

OPTICAL REORIENTATION IN DYE-DOPED LIQUID CRYSTALS

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The light-induced reorientation of nematic liquid crystals is discussed with special emphasis on the effect of dye-dopants. A molecular model is presented which accounts for the large increase of the optical torque, observed in absorbing nematics. An analogous process is described for dye-doped isotropic liquids and the role of photoisomerization is considered as well.

1. Introduction

The nonlinear optical properties of liquid crystals received considerable attention in the past decades and were reviewed by various authors.¹ Harmonic generation in liquid crystalline phases and optical reorientation of nematics are examples of nonlinearities studied in detail. The present paper deals with the latter effect, paying special attention to the influence of absorption on the process.

Absorption of the light beam can be due to the liquid crystal molecules themselves, but often dyes are added to the system to induce significant absorption in the visible range. Dye-doped liquid crystals (guest–host mixtures) have important display applications and a range of suitable dyes and host materials were developed for such systems. The dyes are typically azo or anthraquinone derivatives, they dissolve in the host up to concentrations of a few percent and show pronounced photostability. The transition dipole moment normally tends to align parallel to the preferred direction of the system (the director), hence guest–host mixtures usually exhibit large positive dichroism.

A straightforward consequence of light absorption is heating, which leads to various thermo-optical effects.² There are, however, more sophisticated phenomena, related to the formation of metastable states in the absorption process. Metastable state can mean an excited electronic structure (singlet or triplet) or a metastable configuration of the nuclear positions, like the *cis* configuration of azo compounds. The presence of metastable molecules can affect the properties of the liquid crystal in different ways. First, there is a direct effect, due to the fact that the contribution

of a dye molecule to various physical parameters, such as the optical constants, is not the same in the ground state and the metastable one. Second, in the metastable state molecules interact with the surrounding host molecules differently than in the ground state. As it will be discussed in the following, the change of interaction modifies the collective behavior of the liquid crystal and thus causes large optical effects.

Let us consider first the case when the lifetime of the metastable state is much longer than the characteristic time for molecular reorientation in a nematic. The latter is typically 10^{-9} sec, while the lifetime of e.g. a cis configuration in a liquid crystal can be of the order of seconds or even much longer.³ Under such circumstances, the transformed molecules may be regarded as special kind of “impurities,” the concentration of which is controlled through the intensity of the exciting light beam. The photoinduced component — like all other components in the mixture — exhibits an axially symmetric orientational distribution around the director with its own characteristic order parameter, that can deviate from the order parameter of the ground-state component considerably.⁴ The presence of metastable molecules can influence also the order parameter of the host molecules; this effect is especially strong in the vicinity of the nematic-isotropic phase transition.^{5,6} In chiral liquid crystal they can change the helical pitch and the value of the spontaneous polarization.⁷ It was also shown that the photoinduced metastable molecules alter the layer spacing in the smectic phase.⁸

The effects described above can become quite large already at very low light intensity levels. The fraction of the transformed molecules is of the order of $(I/I_S)/(1+I/I_S)$ where I is the light intensity. The saturation of the concentration of the metastable molecules starts around the characteristic intensity I_S , which can be related to the photon energy $h\nu$, the absorption cross-section, σ , the lifetime of the metastable state, τ_l , and the quantum efficiency of the transition Φ , as $I_S = h\nu/\Phi\sigma\tau_l$. With typical numbers ($\sigma = 10^{-21}$ m², $\Phi = 0.5$, $h\nu = 4 \cdot 10^{-19}$ J) one finds that for $\tau_l = 1$ sec, I_S is in the order of a mW/mm².

We now consider the case when electronic excitation of a dye molecule is not followed by a transition to a metastable configuration. This situation can apply, e.g. to anthraquinone derivatives which have rigid structures. The typical lifetime of an electronic excited state is around 10^{-9} sec. The saturation intensity is in this case in the order of 10^5 W/mm², a value that can be hardly achieved under steady-state conditions. Conversely, at the highest input powers that can be applied to an absorbing layer without heating it significantly, the concentration of the excited molecules is very low. One expects therefore that the modification of the physical parameters of the host material is negligible in this case.

On the other hand, the orientational distribution of the excited dye molecules has the specific feature that it deviates from thermodynamical equilibrium. In polarized light, the probability of an electronic transition is proportional to $\cos^2 \psi$, where ψ is the angle between the electric field vector of the light beam and the transition dipole moment. The orientationally selective probability of excitation

breaks the axial symmetry of the dye molecules around the director. The lifetime of the excited state and the rotational relaxation time are usually of the same order of magnitude, hence rotational Brownian motion restores the axial symmetry only partially.

In the paper, we show that the asymmetric distribution of the dye molecules can lead to a strong enhancement of the optical reorientation process, provided that the interaction between a dye molecule and the host is different in the excited state and the ground state of the molecule. Such an enhancement was first noticed experimentally; the details of the observations are given in Sec. 2. The quantitative theory of the “dye-induced” optical torque is presented in Sec. 3, based on the ideas described above. We point out that the internal field, created by the excited dye molecules is equivalent to that of an external electric field, at least regarding the director motion. The dye-induced torque can, however, exceed the light-induced director torque by orders of magnitude and in many cases inverts the sign of the total optical torque.

In Sec. 4, a related effect in the isotropic phase is discussed and it is shown that the same mechanism can explain the enhancement of the optical Kerr effect in dye-doped liquids.

Finally, we return to the case when electronic excitation is followed with a certain probability by a configurational transition. In accordance with the considerations presented earlier, we regard the isomers as separate components which contribute independently to the internal molecular field. It is demonstrated that the combined effect of photoisomerization and dye-induced torque leads to novel optical phenomena, such as anomalous angular dependence of optical reorientation, or the possibility to regulate the orientational nonlinear coefficient by an ordinarily polarized beam.

2. Experimental Background

The reorientation of *transparent* nematic liquid crystals by optical fields was studied by numerous authors. Presumably it was first demonstrated by A. Saupe in 1969, but his results have not been published until very recently.⁹ From 1980, at least four groups began intensive work on this phenomenon.¹ Although the details of the light-induced reorientation process are complex, the underlying physical mechanism is clear; it originates from the torque exerted by the electric field of the light beam on the induced polarization. Nematics are uniaxial media, hence the induced polarization, from symmetry, can be given as

$$\mathbf{P}/\varepsilon_0 = \varepsilon_{\perp} \mathbf{E} + (\varepsilon_{\parallel} - \varepsilon_{\perp})(\mathbf{n} \cdot \mathbf{E})\mathbf{n}, \quad (1)$$

where \mathbf{E} is the electric field vector, \mathbf{n} is a unit vector along the optical axis, i.e., the director, ε_{\perp} and ε_{\parallel} are the principal dielectric constants, measured perpendicularly and parallel to \mathbf{n} respectively.

For an optical field, $\mathbf{E} = \sqrt{2}E_0\mathbf{e} \cos \omega t$ one has $\varepsilon_{\parallel} = n_e^2$, $\varepsilon_{\perp} = n_o^2$, where n_e and n_o are the extraordinary and ordinary refractive indices respectively. The “optical” torque-density is

$$\mathbf{\Gamma}^{\text{opt}} = \langle \mathbf{P} \times \mathbf{E} \rangle = \varepsilon_0(n_e^2 - n_o^2)(\mathbf{n} \times \mathbf{e})(\mathbf{n} \cdot \mathbf{e})E_0^2. \quad (2)$$

In nematics $n_e > n_o$, thus the stable orientation corresponds to $\mathbf{n} \parallel \mathbf{e}$, i.e., the optical field tends to orient the director parallel to its electric vector.

In the illuminated area, due to director reorientation, the effective refractive index increases, hence self-focusing takes place. This can be easily observed e.g. in a homeotropically or planarly oriented nematic cell, irradiating it with a light beam at oblique incidence, polarized in the plane of incidence. A special situation occurs in a homeotropic sample (director aligned perpendicularly to the walls) at normal incidence. In this case, director deformation starts at a threshold intensity (optical Fredericksz transition). In plane wave approximation, the threshold can be calculated in a way similar to the one used for static fields.¹⁰ The result is

$$I_{\text{th}} = (\pi/L)^2 \frac{n_e^2}{n_o} \frac{K_3 c}{n_e^2 - n_o^2}, \quad (3)$$

where K_3 is the bend elastic constant. Experimental results — when corrections for the finite beam size are taken into account — are in satisfactory agreement with the above relation.¹¹

The very strong influence of *dye dopants* on optical reorientation was discovered during the study of thermo-optical effects and was first published in 1990.¹² It was observed in a guest–host mixture, containing a small amount of the anthraquinone dye AQ1 that the optical Fredericksz threshold is anomalously low. (For the chemical structures of the dye and host materials, see Table 2.) In Fig. 1, the threshold power is shown as a function of dye concentration. The threshold powers expected for the undoped host are 120 and 70 mW for the two spot sizes, i.e., two orders of magnitude higher than the threshold at a concentration of 1%. It should be noted that the material parameters involved in Eq. (3) (elastic constant, refractive indices) are basically unaffected by the presence of dye.

Further experimental investigations of the anomaly^{13–17} showed that optical reorientation is *qualitatively* very similar in dyed and undoped systems; *quantitatively*, however, the corresponding effects may take place at very different power levels. One example is the reduction of the Fredericksz threshold for AQ1, described above. As a further example, we mention the case of Fredericksz transition, induced by circularly polarized light. It is known for transparent materials that in circularly polarized optical fields director precession around the layer normal takes place above the threshold.¹⁸ The same phenomenon was found in the AQ1-doped nematic, but at power levels reduced by the same factor as the threshold.¹²

On the basis of these observations, it was suggested that the effect of dye dopants can be described by adding a new term, $\mathbf{\Gamma}^{\text{dye}}$ to the expression of the optical torque

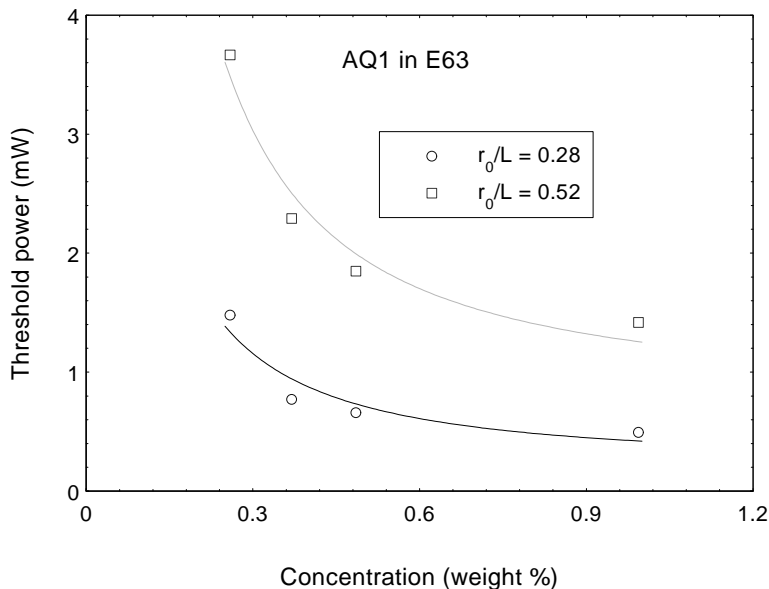


Fig. 1. Optical Freedericksz threshold as a function of the concentration of AQ1. Sample thickness $L = 60 \mu\text{m}$. r_0 is the spot radius of the laser beam. $\lambda = 633 \mu\text{m}$.

(Eq. (2)). Γ^{dye} is connected to the exciting light beam in a similar way as in Eq. (2), except that the birefringence factor is replaced by a new coefficient ζ

$$\Gamma^{\text{dye}} = \varepsilon_0 \zeta (\mathbf{n} \times \mathbf{e})(\mathbf{n} \cdot \mathbf{e}) E_0^2. \quad (4)$$

The expression for the optical torque can therefore be generalized as

$$\Gamma^{\text{opt}} = \varepsilon_0 (\zeta + [n_e^2 - n_o^2]) (\mathbf{n} \times \mathbf{e})(\mathbf{n} \cdot \mathbf{e}) E_0^2. \quad (5)$$

The coefficient ζ vanishes for the undoped material and it is plausible to assume that, for low dye contents, it is proportional to the dye concentration. In the same limit, the absorption coefficients of the guest–host system are also proportional to the dye concentration, hence it is useful to introduce another dimensionless coefficient, ξ , through the relation

$$\xi = \zeta / \bar{\alpha} \lambda \quad \text{with} \quad \bar{\alpha} = \frac{1}{3} (n_e \alpha_e + 2n_o \alpha_o). \quad (6)$$

α_e and α_o are the extraordinary and ordinary absorption coefficients, $\bar{\alpha}$ is their orientational average; λ is the wavelength of the light. For a given host, ξ depends only on the chemical structure of the dopant and is independent from the absorption cross section. In the followings, we refer to ξ as the *molecular coefficient*. In some cases, we will consider the ratio between the dye-induced and dielectric torque (*enhancement factor*), which is equal to $\zeta / (n_e^2 - n_o^2)$.

According to the above empirical relation, the effect of dye-dopants on optical reorientation can be characterized through a single molecular coefficient, ξ , which

can be deduced from the ζ coefficient. Different methods were used to measure ζ quantitatively. In the initial experiments, its value was deduced from the optical Freedericksz threshold. This method is, however, not precise and for several dyes it does not work at all, because thermal effects dominate over the reorientation process. Study of self-focusing in non-threshold geometries (e.g. oblique incidence on a homeotropic sample) proved to be a more efficient method. In the measurements the Z-scan technique¹⁹ was applied^{14,20,21} or a weak probe beam was used to measure the optical path change induced by the reorienting beam.^{22,23} The thermal component of the nonlinearity can be separated in this case e.g. by suppressing reorientation with the help of a strong stabilizing electric field. From the data an effective nonlinear refractive index is obtained, which can be related to the optical torque in a direct way if the material parameters are known. Alternatively, it can be compared with the corresponding nonlinear coefficient in the undoped material, measured under identical geometrical conditions. As an example, in Fig. 2 Z-scan curves are shown for doped and undoped samples.

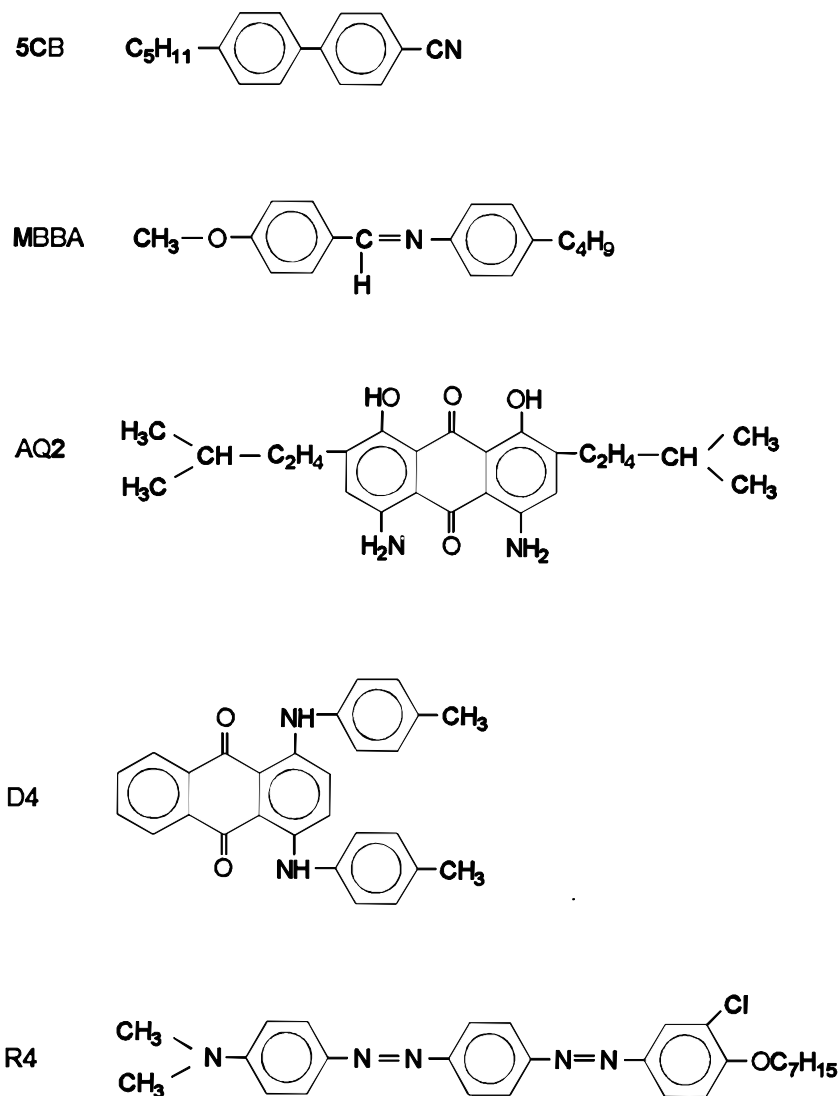
Investigations of different dopants showed that the value of the molecular coefficient, ξ , is very sensitive to the detailed *structure* of the dye. For AQ1, AQ2 and a few other anthraquinone derivatives ξ has a large positive value, while for many other anthraquinone dyes ξ is negative. A negative ξ value means that the dye-induced torque tends to orient the director perpendicularly to the electric field vector of the light beam. In this situation optical reorientation causes self-*defocusing*, as it can be seen e.g. in Fig. 2 for the dye D4. The value of ξ depends on the *host* material as well. In Table 1 ξ is given for AQ2 and D4 for 3 different hosts; the numbers are based on the data reported in Ref. 22. We also include the ζ coefficients, which refer to a dye concentration around 0.1%. The birefringence factor, $n_e^2 - n_o^2$ is in the order of 0.7; thus one can see from the Table that enhancement factor is well above unity, i.e., the dye-induced torque dominates the reorientation process even at this very low concentration.

The *wavelength* dependence of the dye effect was measured for D4 and AQ2.^{20,22} In the former case, only weak variation of the molecular coefficient was found within the absorption band, while in the latter case an increase of ξ was observed around the absorption peak. It should be noted, however, that the dye-induced torque itself is proportional to the absorption coefficients and vanishes outside the absorption band.

Table 1. The molecular coefficients (ξ) and ζ coefficients at 0.1% concentration, for different dyes and hosts. $T = 24^\circ\text{C}$, $\lambda = 633 \text{ nm}$. (After Ref. 22)

Host	ξ (AQ2)	ξ (D4)	ζ (AQ2)	ζ (D4)	$n_e^2 - n_o^2$
5CB	6120	-1170	58	-16	0.58
E63	5625	-1057	170	-22	0.72
MBBA	1332	-990	18	-2.6	0.73

Table 2. Chemical structures of the host and dye materials.



E63 is a commercial mixture, containing cyanobiphenyls. AQ1 has the same structure as AQ2, except that the isopentyl groups are replaced by isobutyl groups.

In particular, dye-doping has no effect on the low-frequency electric Freedericksz threshold.

The *temperature* dependence of the ξ coefficient was determined for the dyes AQ1 and AQ2.²⁴ It was found that ξ decreases with temperature. However, the enhancement factor increases near the nematic-isotropic phase transition and seems to tend to a finite value at the clearing point.

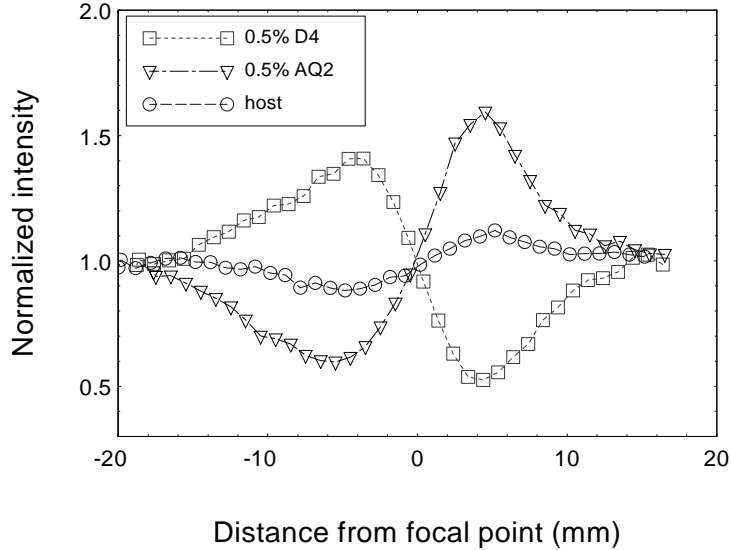


Fig. 2. Z-scan curves of the host E63 ($P_{in} = 8$ mW), AQ2 doped sample ($P_{in} = 0.19$ mW) and D4 doped sample ($P_{in} = 0.46$ mW). Homeotropic sample, angle of incidence 42° . $\lambda = 633$ nm. Note that for the pure host and AQ2 self-focusing takes place (valley before peak), while for D4 self-defocusing is observed (peak before valley).

Finally, we mention that some dyes do not cause any significant enhancement of the optical torque. It may be interesting to note that — to the knowledge of the present author — all guest–host systems with negative dichroism fall into this category.^{16,17,25}

3. Interpretation

The process of optical reorientation in transparent nematics can be adequately described with the help of classical electrodynamics and the standard continuum theory of liquid crystals. The interaction energy between the electric field and the matter, in the electric-dipole approximation, is $\mathbf{P} \cdot \mathbf{E}$, where \mathbf{P} is the polarization. For uniaxial media and optical frequencies this interaction leads to the optical torque given in Eq. (2).

The effect of dye-dopants, on the other hand, is not implied in the usual classical description. At the very low dye concentrations used in the experiments the only physical parameter that changes appreciably is the absorption coefficient of the system. Typical α values ($\sim 10^2$ cm $^{-1}$) are, however much too low to influence significantly the polarizability of the system. Clearly, to explain the observations, an additional mechanism connected with the excitation of dye molecules has to be taken into account.

A formal way to describe the effect of absorbing molecules is to add a “photoinduced” term to the irreversible part of the stress tensor, containing terms proportional to (the time average of) $j_k E_l$, where \mathbf{j} is the electric current density.

The antisymmetric part of the photoinduced stress tensor can be related to the dye-induced part of the optical torque, introduced in the previous section. Such a phenomenological approach shows that the empirically established similarity between the dye-induced and dielectric torque is a consequence of the symmetry of the system alone; furthermore it predicts anomalous photoinduced flow effects in inhomogeneous optical fields.²⁷ To understand, however, why can photoinduced effects be so strong, molecular models are needed.

A hypothesis about the microscopic origin of the dye-induced torque was already outlined in the Introduction. The main points of the model are (i) orientationally selective excitation of the dye molecules; (ii) change of the interaction between a dye molecule and the surrounding host molecules upon excitation. As a consequence of these two effects, the dye molecules become asymmetrically distributed around the director, thus exert a nonvanishing total torque on the host molecules.

To make the considerations quantitative, one can determine the orientational distribution of the dye molecules from a rotational diffusion equation.^{26–28} Let $f_e(\mathbf{s})d\Omega_s$ and $f_g(\mathbf{s})d\Omega_s$ give the number of excited and ground state dye molecules respectively, oriented in an element of solid angle $d\Omega_s$ around the unit vector \mathbf{s} . The rate equations for f_e and f_g can be written as

$$\frac{\partial f_e}{\partial t} + \bar{\nabla} \mathbf{J}_e = p f_g - f_e / \tau_l, \quad (7)$$

$$\frac{\partial f_g}{\partial t} + \bar{\nabla} \mathbf{J}_g = -p f_g + f_e / \tau_l. \quad (8)$$

Here $\bar{\nabla}$ is the angular part of the ∇ operator; \mathbf{J}_e and \mathbf{J}_g are the rotational currents of the excited and ground-state dye molecules respectively; $p = p(\mathbf{s}) \propto E_0^2(\mathbf{e} \cdot \mathbf{s})^2$ is the probability per unit time that a ground-state molecule, oriented along \mathbf{s} absorbs a photon. The currents obey the constitutive equation

$$\mathbf{J}_i = -D_i \bar{\nabla} f_i - \mu_i (\bar{\nabla} U_i) f_i \quad (i = g, e). \quad (9)$$

The first term on the right-hand side of the above equation represents the rotational Brownian motion of the molecules, D_i is the relevant diffusion coefficient. The second term describes the drift motion of the molecules in the mean-field nematic potential, U_i . Usually it is assumed that $\mu_i = D_i/kT$. With the help of the above equations the steady-state distributions of the dye molecules can be calculated for any specified form of the mean-field potentials. Once the distribution functions are known, the internal torque exerted by the dye molecules on the nematic host can be calculated as

$$\Gamma^{\text{int}} = - \int (\mathbf{m}_g f_g + \mathbf{m}_e f_e) d\Omega_s, \quad (10)$$

where \mathbf{m}_g and \mathbf{m}_e denote the torque acting on a single ground-state or excited dye molecule respectively, $\mathbf{m}_i = -(\bar{\nabla} U_i) \times \mathbf{s}$ with $i = g, e$.

In the following, we discuss the case of low light intensities, skipping mathematical details. In the absence of illumination $f_e = 0$ while the ground-state molecules

follow a Boltzmann distribution, $f_g^0 \propto \exp(-U_g/kT)$. For weak optical fields, f_e and the function $f_h = f_g^0 - f_g$ (distribution of “holes”) are linear in E_0^2 , i.e., the intensity. The distribution function can be decomposed into a symmetric and antisymmetric part with respect to reflection of the \mathbf{s} vector in a line parallel to the director. The symmetric part gives no net torque on the host molecules, instead it influences the order parameter of the nematic. However, as it was already pointed out in Sec. 1, this effect is negligible because of the very low density of the excited molecules. The internal torque arises from the antisymmetric parts of the f_i functions. As a detailed calculation shows, Γ^{int} can be given in the form

$$\mathbf{\Gamma}^{\text{int}} = \varepsilon_0 \zeta' (\mathbf{n} \times \mathbf{e})(\mathbf{n} \cdot \mathbf{e}) E^2 \quad \text{with} \quad \zeta' = \frac{3\bar{\alpha}\lambda}{2h\mu_e} Q, \quad (11)$$

where Q is a dimensionless factor, depending on the dimensionless quantities $D_e\tau_l$ and μ_e/μ_g , furthermore on the reduced mean-field potentials U_g/kT and U_e/kT . An example of the calculated Q values is shown in Fig. 3. Here the $D_e\tau_l \gg 1$ and $\mu_e/\mu_g = 1$ cases are considered. The mean-field potentials are assumed to have the Maier–Saupe form, $U_i = -u_i(\mathbf{n} \cdot \mathbf{s})^2$.

In order to compare the above model with experiments, a connection has to be found between the internal and the dye-induced torque. An obvious possibility is to suppose that they are equal, $\mathbf{\Gamma}^{\text{dye}} = \mathbf{\Gamma}^{\text{int}}$, as both represent the torque acting on the nematic molecules in the presence of excitations. This relation is adopted in most of the literature. We do not analyze the problem here in detail, only briefly discuss the question of angular momentum conservation.

At first sight, identifying the dye-induced torque with $\mathbf{\Gamma}^{\text{int}}$ may seem to contradict to the law of angular momentum conservation, because it allows for director

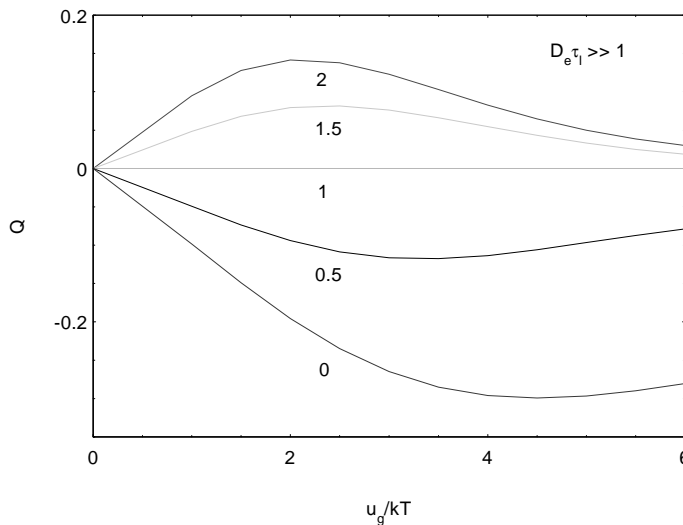


Fig. 3. Calculated values of the Q factor at different u_e/u_g ratios, assuming $\mu_e/\mu_g = 1$.

rotations on the expense of internal interactions alone. It should be noted that the angular momentum exchange between the optical field and the liquid crystal is already fully taken into account in the dielectric part of the optical torque; no further angular momentum is supplied by the light due to absorption. The solution of this apparent difficulty comes from the model itself. The rotational currents, \mathbf{J}_i , associated with the antisymmetric parts of the distribution functions are symmetric with respect to reflections through the director; hence their orientational average are finite. In other words, due to the continuous photoinduced electronic transitions, the dye possess a nonzero average angular velocity, even if the director and the light intensity are constant in time.^{26,27} The angular momentum carried by the internal rotation of the dye molecules is equal to the angular momentum “missing” from the exchange process in the light-liquid crystal interaction. In a very recent publication, P. Palfy-Muhoray pointed out the analogy between the optically induced dye rotation in nematics and translational ratchets proposed lately.²⁹

Taking the dye-induced and internal torque equal, from Eqs. (4) and (11) one finds $\zeta = \zeta'$ and obtains the theoretical expression for the molecular coefficient

$$\xi = \frac{3Q}{2\mu_e h}. \quad (12)$$

A precise quantitative comparison of the model with experiments for the time being is not possible, because some of the molecular parameters involved in the model are not known. The ground-state energy parameter, u_g , can be deduced from the dye-order parameter; the rotational mobility in the excited state can be obtained from time-resolved fluorescence measurements.³⁰ There are, however, no direct informations on u_e and μ_g . Nevertheless, it seems plausible to assume that these quantities are of the same order of magnitude than their counterparts in the ground state and excited state, respectively. With a typical number $D_e = kT\mu_e \approx 2 \cdot 10^8 \text{ sec}^{-1}$, one finds at room temperature $\xi \approx 5 \cdot 10^4 Q$. As it can be seen from Fig. 3, for reasonable values of the molecular parameters, Q is in the range of 0.05–0.2, yielding ξ values $10^3 - 10^4$. This is the order of magnitude observed in the experiments (see Table 1).

According to the model, the sensitivity of the molecular coefficient on the chemical structure of the dye and the host is connected to a corresponding sensitivity of the change of guest–host interaction at excitation. For equal mobilities, $\mu_g = \mu_e$, a positive ξ value means that the excited-state molecules are aligned more effectively than the ground-state ones; $\xi < 0$ reflects the opposite situation.

It is interesting to note that in the case $\mu_g \neq \mu_e$, there is a dye-induced torque even when the mean-field potentials are equal. To understand this fact, consider the case when the rotational mobility in the excited state becomes very low. At excitation, the dye molecules are “blocked” in their position, hence they accumulate around the polarization direction of the light beam. Due to this asymmetry, there will be a net torque on the host molecules, rotating the director towards the electric field vector ($\xi > 0$). There are indications that this is the dominant effect for the

dyes AQ1 and AQ2.^{27,31} It may be possible that in the excited state there is a charge-transfer interaction between the AQ dyes and the host molecules, leading to a strong reduction of the mobility.

The theoretical expression for the molecular coefficient, (Eq. (12)), does not contain the wavelength. For D4 the experiments are in agreement with this prediction. The wavelength dependence found for AQ2 may be related to the double-band absorption spectrum of this dye.²² In the visible range two distinct electronic excited states contribute to the dye-induced torque and their relative strengths may change as λ is varied.

The temperature is involved in a complex way in Eq. (12). Far from the nematic-isotropic phase transition, the main effect comes from the temperature increase of the mobility, which follows an Arrhenius plot. According to Eq. (12), this corresponds to a decrease of ξ , that was, in fact, observed. Near the phase transition u_g and u_e are also strongly temperature dependent — this case was analyzed in detail in Ref. 22.

4. Optical Kerr Effect in Absorbing Liquids

Light-induced birefringence in isotropic liquids (optical Kerr effect³²) is a phenomenon strongly related to optical reorientation in nematic liquid crystals. In transparent organic liquids on nanosecond time scale it results first of all from molecular reorientation in the electric field of the light beam. The torque exerted by an optical field on the molecules tends to orient them parallel to the polarization direction; this process is counteracted by thermal rotational movements. The difference between the effects taking place in isotropic and anisotropic fluids is that in the former case molecular rotations are more or less independent, while in the latter one director reorientation is a collective response.

In 1997, two groups demonstrated simultaneously that dye-doping cause an enhancement of the optical Kerr effect analogous to the one observed in nematic liquid crystals.³³ The guest–host systems investigated in the experiments were similar to those used for the nematic phase. Typically 0.05–0.3% of anthraquinone dyes were dissolved in various hosts, some of which exhibited nematic phase, while others not. In all cases, a strong increase of the Kerr coefficient was found; the enhancement of the induced birefringence was of the same order of magnitude than the corresponding enhancement of the optical torque in nematics.

The close connection between dye-induced enhancements of reorientation in liquids and liquid crystals becomes particularly clear in the pretransitional behavior near the isotropic-nematic phase transition. It was shown long time ago in transparent materials that, due to pretransitional orientational correlations, the strength of optical Kerr effect increases with temperature proportional to $1/(T - T^*)$ as the phase transition is approached; here T^* is a temperature slightly lower than the clearing point.³⁴ A similar relation was found to hold in dye-doped samples. The enhancement ratio, however, does not show critical behavior; it turned out to be

basically constant in this temperature range. In the nematic phase, the enhancement factor, as determined from the reduction of the optical Freedericksz threshold few degrees below the clearing point, was found to be only 30% lower than in the isotropic phase.³³ The above observations suggest a common mechanism for the two phases.

The model proposed for the nematic phase works for isotropic liquids as well. The main ideas are again orientationally selective excitations of the dye molecules and the change of guest–host interaction upon excitation. In isotropic phase, the equilibrium distribution is spherically symmetric. Due to selective excitations, the dye orientational distribution functions become axially symmetric around the polarization direction of the exciting light beam. As a consequence, there will be a molecular field associated with the dye molecules which modifies the order parameter of the host molecules, without exerting a net torque on them (just like the symmetric part of the distribution functions in a nematic; see the previous section). In nematics, such a change gives a very small relative variation of the birefringence. On the other hand, in the isotropic phase, where the order is initially zero, it becomes the main source of the measured Kerr signal.

In a quantitative description, the same parameters are involved in both phases, namely the dye–host interaction energies and the rotational mobility of the ground-state and excited-state molecules. These quantities do not change drastically in a nematic-isotropic phase transition, therefore the model predicts a comparable enhancement factor at both sides of the transition.³³

5. The Influence of Photoisomerization on Optical Reorientation

In this section, we consider the case when dye molecules are transformed with certain probability from the excited state to a metastable state, that has a much longer lifetime than the rotational diffusion time. As it was discussed in Sec. 1, metastable molecules with long lifetime can be regarded as additional dopants. This new component can contribute to the dye-induced enhancement of optical reorientation as well, provided that its absorption cross section is significant at the wavelength of the exciting light beam. Such a situation occurs at *trans-cis* isomerization of azo dyes, as the absorption bands of the two isomers normally overlap almost entirely.

It was shown by various authors that azo dyes cause a similar effect on optical reorientation than anthraquinone compounds.^{15,20,21} Barnik *et al.*, however, noted an interesting anomaly in a guest–host system containing a di-azo derivative.³⁵ They found that in a homeotropic sample at small angles of incidence self-defocusing occurs (corresponding to a negative ζ), while above a critical angle of incidence self-focusing takes place ($\zeta > 0$). The experiment was repeated by Szabados *et al.* on a similar di-azo dye (R4).³⁶ Representative Z-scan curves are shown in Fig. 4.

The observed angular dependence of the dye-induced torque seems to contradict to the model outlined in Sec. 3, which requires — from general symmetry

considerations — that ζ should be independent of the direction of light propagation. The reason behind the peculiar behavior of the azo-dye doped guest–host system, was clarified in Ref. 23. The explanation is based on two main points: (i) the trans and cis isomers contribute independently and with opposite signs to the resultant ζ coefficient; (ii) the fraction of cis molecules depend on the angle between the polarization direction of the light wave and the director.

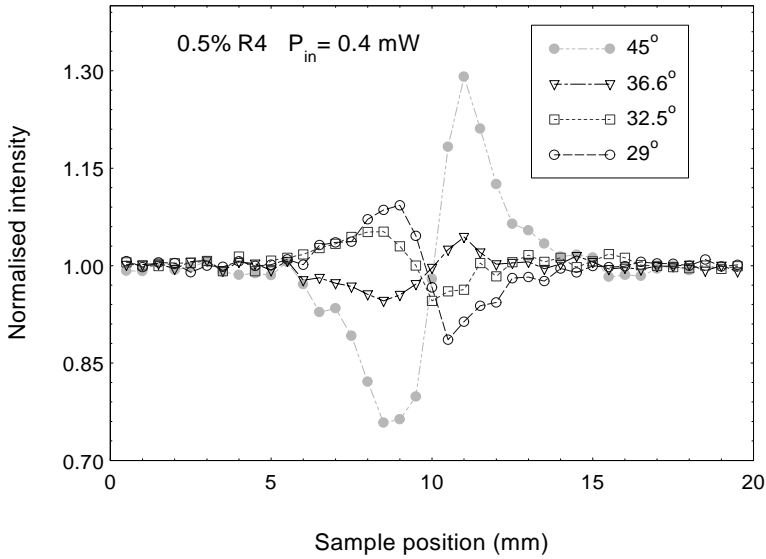


Fig. 4. Z-scan curves of R4 doped E63 at different angles of incidence. $\lambda = 514$ nm. Note the change from self-defocusing to self-focusing as the angle of incidence is increased.

In connection with the second point, we note that light induces both trans-cis and cis-trans transitions. At typical intensity levels used in reorientation experiments, thermal cis-trans transitions can be neglected in comparison with light-induced transitions. The steady-state cis concentration is determined by the absorption cross-sections of the two isomers and the quantum efficiencies of the transitions. To demonstrate why does the cis concentration depend on the light propagation direction, consider a guest–host system, in which the trans molecules are perfectly aligned with their transition dipole moments along the director, while the cis isomers exhibit disorder. If the light beam propagates along the director, the electric field is perpendicular to the transition dipole of the trans isomers, hence no cis isomer is formed. When the wave vector is perpendicular to the director, for extraordinary polarization, trans molecules *are* excited, consequently the cis concentration will be finite.

In the general case, the steady-state fraction of the cis dye molecules, X , can be given as²³

$$X = X_{\text{ord}} \frac{1 + g \cos^2 \Psi}{1 + h \cos^2 \Psi}, \quad (13)$$

where X_{ord} is the cis fraction generated by an ordinarily polarized beam; Ψ is the angle between the electric vector and the director; g and h are molecular parameters. As shown in Ref. 4 X_{ord} , g and h can be determined from simple transmission measurements.

The ζ coefficient can be given as

$$\zeta = X\zeta_C + (1 - X)\zeta_T, \quad (14)$$

where ζ_C and ζ_T refer to hypothetical states in which all dye molecules are in cis or trans configuration respectively. The cis and trans coefficients are independent of Ψ , but the resultant ζ has an angular dependence through X . ζ_C and ζ_T can be determined by measuring the reorientational nonlinearity as a function of the angle of incidence of the light beam. For 0.3% R4 added to E63, $\zeta_C = 467$ and $\zeta_T = -294$ were found.²³ These numbers are comparable with the values found for the most effective anthraquinone dyes extrapolated to similar concentrations (see Table 1).

In Ref. 23, it was suggested that the large values and opposite signs of the trans and cis coefficients are connected with changes of the molecular shape during trans-cis isomerisation. The trans isomer has an elongated form, similar to the host molecules, therefore it is much more effectively oriented along the director than the V-shaped cis isomer. Quantum-chemical calculations show that in the excited states the shape anisotropy is somewhere between the anisotropy of the trans and cis ground states.³⁷ As a consequence, upon excitation a trans isomer is transformed to a configuration which is less ordered than the ground state. According to the theory presented in Sec. 3, this means $U_g > U_e$ and thus $\xi < 0$. For the cis isomer the situation is reserved; in this case excited state is more ordered than the ground state, hence $U_e > U_g$ and ξ is positive. In addition, it is plausible to assume that the rotational mobility increase with decreasing shape anisotropy, i.e., $D_{\text{trans}} < D_{\text{exc}} < D_{\text{cis}}$. Such a sequence can also explain the observed signs of the ξ coefficients.

From a macroscopic point of view, the anomalous angular dependence of the dye-induced torque leads to a number of original optical phenomena, especially in the case when change of sign of ζ occurs. For example Terskov *et al.*³⁸ observed a bistable behavior at normal incidence of the light beam. This observation is readily explained by the suggested interpretation of the anomaly. For normal incidence ζ is negative, hence the dye-induced torque stabilizes the homeotropic alignment. If, however, the director is rotated by some method over the critical angle, the dye-induced torque becomes positive and will stabilize the distorted director configuration.

A further example is the control of the strength of orientational nonlinearity by superposing an ordinarily polarized beam on the reorienting light wave. Although an o-ray in itself does not cause reorientation, its presence modifies the cis content within the illuminated area and thus influences ζ . In an actual experiment, even a change of sign was achieved using this method.²³

6. Conclusions

The presence of dye-dopants in liquid crystals gives rise to various nonlinear optical processes. In this paper, we discussed in detail a particular effect connected to light-induced non-equilibrium orientational distribution of the dye molecules. The deviation from the equilibrium distribution results from the orientationally selective excitation probability of the dye molecules. It was shown that in the non-equilibrium state, the molecular fields associated with the excited-state and ground-state molecules enhance significantly the orienting effect of the light beam. The magnitude and sign of the enhancement of the optical torque depend on the change of dye–host interaction upon excitation. For many dyes it can be one or two orders of magnitude at concentrations below 1%. The mechanism is effective in dye-doped isotropic liquids as well, where a similar increase of the optical Kerr effect was observed. According to Ref. 28, light-induced reorientation of Langmuir–Blodgett films involves also an analogous mechanism.

The influence of a given dopant on the optical torque is reproducible and reversible. On the other hand, the strength of the effect is highly dye-specific and also depends on the host material. The study of optical reorientation in various guest–host systems can provide valuable information about the interaction between an excited-state dye molecule and the surrounding host molecules. In this aspect, time-resolved measurements with pulsed lasers may be particularly useful.

The large increase of the optical nonlinearity may be interesting also from the point of view of applications, especially because the enhancement is *not* accompanied by a corresponding increase of the response time. The main drawback of this type of nonlinearity is that it requires light absorption. The absorption losses are, however, material dependent and using properly chosen guest–host systems, they might be kept on a tolerable level.

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