PHYSICAL REVIEW E VOLUME 58, NUMBER 4 OCTOBER 1998

Optical reorientation of nematic liquid crystals in the presence of photoisomerization

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(Received 21 April 1998)

The optical reorientation of nematic liquid crystals doped with azo dyes is studied. It is shown that in the presence of absorption both the *trans* and *cis* isomers enhance significantly the optical torque; they contribute, however, with opposite signs to the net enhancement and tend to cancel each other's effect. The anomalous angular dependence of optical reorientation reported by Zolotko *et al.* is explained by considering the photoinduced *trans-cis* equilibrium. [S1063-651X(98)03510-7]

PACS number(s): 61.30.−v, 42.65.Vh

I. INTRODUCTION

The reorientation of nematic liquid crystals (NLC's) by optical fields was investigated extensively in the past [1]. In transparent materials, the observations can be fully understood with the help of classical electrodynamics and the standard continuum description of liquid crystals. The electromagnetic field exerts a torque on the liquid crystal molecules due to their anisotropic molecular polarizibility; this torque is balanced by the elastic and viscous torque associated with the spatial nonuniformity and rotation of the nematic director. In the presence of light absorption, however, puzzling new effects were discovered that could not be interpreted within the framework of the macroscopic phenomenological theory. It was found that when small amounts of absorbing dyes are added to NLC's (typically less than 1%), the optical torque increases significantly, in some cases by more than two orders of magnitude [2–5]. The strength of the additional absorption-induced torque is highly dye specific and does not show any direct correlation with the absorption coefficient of the system. For some dyes the absorption-induced torque was found to have the same sign as the dielectric optical torque, while for others the signs are opposite.

In order to explain the effect described above, molecular models were worked out [6–8]. The common starting point of the models is the fact that in the presence of absorption the orientational distributions of the ground-state and excited-state dye molecules are not axially symmetric around the director. Due to this asymmetry, the molecular mean field associated with the dye molecules exerts an effective torque on the director. In Ref. [6], the change of the dye-host interaction energy upon excitation was considered as the main source of the absorption-induced torque. In Ref. [8] it was shown that the difference between the rotational mobility of the ground-state and excited-state molecules can contribute also to the enhancement of the optical torque. The models successfully describe the basic experimental facts and account for the order of magnitude of the observed enhancement. Recently, it was shown that the same idea can be applied even to dye-doped isotropic liquids, in which a similar amplification of the optical Kerr effect was found [9].

On the other hand, Barnik *et al.* reported observations in a NLC doped with azo dyes, which seem to contradict the existing models [10]. These authors found that, in their particular system, the absorption-induced torque changes sign as the angle between the wave vector of the light beam and the director is varied; namely, it is negative for small angles and becomes positive above a critical angle. Such behavior disagrees with theoretical predictions as well as with observations on anthraquinone dyes. Considering the symmetry properties of the nematic phase, one expects that the ratio of the absorption-induced and dielectric torque (''enhancement factor'') is independent of the direction of light propagation. The anomaly found by Barnik *et al.* indicates, on the contrary, a pronounced angular dependence of the enhancement factor.

In a very recent publication, we suggested that the observed angular dependence of the absorption-induced torque in azo dye doped NLC's is caused by *trans-cis* photoisomerization [11]. The basic point of our model is that *trans* and *cis* forms of azo compounds can be regarded as two separate dye dopants that contribute with different strengths or even signs to the overall optical torque. It was demonstrated earlier that the photoinduced equilibrium *cis* concentration depends on the angle of incidence of the light beam [12]. As a consequence, the net optical torque, which is a superposition of the contributions from the two isomers, also depends on this angle.

The aim of the present paper is to investigate in detail the process of optical reorientation in the presence of photoisomerization and to provide further evidence of the proposed mechanism. In Sec. II, a simple relation is given for the equilibrium *cis* concentration as a function of the beam propagation direction. The relation is verified experimentally for an azo dye. In Sec. III, measurements of the enhancement factor for the same dye are presented as a function of the angle of incidence. It is found that the enhancement factor is a linear function of the *cis* concentration, as expected from the suggested model. The *trans* and *cis* enhancement factors are deduced separately from the data; the former has a large negative, the latter has a large positive value. For comparison, another azo dye was investigated too, which does not show photoisomerization. In this case, no angular dependence of the enhancement factor was found.

To provide further verification of the role of *trans-cis* transitions in optical reorientation, we carried out an experiment in which the equilibrium *cis* concentration was regulated independently from the reorientation process (Sec. IV). In the experiment, an ordinarily polarized component was superposed on the reorienting beam. Although the *o* ray in itself did not cause any director reorientation, its presence modified the *cis* content within the illuminated area and thus influenced the enhancement factor. By increasing the strength of the ordinary component, even a change of sign of the enhancement factor was achieved. This observation provides a strong support of our idea about the mechanism of optical reorientation in azo dye doped NLC's.

In Sec. V, we discuss the possible reasons for the opposite signs of the enhancement factors found for the two isomers. We point out that changes of the geometrical shape of the dye molecule during *trans-cis* photoisomerization can be the source of the observed behavior.

II. PHOTOINDUCED *trans-cis* EQUILIBRIUM

Most azo dyes have two stable configurations. In the energetically more favorable *trans* form, the two chemical bonds attached to the central nitrogen group are parallel to each other, resulting in an elongated form of the molecule. In the *cis* form, the angle between these bonds is 120° and the molecule adopts a V-like shape. The two isomers differ in their absorption spectra. In addition, their orientational order in NLC's are different too, namely, the *trans* form is significantly more ordered than the *cis* one [12].

In thermal equilibrium the molecules are in the *trans* form. Light irradiation converts a fraction of the molecules to the *cis* form [13]. In a previous publication [12], we showed that the equilibrium *cis* concentration and other parameters can be deduced from simple transmission measurements. Here, we follow a slightly different approach, which is more suitable for our present aim, i.e., the determination of the angular dependence of the fraction of the *cis* isomers.

The starting point of the discussion is the rate equation for the number of *cis* isomers per unit volume, N_C:

$$\frac{dN_C}{dt}=-N_C(p_C\Phi_{CT}+1/\tau)+N_Tp_T\Phi_{TC}. \tag{1}$$

Here N_T is the number of *trans* isomers per unit volume, p_C and p_T are the probability that a *cis* or a *trans* molecule is excited within a unit time, respectively, Φ_{CT} and Φ_{TC} denote the quantum efficiency of a *cis-trans* or *trans-cis* transition, respectively, finally τ is the thermal relaxation time for *cis-trans* transitions. We write $N_C=NX$ and $N_T=N(1-X)$ where N is the total number of dye molecules per unit volume and X is the fraction of *cis* molecules. From Eq. (1), in steady state

$$X=\frac{X_S}{1+\tau_0/\tau}\quad\text{with}\quad X_S=\frac{p_T\Phi_{TC}}{p_T\Phi_{TC}+p_C\Phi_{TC}},$$

$$1/\tau_0=p_T\Phi_{TC}+p_C\Phi_{TC}. \tag{2}$$

τ_0 is the characteristic time for the formation of the steady-state *cis* concentration. It decreases as the light intensity is increased; in the limit $\tau_0/\tau\ll 1$ the fraction of the *cis* isomers approaches the saturation value X_S. In typical reorientation experiments the light intensity is high enough to saturate the number of *cis* isomers.

In order to find out how p_C and p_T depend on the light propagation direction, let us first consider a single dye dopant. The dissipated energy per unit time and volume is

$$\mathcal{D}=\hbar\omega Np, \tag{3}$$

where p is the excitation probability per unit time. Macroscopically, the dissipation is given as

$$\mathcal{D}=\varepsilon_0\omega\vec{e}\boldsymbol{\varepsilon}''\vec{e}E^2, \tag{4}$$

where $\boldsymbol{\varepsilon}''$ is the imaginary part of the dielectric tensor, E is the effective field strength, and $\vec{e}$ is a unit vector along the electric field. The components of $\boldsymbol{\varepsilon}''$, as for any tensor in a NLC, can be written as $\varepsilon''_{ij}=\varepsilon''_\perp\delta_{ij}+(\varepsilon''_\parallel-\varepsilon''_\perp)n_in_j$ where $\vec{n}$ is the director, i.e., the symmetry axis of the system. Therefore $\vec{e}\boldsymbol{\varepsilon}''\vec{e}=\varepsilon''_\perp+(\varepsilon''_\parallel-\varepsilon''_\perp)\cos^2\Psi$ where Ψ is the angle between the director $\vec{n}$ and the polarization direction $\vec{e}$. Inserting this expression into Eq. (4) and comparing it with Eq. (3), one finds

$$p=[f_\perp+(f_\parallel-f_\perp)\cos^2\Psi]E^2\quad\text{with}\quad f_\perp=\varepsilon''_\perp/N\hbar,$$

$$f_\parallel=\varepsilon''_\parallel/N\hbar. \tag{5}$$

Returning to the azo dyes, in the limit of low concentrations and low light intensity levels we can regard the two isomers as independent dopants and assume that their orientational distributions correspond to a thermal equilibrium. In this case the above argument can be applied separately to p_C and p_T, hence

$$\begin{aligned}p_C&=[c_\perp+(c_\parallel-c_\perp)\cos^2\Psi]E^2,\\ p_T&=[t_\perp+(t_\parallel-t_\perp)\cos^2\Psi]E^2.\end{aligned} \tag{6}$$

The *c* and *t* coefficients depend on molecular parameters and the orientational order of the isomers, but they are independent of the dye concentration and *X*. Equation (6) could have been also derived from microscopic considerations by averaging over the orientational distributions; the present argument is, however, more general.

Inserting Eq. (6) into Eq. (2) we find

$$X_S=X_{\text{ord}}\frac{1+g\cos^2\Psi}{1+h\cos^2\Psi} \tag{7}$$

with

$$X_{\text{ord}}=\frac{At_\perp}{At_\perp+c_\perp},\quad g=\frac{t_\parallel-t_\perp}{t_\perp},\quad h=\frac{A(t_\parallel-t_\perp)+c_\parallel-c_\perp}{At_\parallel+c_\perp},$$

$$\text{and}\quad A=\Phi_{TC}/\Phi_{CT}.$$

X_{ord} gives the saturated *cis* concentration for an ordinarily polarized beam; it is independent of the light propagation direction.

To verify the angular dependence of X_S, predicted in Eq. (7), and to determine the values of g and h, we carried out pump-probe experiments on a guest-host system, containing 0.3% 4′-dimethylaminophenyl-[1,4-phenylenebis(azo)]-3-chloro-4-heptyloxy benzene ($R4$) in the nematic mixture

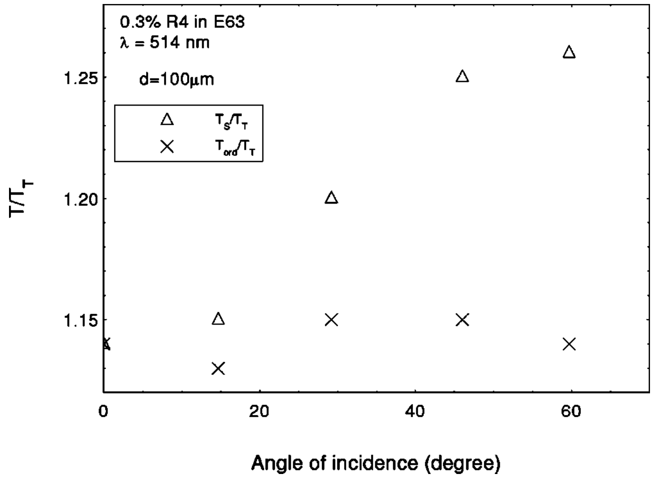

FIG. 1. Transmission of the probe beam, normalized to the initial transmission, T_T, at different angles of incidence of the pump beam. Pump power 6 mW, spot radius 1 mm. Angle of incidence of the probe beam 45°.

$E63$. A homeotropically aligned cell was prepared with a sample thickness of 100 μm. An Ar laser beam was split to a pump and a probe beam. The former was unfocused, the latter was focused to the center of the pump beam and sufficiently attenuated to avoid its influence on the photoisomerization process. The probe beam had a fixed angle of incidence and was polarized in the plane of incidence. Its transmission was measured without the pump beam, with pump at extraordinary and with pump at ordinary polarization, for various propagation directions of the pump.

The transmission of the probe is $T=T_0e^{-\alpha_z d}$ where T_0 is the transmission of an undoped sample, d is the sample thickness, α_z gives the attenuation of the probe beam along the z direction (normal to the plates). α_z can be given as a linear superposition of the contributions from the two isomers:

$$\alpha_z=X\alpha_C+(1-X)\alpha_T. \tag{8}$$

The measurements without a pump correspond to $X=0$, those with an e-polarized pump to X_S, and those with an o-polarized pump to X_{ord}. Denoting the corresponding transmissions by T_T, T_S, and T_{ord} we have

$$T_T=T_0e^{-\alpha_T d}, \quad T_S=T_Te^{-(\alpha_C-\alpha_T)X_S d},$$

$$T_{\mathrm{ord}}=T_Te^{-(\alpha_C-\alpha_T)X_{\mathrm{ord}}d}. \tag{9}$$

From these relations we obtain

$$X_S/X_{\mathrm{ord}}=\frac{\ln T_S/T_T}{\ln T_{\mathrm{ord}}/T_T}. \tag{10}$$

In Fig. 1 the measured transmission ratios are shown. As expected, T_{ord}/T_T was found to be independent of the beam propagation direction. On the other hand, T_S/T_T varied in a systematic way as the angle of incidence, β, was increased. In Fig. 2, we plot the X_S/X_{ord} values, deduced from the measured transmissions. The Ψ angle was calculated from β, as

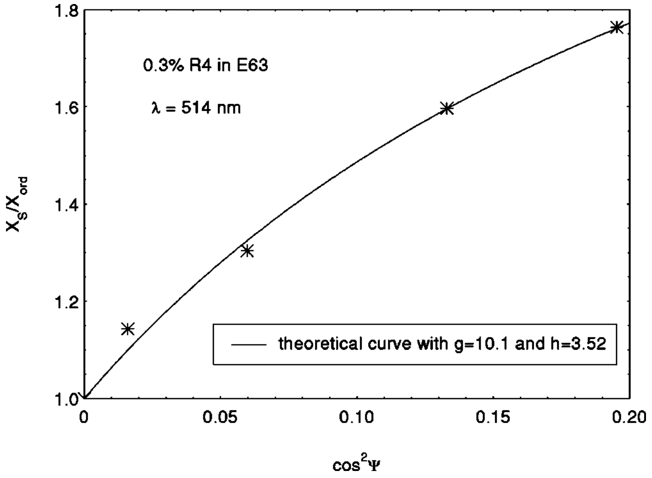

FIG. 2. Comparison of the theoretical curve [Eq. (7)] with the experimental points. To calculate the Ψ angle, the refractive indices of $E63$ were used, $n_o=1.52$ and $n_e=1.75$.

$$\cos^2\Psi=\frac{n_o^2\sin^2\beta}{n_e^4-(n_e^2-n_o^2)\sin^2\beta}. \tag{11}$$

The fitted curve in Fig. 2 corresponds to Eq. (7), with the fit parameters $g=10.1$ and $h=3.52$.

From these measurements alone, it is not possible to determine X_{ord}. As discussed in Ref. [12], one can obtain the full set of parameters if further measurements are performed with ordinarily polarized probe beam. Here we do not repeat this rather sophisticated procedure; we adopt the value $X_{\mathrm{ord}}=0.26$, that was reported in Ref. [12] for the same guest-host system.

III. MEASUREMENT OF THE ENHANCEMENT FACTOR

In transparent materials, the optical torque is

$$\vec{\Gamma}_{\mathrm{opt}}=\varepsilon_0(n_e^2-n_o^2)(\vec{n}\cdot\vec{E})\vec{n}\times\vec{E}. \tag{12}$$

The additional absorption-induced torque can be given in the form

$$\vec{\Gamma}_a=\eta\vec{\Gamma}_{\mathrm{opt}}, \tag{13}$$

where η is the enhancement factor. As explained in the Introduction, for a single dye dopant η should be independent of the direction of light propagation. In the presence of *trans-cis* photoisomerization, we can regard again the two isomers as separate dyes, which give independent contributions to the absorption-induced torque. The enhancement factor can be written as

$$\eta=X\eta_C+(1-X)\eta_T=\eta_T+(\eta_C-\eta_T)X, \tag{14}$$

where η_C and η_T characterize the strength of the absorption-induced torque for the *cis* and *trans* isomers, respectively. η_C and η_T have no angular dependence, but X and thus η depend on the Ψ angle between the director and the polarization direction. If the light intensity is sufficient to saturate the *cis* concentration ($X=X_S$), the angular dependence of η is

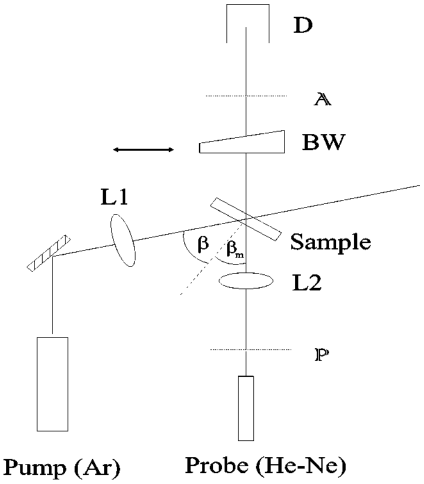

FIG. 3. Experimental setup used to measure the enhancement factor. *P*: polarizer; *A*: analyzer; BW: birefringent wedge; *D*: detector. The focal length of the *L*1 and *L*2 lens was 27 and 10 cm, respectively.

$$\eta = \eta_T + (\eta_C - \eta_T) X_S, \tag{15}$$

where X_S is given by Eq. (7).

To determine the enhancement factor, one has to compare optical reorientation in a doped and an undoped sample under the same geometrical conditions. In previous works, the *Z*-scan method was used to measure quantitatively the director reorientation [14,15]. In the present work, we applied a pump-probe method, in some aspects similar to the one reported in [16]. The experimental setup is sketched in Fig. 3. The optical torque was induced by an Ar laser, and focused on the sample with lens *L*1. The probe beam was the 633-nm line of a He-Ne laser; at this wavelength the investigated guest-host mixtures were transparent. The probe was polarized in 45° with respect to the plane of incidence and focused with the lens *L*2 on the center of the illuminated region of the sample. Behind the sample, a movable birefringent wedge was placed, followed by an analyzer, crossed to the polarizer. The detector signal was recorded as a function of the wedge position, with and without the pump beam.

In plane-wave approximation, the intensity at the detector is

$$I = A_0 \sin^2(q\xi + \Phi/2), \tag{16}$$

where ξ is the position of the wedge, and q is a constant depending on the wedge angle. Φ is the phase difference between the *e* and *o* components of the probe beam behind the sample. The $\Delta\Phi$ difference between the Φ values in the undistorted and the reoriented samples was calculated in Ref. [16]. For a homeotropic layer, in the linear approximation it is

$$\Delta\Phi = (1+\eta) k \sin(2\beta) \sin(\beta_m) d^3 T_0 f I_d, \tag{17}$$

where β_m is the angle of incidence of the probe beam; k is a factor that depends on material parameters of the host [$k = \pi/12\ (n_e^2 - n_o^2)^2/\lambda c n_e^4 K_3$ where K_3 is the bend elastic constant]. I_d is the input intensity and f is an averaging factor:

$$f = \frac{12}{(\alpha_z d)^2}\left[1 - \left(\frac{1}{2} + 1/\alpha_z d\right)(1 - e^{-\alpha_z d})\right]. \tag{18}$$

For an undoped sample $\eta = 0$ and $f = 1$, hence the $\Delta\Phi_u$ phase shift measured in this case, at an intensity I_u is

$$\Delta\Phi_u = k \sin(2\beta) \sin(\beta_m) d^3 T_0 I_u. \tag{19}$$

From Eqs. (17) and (19) one finds

$$\eta = \frac{\Delta\Phi / f I_d}{\Delta\Phi_u / I_u} - 1. \tag{20}$$

For finite beam sizes, the input intensities I_d and I_u can be replaced by the corresponding input powers, P_d and P_u, hence η can be calculated from the measured $\Delta\Phi$'s as

$$\eta = \frac{\Delta\Phi / f P_d}{\Delta\Phi_u / P_u} - 1. \tag{21}$$

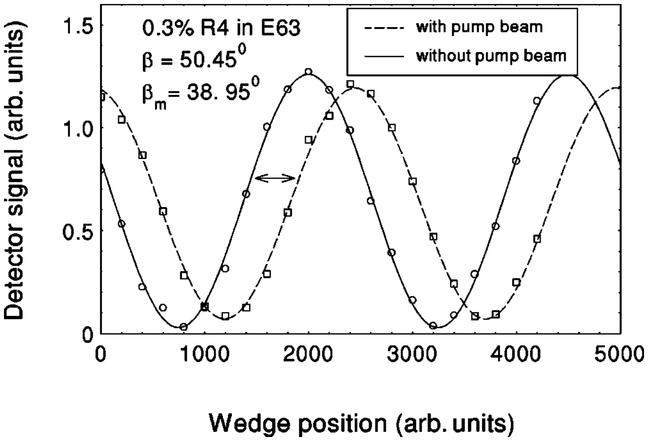

FIG. 4. Example of the recorded curves. Input power 0.13 mW. The fitted curves correspond to Eq. (22); the phase shift between the two curves is 62.2°.

In Fig. 4, experimentally recorded curves are shown. The data points were fitted with the function

$$I = (A_0 - 2\delta) \sin^2(q\xi + \Phi/2) + \delta, \tag{22}$$

where the factor δ accounts for the depolarization of the beam. δ was significant only in the distorted state, indicating that the main source of depolarization was the finite beam size. We note that—in linear approximation—depolarization does not effect the $\Delta\Phi$ values, provided that the probe beam is properly centered within the distorted region. The $\alpha_z d$ values, necessary to calculate *f*, were determined from transmission measurements.

In Fig. 5 the η values are shown for the *R*4 dopant as a function of the angle of incidence of the pump beam. In the dyed sample typical intensities at the center of the beam were around 50 mW/mm^2, so complete saturation of the *cis* concentration was ensured. In Fig. 6 η is plotted as a function of X_S, calculated according to Eq. (7) with the *g* and *h* values

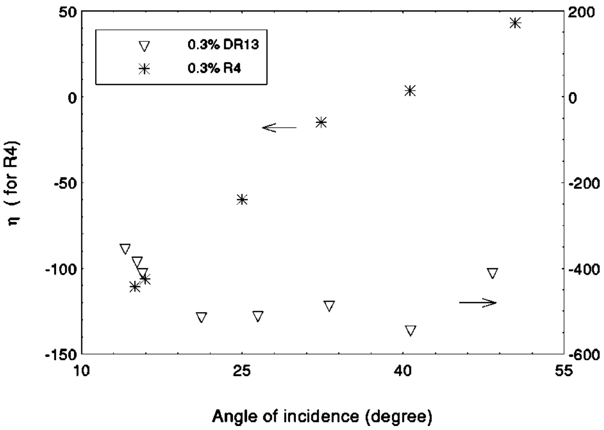

FIG. 5. η as a function of the angle of incidence for $R4$ and DR13.

reported in Sec. II. As can be seen from the figure, the predicted linear relation [Eq. (15)] is satisfied, with the values $\eta_C = 610$, $\eta_T = -450$.

For comparison, we carried out the same measurement with the dye dopant Disperse Red 13 (2-[4-(2-chloro-4-nitrophenylazo)-*N*-ethyl-phenylamino]ethanol). With this dye no photoisomerization can be observed [12]. In accordance with our expectations, no significant angular variation of η was found in this case (Fig. 5); η has a large negative value through the range of β angles studied. A slight decrease of η was observed as the incidence approached to the normal direction. This fact might be due to the increasing difficulty to measure in the linear regime in the limit $\beta \to 0$. The experiments clearly show, however, the striking qualitative difference in the behavior of isomerizable and nonisomerizable dyes.

IV. CONTROL OF THE ENHANCEMENT FACTOR BY AN o-RAY

According to our suggestion, the angular dependence of the enhancement factor is a consequence of the variation of the equilibrium *cis* fraction with the light propagation direction. In the experiments described in the previous section, the pump beam was extraordinarily polarized; its propagation direction determined X_S and thus η. In this section, we discuss the effect of a superposed ordinarily polarized component. It is evident that the presence of an *o* ray modifies the *trans-cis* equilibrium. Thus we expect that although an ordinary component in itself does not induce director reorientation, it should influence the optical torque exerted by the *e* ray through changing the value of X_S and therefore the enhancement factor.

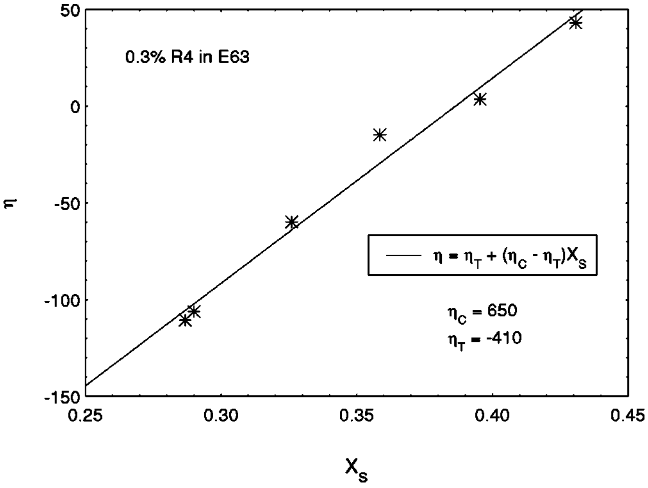

FIG. 6. η as a function of the *cis* fraction, X_S. X_S was calculated using Eq. (7) with $X_{\text{ord}} = 0.26$, $g = 10.1$, and $h = 3.52$.

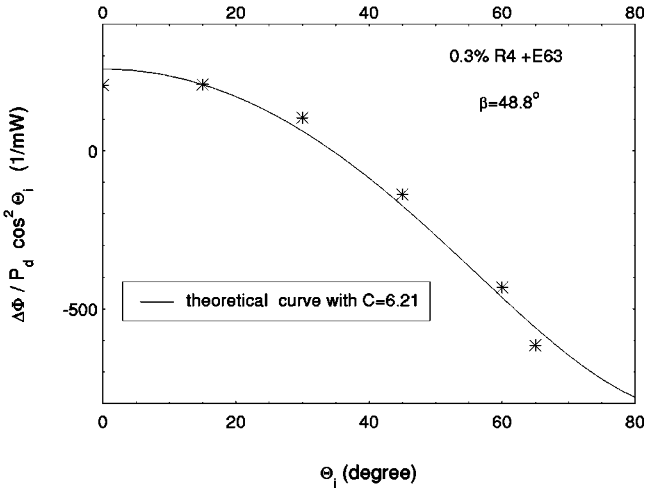

FIG. 7. Normalized phase shift as a function of the polarization angle of the input beam. Input powers were in the range 0.1–0.2 mW. The fitted curve corresponds to Eq. (26).

We consider a light beam, with an electric field $\vec{E} = E_e \vec{e}_e + E_o \vec{e}_o$, where $\vec{e}_e$ and $\vec{e}_o$ are the polarization vectors for the *e* ray and *o* ray, respectively. Taking into account that $\vec{e}_o$ is orthogonal to both $\vec{n}$ and $\vec{e}_e$, one finds from Eq. (4) that the dissipated energy is an independent superposition of the dissipations of the components. The same must hold for the excitation probabilities, hence

$$p_C = [c_\perp + (c_\parallel - c_\perp)\cos^2\Psi]E_e^2 + c_\perp E_o^2,$$

$$p_T = [t_\perp + (t_\parallel - t_\perp)\cos^2\Psi]E_e^2 + t_\perp E_o^2. \tag{23}$$

Inserting the above expressions into Eq. (2), we find after a simple calculation

$$X_S = X_{\text{ord}} \frac{1 + g\cos^2\Psi\cos^2\Theta}{1 + h\cos^2\Psi\cos^2\Theta} \quad \text{with} \quad \tan\Theta = E_o/E_e. \tag{24}$$

The enhancement factor is therefore

$$\eta = \eta_T + (\eta_C - \eta_T)X_{\text{ord}} \frac{1 + g\cos^2\Psi\cos^2\Theta}{1 + h\cos^2\Psi\cos^2\Theta}. \tag{25}$$

For dopants with $g > h$ (like $R4$), the superposed *o* ray decreases the *cis* concentration and shifts η towards negative values. An experimental verification of this effect is shown in Fig. 7. In the experiment, $\Delta\Phi$ was measured as a function of the polarization angle of the pump beam, Θ_i, at an angle of incidence $\beta = 48°$ ($\Psi = 67.5°$). In agreement with our considerations, the $\Delta\Phi$ phase shift changed from positive values to negative ones as the Θ_i angle was increased. No similar effect was observed in the case of the undoped sample.

A somewhat simplified quantitative interpretation of the data can be given if we substitute the Θ angle in Eq. (24) with the angle at the entrance face of the sample, i.e., Θ_i. (In reality, the ratio of E_o to E_e, which defines Θ, changes to a certain extent along the beam path, because the *o* ray and *e* ray are differently attenuated.) We can, furthermore, neglect the effect of interference between the *o* ray and *e* ray, which leads to an optical torque component in the plane of incidence and rotates the director out of this plane. This torque component oscillates spatially along the beam path, therefore, the director deformation caused by it is much smaller than the one caused by the *e* ray. In addition, it can be seen that such rotations of the director have only a quadratic effect on $\Delta\Phi$, hence they do not influence the results obtained in the linear regime. In this approximation, $\Delta\Phi$ is proportional to $1+\eta(\Theta_i)$ and to the input power of the *e* ray, $P_d\cos^2\Theta_i$. From Eq. (25)

$$\Delta\Phi/P_d\cos^2\Theta_i = C\left[1+\eta_T+(\eta_C-\eta_T)X_{\mathrm{ord}}\frac{1+g\cos^2\Psi\cos^2\Theta_i}{1+h\cos^2\Psi\cos^2\Theta_i}\right]. \tag{26}$$

The fitted curve is shown in Fig. 7. The only fit parameter was the constant *C*; the other parameters η_C, η_T, X_{ord}, *g*, and *h* were set equal to the values obtained from the previous measurements. We think that the reasonable agreement between the measured points and the fitted curve indicates the validity of the model discussed in this paper.

V. DISCUSSION

The experimental findings presented in Sec. III show that azo dyes can induce very strong optical torque. The *trans* and *cis* enhancement factors of *R*4, furthermore the enhancement factor of DR13, are comparable with the values measured for the most effective anthraquinone dyes at similar dye concentrations [16]. In addition, it was found that the optical torque, generated by *trans* and *cis* isomers are of opposite signs, namely, negative for the former and positive for the latter isomer. In the presence of photoisomerization the resultant enhancement is significantly reduced because the contributions from the two isomers tend to cancel each other.

According to the theoretical models [6,8], the absorption-induced torque is associated with the molecular field created by the dye dopants. Without illumination, this field is axially symmetric around the director. In the presence of excitations, the axial symmetry is broken and the molecular field exerts an effective torque on the director. If the rotational mobilities of the ground-state and excited-state molecules are equal, the difference between the molecular field strengths of the two electronic states determines the magnitude and the sign of the torque. When the ground-state molecular field is stronger than the excited-state one the enhancement is negative; in the opposite case it is positive.

We suggest that in the presence of *trans-cis* photoisomerization there are basically three different molecular fields connected to the dye. The first two are the fields created by the ground-state *trans* and *cis* isomers; the third one is the molecular field of the excited-state molecules. (For simplicity, we assume that the excited states of the *trans* and *cis* isomers is identical.) From the observed signs of η_C and η_T one can deduce that the molecular field of the trans ground-state molecules is stronger than that of the excited molecules, which is, in turn, stronger than the field of the *cis* ground-state molecules.

The sequence of the decreasing magnitude of the molecular field may be related to a corresponding decrease of the orientational order of the different configurations of the dye molecule. Although the explicit relation between the orientational order parameter of a dopant and the associated molecular field is complicated, it is evident that a significant decrease of the order is accompanied with an important reduction of the molecular field. The large difference between the dye order parameters of the ground-state *trans* and *cis* isomers of *R*4 were reported in Ref. [12]; for $\lambda=514$ nm, they are 0.78 (*trans*) and 0.25 (*cis*). The reason for the small order parameter in the case of the *cis* isomer is a consequence of its geometrical shape; the elongated *trans* molecules are much more effectively oriented in the nematic host than the more spherelike *cis* isomers.

In connection with the orientational order of the excited molecules, we note that the excited state is formed in two steps. First, an electronic transition takes place with fixed nuclear coordinates. This process is followed by a fast configurational relaxation of the nuclei towards a new equilibrium position. As can be seen, e.g., from the energy diagrams reported in Ref. [13], in terms of configurational coordinates the excited state is stabilized near half-way between the *trans* and *cis* configurations. It seems therefore plausible to assume that its order parameter is also intermediate between the *trans* and *cis* order parameters, hence the associated molecular field strength is significantly lower than that of the *trans*, but much higher than that of the *cis* isomer.

It was pointed out in Ref. [8] that change of the rotational friction occurring at excitation can also cause an enhancement of the optical torque. If the rotational diffusion constant is lower in the ground state than in the excited state, an enhancement with negative sign is expected. In the case of azo dyes, a sequence $D_{trans}<D_{\mathrm{exc}}<D_{cis}$ (*D*: rotational diffusion constant) could also explain the observed signs of η_C and η_T. Such a sequence might be also connected to the corresponding geometrical shapes of the dye molecule.

From a macroscopic point of view, the angular dependence of the enhancement factor can lead to a number of interesting new optical phenomena, especially in the case when change of sign of η occurs. Interesting observations of this kind were already reported by Zolotko's group [10,17]. In their interpretation, however, an *ad hoc* angular dependence of η was introduced, without clarifying the physical mechanism behind it. The angular dependence derived in our paper may help to analyze the optical reorientation process in azo-dye doped NLC's in a more systematic way.

ACKNOWLEDGMENT

This work was supported by the Hungarian National Science Foundation, OTKA, under Contract No. T 024098.

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