burning (Weigert effect). However, in low-molecular mass nematics the rotational mobility of the dye-dopants is very high, rendering inefficient the mechanism responsible for the Weigert effect. A more general model valid for both azo and anthraquinone dyes is based on the idea that intermolecular forces are changed due to the excitation from the ground state to the excited state [4]. According to this model, the angular distribution of excited dye molecules is anisotropic and is related to the direction of the electric field of the optical wave. It has been shown in a mean field model that both a change of intermolecular interaction and of rotational diffusion constants due to the excitation can lead to a photoinduced torque which has the same symmetry as and acts in addition to the optically induced torque on the nematic director. The result is an enhancement of the optical torque and thus of the material's sensitivity:

$$\tau_{light} = \tau_{opt} + \tau_{photo} = (1+\eta)\tau_{opt}, \tag{1}$$

where τ_{opt} is the optical torque, τ_{photo} the photoinduced torque, and η the enhancement factor. The model implies that the photoinduced torque can have the same or the opposite sign of the optical torque depending on the details of the dye-host interaction. Indeed, in the experiments both positive and negative enhancement was observed for different dopants. The model, however, does not take into account the trans-cis photoisomerization of azo dyes.

Barnik et al observed an anomalous dependence of the enhancement factor on the light beam's angle of incidence using a bis-azo dye as dye dopant [5]. This anomalous angular dependence has been interpreted as the interplay of the two photoinduced processes, namely photoinduced reorientation and photoisomerization. Since the details of this model have already been published [1], we only follow a qualitative argumentation here. Similarly to two independent non-isomerizable dye dopants, each of the isomers causes an individual photoinduced torque. The overall photoinduced torque is a superposition of these two contributions, therefore it depends on the concentration ratio between the isomers. The trans-cis-ratio is determined by the photoisomerization process. As for the photoinduced torque, the superposition also applies to the enhancement factor:

$$\eta = C\eta_{cis} + (1-C)\eta_{trans}, \tag{2}$$

with the individual enhancement factors η_{trans} and η_{cis} of the pure isomers and C as the fraction of dye molecules in the cis conformation. It must be pointed out that this model is independent of the mechanism for the photoinduced torque, particularly it is not excluded that the isomerization itself is involved in the enhancement mechanism. The aim of the presented work is to check the model by investigating the dependence of the enhancement factor on variations of the trans-cis ratio in several experimental ways.

Photoisomerization of azo, stilbene and other dyes has been investigated extensively for more than three decades and still is subject of topical research [6-8]. In the following, we will focus on the case of azo dyes. The bent cis isomer is metastable with a certain lifetime due to relaxation to the thermodynamically stable trans state. Photoinduced transitions between the isomers are initiated by absorption of photons by the trans or cis ground state. Subsequently, a fast (~200fs) change to the minimum of the excited state hypersurface [8] and a relaxation to the trans and cis ground states with the quantum efficiencies ϕ_{CT} and ϕ_{TC} follow. Depending on the number of photons absorbed by the trans and cis state, respectively, a dynamic equilibrium between trans and cis isomers results. The absorption spectra of azo trans and cis isomers are generally quite distinct from each other. Trans isomers typically have a strong peak in the blue range, whereas cis isomers have two much weaker absorption peaks: One at shorter and one at longer wavelengths than the trans isomer. For steric reasons, the trans isomer aligns in the NLC host with a higher order parameter than the cis isomer. The unequal order parameters correspond to different dichroism of the isomers. As a consequence, there are four absorption coefficients, for each isomer respectively one for the electric field parallel to the nematic director and one perpendicular to it: $\alpha_{\parallel}^{t}, \alpha_{\perp}^{t}, \alpha_{\parallel}^{c}, \alpha_{\perp}^{c}$. The trans-cis equilibrium depends on the excitation probabilities for the isomers. These excitation probabilities depend on the four absorption coefficients and on the electric field components of the optical wave parallel and perpendicular to the nematic director, $E_{\parallel}$ and $E_{\perp}$. For a single extraordinarily polarized beam, these components are determined by the angle Ψ between the electric field vector and the director. This angle can be varied via the beam's angle of incidence. By the intensity of an additional ordinarily polarized beam, the $E_{\perp}$ component can be varied independently of the extraordinary beam.

Besides the dependence of the *trans-cis* ratio on the light field components and on the wavelength, the intensity-dependent photoinduced *trans-cis* transition competes with the thermal relaxation from cis to trans. At low intensities, the thermal relaxation dominates and at high intensities it can be neglected. The photostationary trans-cis ratio is a saturation function of the intensity, with a saturation intensity I_s inversely proportional to the thermal relaxation time τ.

In this paper we consider at first dyes with long *cis-trans* thermal relaxation times, where the experiments can be performed with intensities well above the saturation intensity. Two different ways of modifying the trans-cis ratio are presented for a number of different azo dyes. First, we vary the angle Ψ via the light beam's angle of incidence. Here we extend the angular range of earlier investigations by complementary measurements in both homeotropic and planar cells. Second, we use an additional ordinarily polarized beam. We will show that both the magnitude and even the sign of the enhancement factor η, i.e. the type of the nonlinearity and its sensitivity can be controlled with the intensity of the ordinary beam. Subsequently, we discuss briefly the case of dyes with high saturation intensities, where in reorientation measurements the intensity is much less than I_s.

EXPERIMENTS

We report results obtained with the azo dyes R4 from Hoffman-Roche, DO3, Para red, DR13 from Aldrich and KI288 from Nematel as dye dopants in the nematic mixture E63 from Merck as host material. The absorbance $\alpha_z d$ of the dye doped samples (dye concentrations ~0.3% w/w) is of the order of 1 and the thickness of the cells is $d = 50\mu\text{m}$.

For an experimental verification of the model proposed in [1] with a number of different isomerizable dyes, information about the photoisomerization of the dyes on the one hand, and about enhancement factors η under a variation of the trans-cis ratio on the other hand has to be gained from independent measurements. Polarization sensitive pump-probe transmission measurements yield the parameters of the dyes which characterize the photoisomerization. Hence, the trans-cis ratio under different experimental circumstances can be calculated and it can be checked if the model fits the experimental data of the measurements of η.

Furthermore, the individual contributions of the pure isomers to the enhancement factor can be determined.

Measurement of enhancement factors in homeotropic samples

In the experiments, the enhancement factor η should be determined both in homeotropic and in planar cells. In the homeotropic case, this is done by measuring the induced birefringence by a pump-probe technique in the dye doped and in an undoped reference cell. The factor η results from [1, 9]:

$$\eta = \frac{\Delta\Phi_d I_r}{\Delta\Phi_r I_d f} - 1, \qquad f = \frac{12}{(\alpha_z d)^2}\left[1 - \left(\frac{1}{2} + \frac{1}{\alpha_z d}\right)\left(1 - e^{-\alpha_z d}\right)\right], \tag{3}$$

where $\Delta\Phi_d$ and $\Delta\Phi_r$ are the induced birefringences in the dye doped and in the reference sample, I_d and I_r are the respective pump intensities, and f is a factor averaging the intensity gradient due to absorption inside the dye doped sample.

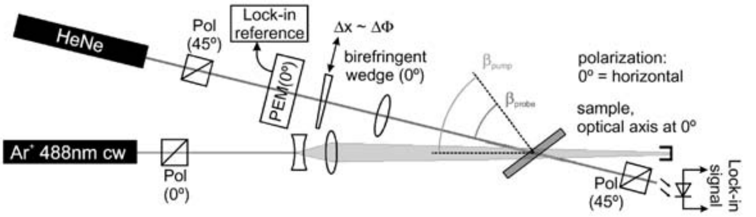

FIGURE 1 Pump-probe setup for the detection of the induced birefringence in homeotropic cells

The experimental setup is shown in figure 1. A horizontally polarized cw pump beam from the 488nm line of an Ar^+ laser impinges the sample at the angle of incidence β_{pump}. The $1/e^2$ beam diameter at the sample is 400μm. The probe wavelength 633nm is outside the absorption band of the dyes, i.e. the probe beam only detects changes in birefringence. The determination of the induced birefringence in the probe line is based on a crossed polarizer arrangement. Between the crossed polarizers, which include an angle of 45° with the pump polarization, three birefringent elements are aligned with their optical axes horizontally: A photoelastic modulator (PEM), a birefringent wedge and the sample. The birefringence of the PEM is modulated at 42kHz. The first harmonic I_1 of the intensity behind the analyzer is detected by means of a lock-in amplifier. For this configuration, it can be shown that

$$I_1 = \hat{I}_1 \sin(\Delta\Phi). \tag{4}$$

Ideally, $\hat{I}_1$ is a constant, but in the experiments averaging effects due to the finite beam size and scattering or depolarization inside the sample influence $\hat{I}_1$. However, the zeros of the sine in equation (4) remain unaffected. For this reason, we adjust the position of the birefringent wedge such that $I_1 = 0$ when the pump beam is off. After the pump beam is switched on and transients have ceased, we determine the induced birefringence by shifting the wedge until $I_1 = 0$ again.

In addition to the induced birefringence caused by reorientation of the director, laser heating changes the NLC order parameter and so the refractive indices change as well. In homeotropic cells, the resulting contribution to the induced birefringence can be separated from the reorientational part if two measurements are performed. In the first, both the reorientational and thermal effect are measured. In the second, reorientation is avoided by application of a strong quasi-dc electric field via ITO electrodes on the glass substrates of the cell. Since the reorientation angle is small, no large differences of the absorption due to dichroism or photoisomerization are present between the two experiments. Subtraction of the two measurements yields the pure reorientational contribution.

In the experiments we took care to avoid surface realignment effects, which can also be present in dye doped NLC cells. The surface effect, however, has different dynamics and is, at least on the order of minutes, irreversible. First, we observed the dynamics and verified that the effect is reversible during the experiment. Second, we checked the surface alignment after an experiment under a polarizing microscope. In this way we proved that our observations were due to bulk reorientation.

Measurement of enhancement factors in planar samples

In planar cells, the correction for thermal contribution to the nonlinear phase shift is less straightforward than in the homeotropic case. Superposing an electric field on the light wave would enlarge the director tilt instead of compensating it. In addition, due to the positive dichroism of the dyes, the heating effect is also larger in this geometry.

In order to overcome this problem, we applied a new method [10], which is in first order approximation independent of laser heating. The underlying idea of the method is based on the fact that planar cells prepared with the Polyimide rubbing technique have a pretilt of some degrees (here: ~2°). Photoinduced reorientation can be used to tilt the director in the opposite direction of the pretilt in the area where the beam impinges the sample. If a strong quasi-dc electric field is switched on, the molecules reorient further in the preoriented direction. As a consequence, a disclination line is generated between the area previously reoriented by light and the non-illuminated area. It is clear that there is a critical intensity I^{th} for the creation of such a disclination loop, as the director must be reoriented enough to overcome the pretilt. The loop can easily be observed as a characteristic diffraction pattern on a screen behind the sample. The enhancement factor is determined by the ratio of the threshold intensities in the dye doped and in an undoped reference sample:

$$\eta = \frac{I_d^{th}}{I_r^{th} f} - 1 . \tag{5}$$

The method also allows us to obtain the sign of the nonlinearity. In the plane of incidence containing the director, there exist two directions with the same absolute value of the incident angle. The two beams are not equivalent, because loop formation occurs only with the beam reorienting the director opposite to the pretilt. In the case of positive enhancement, the incidence directions with respect to the pretilt for the undoped and the dye doped sample are the same, while if $\eta + 1 < 0$, they are interchanged.

RESULTS

1) Variation of the trans-cis equilibrium via the angle of incidence

The anomalous angular dependence of the enhancement factor η is investigated in detail for various azo dye dopants. The model that we want to check, predicts the dependence of η on the angle Ψ between the electric field of the optical wave and the director if the pump intensity is above the saturation intensity I_S. Due to refraction, the internal angle of incidence is smaller than the external one β_{pump}. In planar cells, Ψ is a monotonously increasing function of the angle of incidence, whereas in the homeotropic case it is a decreasing one. Hence, the measurements in planar and homeotropic samples are complementary, such enabling us to cover a larger range of Ψ. In the experiments with homeotropic samples, the external angle of incidence is varied between 20° and 50°, in planar cells from 10° to 70°, such covering a range of Ψ between 10° and 80°, with a gap from 42° to 66°.

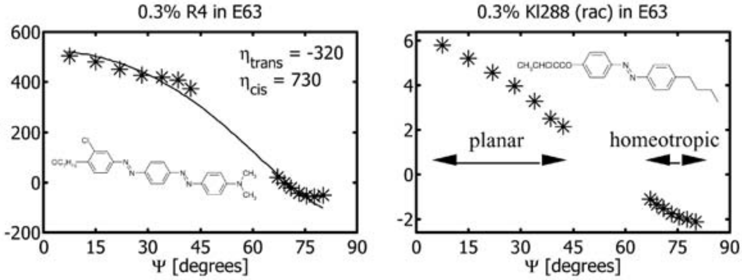

FIGURE 2 Angular dependence of the enhancement factor of two azo dyes (chemical formulas shown in the insets). The data from homeotropic and planar cells are indicated in the rhs plot. The line in the lhs plot is a least square fit with the model from [1], with the fit parameters η_{trans} and η_{cis}.

Figure 2 shows the results of such measurements for two different azo dyes. The least square fit with the only fit parameters η_{trans}= -320 and η_{cis}= 730 for the dye R4 shows a very good agreement between the model and the data. The fit could not be performed in the case of Kl288, because the characteristic dye parameters where not measurable due to a very weak absorption at 488nm. The weak absorption also manifests in relatively small values of the enhancement factor.

We also detect analogous sign-inversion in the case of DO3. In a recent publication Kitaeva et al. report similar results on three further azo dyes [11]. All these cases indicate that the pure trans isomer has a negative and the cis isomer has a positive enhancement factor. This feature is a hint to a general mechanism for the dye enhanced reorientation in azo dye doped NLCs.

2) Control of the trans-cis equilibrium with an independent beam

As mentioned in the introduction, the model predicts a dependence of the enhancement factor on the intensity of an ordinary beam which is independent of the reorienting beam. The dependence of the enhancement factor means a dependence of the nonlinear optical material's sensitivity on the control beam intensity. Furthermore, a change of the sign of η

implies a change of the sign of the nonlinear optical coefficient for the extraordinary beam, i.e. a light-induced change from a self-focussing nonlinearity to a self-defocusing one or vice versa. This is a new functionality not realized in any other material so far. Unambiguous experimental evidence for this unique feature of azo dye doped NLCs is given by the data in figure 3.

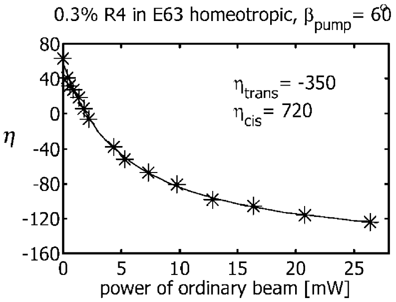

FIGURE 3 Control of the enhancement factor by the power of an additional ordinary beam. The line is a least square fit. The power of the extraordinary beam is 10 mW.

A homeotropic cell is used in this experiment and the external angle of incidence is β_{pump}= 60° ($\Rightarrow\Psi$= 64°). If only the extraordinary beam is present, the enhancement factor is positive in accordance with the lhs plot in figure 2. An ordinary control beam is added from a second, vertically polarized Ar^+ laser to the setup in figure 1. This beam is coupled into the pump line with the polarizing beam splitter. The extraordinary reorienting beam and the ordinary control beam have approximately the same beam diameter at the sample.

In addition to causing the reorientation, the extraordinary beam induces a certain trans-cis ratio. When the power of the control beam is increased, the trans-cis equilibrium is shifted progressively to the trans side, because the ordinary beam is more likely to excite cis molecules due to the lower order of this isomer. As a result, the enhancement factor gradually decreases, changes its sign and decreases further to larger negative values. A least square fit with the model yields the values η_{trans}= -350 and η_{cis}= 720 which is in good agreement with the values determined in the angular dependent measurements for the same dye. A qualitatively similar behavior can be observed with other azo dyes as well.

3) Variation of the trans-cis equilibrium at intensities below I_s

As it can be seen from Table 1, the azo dyes Disperse Red 13 and Para Red are distinguished from other dyes by short thermal cis-trans relaxation times (ms). For these dyes, only a very small change of the absorption coefficients due to photoisomerization is found in pump-probe absorption measurements. In parallel, their behavior in angular dependent measurements and in the experiments with an ordinary control beam differs clearly from the one described above. For DR13 the enhancement factor is found to be negative both in homeotropic and planar cells; its absolute value decreases when the pump intensity is increased or a superposed ordinarily polarized beam is applied.

Dye	R4	DO3	Para Red	DR13
τ	10s	0.9s	7.5ms	1.7ms

TABLE 1 Thermal relaxation times of different azo dyes

In order to interpret the observations, we remark that the thermal relaxation time, τ, is inversely proportional to the saturation intensity I_s. The saturation intensity of DR13 and Para Red is therefore more than two orders of magnitude higher than of the other dyes. We ascribe the observed behavior of DR13 and Para Red to the fact that the intensity is well below the saturation intensity. In this intensity regime the cis concentration is increasing both with the intensity of the pump and the control beam.

The intensities in the reorientation experiments cannot just be increased, because thermal effects or even melting to the isotropic phase make measurements at high intensities impracticable. In addition, the temperature dependence of the enhancement factor due to temperature induced changes of order parameters can give a similar effect as the change of the cis concentration. Further investigations on this topic are currently on the way.

CONCLUSIONS

Azo dye doped NLCs are highly sensitive nonlinear optical materials. Furthermore, the magnitude and the sign of the nonlinearity can be controlled with an independent ordinary beam. Both properties, the sensitivity and the controllability make this material candidates for optically addressable light modulators with a spatially controllable sensitivity. All-optical switches with two inputs and one output performing logical operations could be implemented by using the described control of the nonlinearity.

The angular dependent measurements both in homeotropic and planar samples and the experiments with a control of the enhancement factor for a number of different azo dyes confirm the model that the trans and cis isomers contribute individually to the enhancement of the optical torque. With the exception of two dyes in which the thermal cis-trans relaxation dominates, all dyes show a positive enhancement factor of the cis and a negative one of the trans isomer. This is a hint to a general mechanism of photoinduced reorientation with isomerizable dyes.

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