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Enrico Santamato^a, Giancarlo Abbate^a, Pasqualino Maddalena^a,
Lorenzo Marrucci^a, Domenico Paparo^a & Ettore Massera^a

^a INFM, Dipartimento di Scienze Fisiche, Università di Napoli, Pad. 20,
Mostra d'Oltremare, 80125, Napoli, Italy

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OPTICAL REORIENTATION IN DYE-DOPED NEMATICS

ENRICO SANTAMATO, GIANCARLO ABBATE, PASQUALINO MADDALENA,
LORENZO MARRUCCI, DOMENICO PAPARO, ETTÖRE MASSERA

INFN, Dipartimento di Scienze Fisiche, Università di Napoli, Pad. 20, Mostra
d'Oltremare, 80125, Napoli, Italy

Abstract We present our most recent results on laser-induced optical reorientation in mixtures made by adding small amounts of organic dyes to nematic liquid crystals. The optical reorientation process is biased by the molecular interaction between dye and nematic host, so that the reorientation is dramatically enhanced. Measurements of this enhancement have been performed on several guest-host mixtures in order to get information on the nematic-dye molecular interaction. Our results seem to indicate that the presence of strong dipolar group as *CN* in the nematic host may play a significant role in the observed effect.

INTRODUCTION

The laser-induced optical reorientation in nematic liquid crystals^{1, 2} was extensively studied in the last two decades³, because of its great interest for applications in non-linear optics. The effect can be also used to obtain information about some macroscopic properties of liquid crystals as elastic constants⁴ or viscous coefficient⁵. The optical reorientation in nematics, however, can be fully understood in the framework of a macroscopic phenomenological approach, so that the effect cannot be exploited to obtain informations on the material at the molecular level. The only exception seems to be the laser-induced optical reorientation in dye-nematic mixtures. It was observed, indeed, that the optical reorientation process may be enhanced over two orders of magnitude, when small amounts of absorbing dye are added to the pure nematic host^{6, 7, 8}. The enhancement effect is remarkable, because all other macroscopic properties of the material (except the light absorption coefficient) remain almost unchanged by adding the dye to the nematic. The phenomenon should originate, therefore, in some peculiar feature of the interaction between the dye and

the host molecules. Recently, it was suggested that the enhancement of the optical torque, leading to the host reorientation, could be related to the change in the dye-nematic interaction strength, when the former is put in its excited state by the incoming laser beam⁹. A measurement of the enhancement of the laser-induced optical reorientation could then be used to obtain information on the strength of the interaction between the molecules of the dye and the host in both the ground and excited state of the dye molecule. This strength should be dependent, in turn, on the molecular structures of the dye and the nematic liquid crystal. In order to extract this information, the measurement of the enhancement should be repeated over several combinations of dye-nematic mixtures and the enhancement factor should be related by some theoretical model to the dye-nematic interaction energy.

In this work we present some comparative results about the enhancement of the optical reorientation in several dye-nematic mixtures, obtained by changing both the guest and the host material. The experimental data are then compared with a phenomenological model, that although less detailed than the one already reported⁹, permits to obtain substantially equivalent results in a simpler way. We studied both anthraquinone and azo dyes, observing quite similar effects. The results presented in this work, however, refer to anthraquinone dyes, because azo dyes, unlike anthraquinone dyes, are known to undergo *cis-trans* photoisomerization, when illuminated by green light. Photoisomerization changing the dye molecular conformation may well lead to a reorientation of the nematic host proportional to the incident laser intensity. But, quite surprisingly, anthraquinone dyes, whose molecular conformation is very stable, produce a much larger enhancement of the optical reorientation in the nematic, despite of the small amount of dye (a few percent) present in the mixture. In the anthraquinone dyes, the molecular conformation remains unchanged, and only the electronic state is affected by the photon absorption. We are assuming here that a change of the electronic state in a dye molecule will produce a change in the interaction forces with the surrounding liquid crystal molecules. The change is expected to be small. Thus, the key point of the model will be to prove that a small change in the guest-host interaction at the molecular level can lead to huge changes in the observed macroscopic torque on the liquid crystal, even for very low dye concentration. It is worth nothing that an enhancement of the optical torque is expected whatever the mechanism leading to a difference in the molecular interaction when the dye molecules electronic state is changed. In this sense, the enhancement effect is expected to be quite general and should be observable in the majority of dye-nematic mixtures. This is confirmed by our experiments: we studied 11 dyes in five

different nematic hosts (5CB, MBBA, E7, E63, 3010) and only one dye showed zero torque enhancement, within the experimental errors¹⁰. Moreover, we found both positive and negative enhancement factors. According to the model presented here, this is to be ascribed to the reversing in sign of the difference $\Delta u = u_e - u_g$, between the interaction energies of the dye molecules in their excited and ground state. This is just an example of how the optical reorientation in dye-nematic mixtures can be exploited to obtain important informations on the intramolecular forces.

THE OPTICAL TORQUE ENHANCEMENT

A laser beam linearly polarized in the direction \mathbf{e} propagating in a nematic medium produces a macroscopic optical torque \mathbf{M}_o acting on the molecular director \mathbf{n} given by¹¹

$$\mathbf{M}_o = \frac{\epsilon_a |E_o|^2}{8\pi} (\mathbf{n} \cdot \mathbf{e})(\mathbf{n} \times \mathbf{e}), \quad (1)$$

where E_o is the optical field inside the medium, $\epsilon_a = n_e^2 - n_o^2$, and n_o and n_e are the ordinary and extraordinary refractive indices of the liquid crystal, respectively.

If $p_e = p_e(\mathbf{l})$ is the probability of finding a dye molecule oriented along \mathbf{l} in its excited state, the average total torque that the dye exerts on the nematic is given by

$$\mathbf{M}_d = \frac{N_d}{V} \langle p_e \mathbf{m}_e + (1 - p_e) \mathbf{m}_g \rangle, \quad (2)$$

where N_d is the number of dye molecules in the volume V , and $\mathbf{m}_{e,g}$ are the torques exerted by each dye molecule in its excited or ground state, respectively. The average is made with respect to the angular distribution of the dye molecules. In the first approximation, we may neglect the effect of the rotational diffusion of the dye molecules and perform the average in Eq.(2) with respect to the distribution function $f_0(\mathbf{l})$ of the ground state dye molecules in the absence of the laser beam. In the mean field approximation we may take

$$f_0 = \frac{1}{4\pi Z} e^{m(\mathbf{n} \cdot \mathbf{l})^2} \quad (3)$$

where \mathbf{n} is the nematic director, Z the normalization constant, and

$$m = \frac{u_g S_n}{2k_B T}, \quad (4)$$

S_n being the scalar order parameter of the nematic host, u_g the coupling energy between the dye and the host molecules, T the temperature and k_B the Boltzmann

constant, respectively. In the same mean field approximation, the torques $\mathbf{m}_{e,g}$ are given by

$$\mathbf{m}_{e,g} = u_{e,g} S_n (\mathbf{n} \cdot \mathbf{l}) (\mathbf{n} \times \mathbf{l}). \quad (5)$$

For laser intensity low enough to prevent the dye saturation, the excitation probability $p_e(\mathbf{l})$ at steady-state is given by

$$p_e(\mathbf{l}) = \tau_e w(\mathbf{l}) \quad (6)$$

where $w(\mathbf{l})$ is the transition rate and τ_e the lifetime of the dye excited state. Although we neglected the rotational diffusion in evaluating the dye distribution function, we shall now reintroduce it phenomenologically by taking as lifetime τ_e of the excited level the value

$$\tau_e = \frac{\tau_f \tau_D}{\tau_f + \tau_D}, \quad (7)$$

where τ_f is the dye excited state lifetime and τ_D is the dye rotational diffusion time. The dependence of the transition rate w on the direction \mathbf{e} of the light polarization is given by

$$w = \sigma |E_o|^2 (1 \cdot \mathbf{e})^2 \quad (8)$$

where σ is a constant to be related to the absorption coefficient of the mixture.

Inserting now Eq.(8) into Eq.(6) and the result into Eq.(2) yields

$$\mathbf{M}_d = \frac{N_d S_n \sigma |E_o|^2 \tau_e}{V} (u_e - u_g) \langle (1 \cdot \mathbf{e})^2 (\mathbf{n} \cdot \mathbf{l}) (\mathbf{n} \times \mathbf{l}) \rangle. \quad (9)$$

It is worth noting that the right hand side of Eq.(9) is not zero because the transition probability p_e depends on the azimuthal angle ϕ of \mathbf{l} around the molecular director \mathbf{n} . This lack of cylindrical symmetry of the dye excitation probability is the true foundation of the enhancement of the optical torque in the nematic phase. The average appearing in Eq.(9) is made with respect to the distribution function (3) and can be evaluated in closed form. The final result for \mathbf{M}_d is

$$\mathbf{M}_d = \frac{2k_B T N_d S_d \sigma |E_o|^2 \tau_e}{V} \left(\frac{u_e - u_g}{u_g} \right) (\mathbf{n} \cdot \mathbf{e}) (\mathbf{n} \times \mathbf{e}). \quad (10)$$

Comparing now Eq.(10) with Eq.(1) we see that the torques \mathbf{M}_d and \mathbf{M}_o are indeed proportional, the enhancement factor ξ being

$$\xi = \mu S_n \left(\frac{8\pi h \sigma N_d}{\epsilon_a V} \right), \quad (11)$$

where we introduced the optical wavelength λ and the constant

$$\mu = \frac{2k_B T S_d \tau_e (u_e - u_g)}{h u_g S_n}. \quad (12)$$

In deriving Eq.(12), we used the relationship between σ and the light absorption coefficients α_e and α_o for the extraordinary and ordinary waves

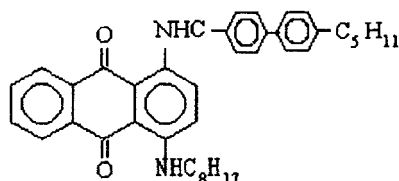
$$\frac{N_d}{V} \sigma = \frac{c n_o (n_e \alpha_e + 2 n_o \alpha_o)}{8 \pi h \nu}. \quad (13)$$

The quantity μ depends on molecular parameters only and is a measure of the angular momentum in units of h that each dye molecule transfers to the nematic hosts. We may use μ as the merit figure characterizing the torque enhancement effect in the mixture. This merit figure can be evaluated from Eq.(11), once all other factors have been expressed in terms of measurable quantities. The enhancement factor ξ is found by comparing the strength of the optical reorientation induced by the laser beam in the dye-nematic mixture and in the pure host, corrected for taking onto account the exponential decay of the beam intensity in the dyed sample. In order to extract the information on the interaction energies u_e and u_g we need to know S_d and τ_e . The first quantity is the scalar order parameter of the dye guest and it can be found from the light absorption anisotropy $\alpha_a = \alpha_e - \alpha_o$, because $S_d = \alpha_a / (\alpha_e + 2\alpha_o)$. The experimental determination of the lifetime of the dye excited state requires more sophisticated techniques as time resolved fluorescence¹².

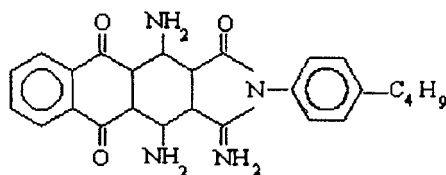
THE EXPERIMENT

We performed a series of experiments to determine the merit figure μ of several nematic-dye mixtures. In the measurements presented here, 5CB, E63, and MBBA have been used as nematic hosts. The dyes were anthraquinone dyes AQ2 and D4 from BDH company, and home made dye 12, and dye 9, whose structure formulas are shown in Fig. 1.

All samples were $50\mu m$ thick and their walls were treated with polyvinyl alcohol surfactant to obtain good planar alignment. The quality of the alignment was tested by a polarizing microscope. During the measurements the temperature was taken constant to $24 \pm 1^\circ C$ by placing the cell in a thermostatic oven. The enhancement factor ξ of the optical torque was determined for AQ2 and D4 in the E63 host, by comparing the birefringence due to laser induced optical reorientation in the pure host and in the mixture. The absolute determination of ξ is not easy and requires laser sources having power in the range of hundred milliwatts or more. We used a



Dye 9



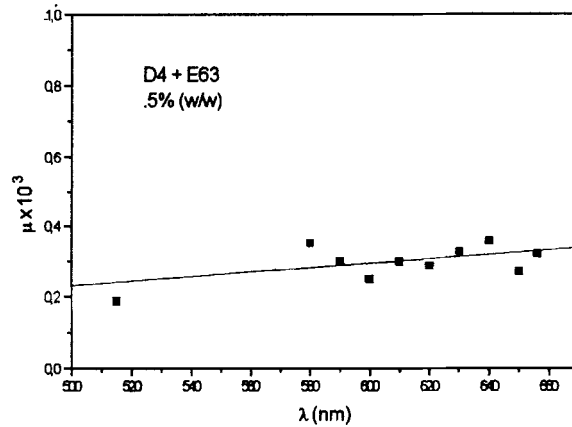
Dye 12

FIGURE 1: Structures of our dye 12 and 9.

dye laser to measure ξ , and hence the merit figure μ , as a function of wavelength. The results of these experiments have been reported elsewhere¹³. The measured enhancement factor ξ was about 200 for AQ2 and about -40 for D4 at $\lambda = 6300 \text{ \AA}$. These factors are huge, as previously noted^{6, 7, 8}, and may render these mixtures very interesting for low power nonlinear optical applications, provided absorption can be tolerated. Moreover, D4 shows a negative enhancement, leading to a defocusing Kerr-like material (pure nematics always behave as focusing Kerr-like materials). According to our model, the merit figure μ should be independent of the laser wavelength. This is indeed the case for D4 dye, as shown in Fig.(2).

It should be noted, however, that in the case of AQ2 μ was found to be an increasing function of λ . This discrepancy was ascribed to the fact that, unlike D4, AQ2 has two absorption bands in the explored spectral region, so that our single-resonance model fails¹³.

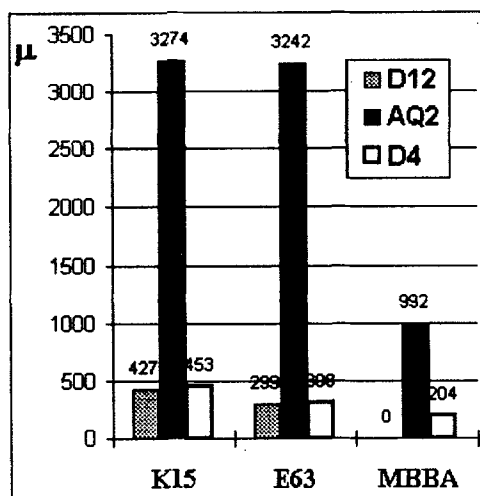
The experiments are made simpler and the errors are greatly reduced, if one is interested only to the relative change of the merit figure in changing the mixture. In this case, the huge nonlinear optical response of dye-nematic mixtures can be exploited to use a low power laser source, in the milliwatt range, to induce the molecular reorientation in the sample. In our experiments, we used a *p*-polarized He-Ne laser focused on a spot of 60μ to induce the optical reorientation. The incidence angle of the pump beam was fixed at 37° to avoid the occurrence of the Fréedericksz transition threshold. The birefringence due to the optical reorientation was probed

FIGURE 2: Merit figure μ for E63-D4 mixture as a function of the laser wavelength.

	AQ2			D4			Dye 12			Dye 9		
	α_e	α_o	S_d	α_e	α_o	S_d	α_e	α_o	S_d	α_e	α_o	S_d
5CB	194	50	.49	223	107	.27	373	90	.51	42	74	-.17
MBBA	190	92	.26	43	22	.24	348	86	.50	30	71	-.24
E63	663	64	.76	362	115	.42	480	49	.74	23	96	-.34

TABLE 1: Absorption coefficients α_{\parallel} and α_{\perp} (in cm^{-1}) and the scalar order parameter S_d for different dye nematic mixtures

by using a second He-Ne laser beam in a suitable interferometric scheme, described elsewhere⁴. The incidence angle of the probe beam was set to 43° . The absorption coefficients at the He-Ne wavelength ($\lambda = 6328\text{\AA}$) were determined in a separated experiment. Their values together with the scalar order parameter of the dye are reported in Table 1. The merit figure μ is reported in Fig. 3. Dye 9 does not appear in the figure, because we found no enhancement for this dye in all nematic hosts. AQ2 yields the strongest enhancement effect in all hosts, while MBBA yields the lowest enhancement for all dyes. If we take 1000 as a typical value for μ and pose $S_d \simeq .5$, $\tau_e \simeq 1\text{ns}$, $k_B T \simeq 4 \cdot 10^{-14}\text{erg}$, we may use Eq.(12) to evaluate the relative difference $\Delta u/u$ in the interaction energy between the nematic and the dye molecule in its excited and ground state. The result is $\Delta u/u \simeq 17\%$. We see therefore, that a relatively small change in the interaction energy may lead to enhancement factors as large as 200, even in dilute dye-nematic mixture. As a consequence, we may imagine

FIGURE 3: Merit figure μ for different dye nematic mixtures.

that the angular distribution function of the dye molecules is poorly affected by the presence of the laser beam. As previously noticed, for each dye the lowest merit figure is found in MBBA host. Also the order parameter is minimum for MBBA, even if the differences are less evident, as shown in Table 1. We think that this may be ascribed to the fact that the MBBA molecule has no strong polar groups in its side chains. On the contrary, 5CB is a cyanobiphenyle and E63 is a mixture of cyanobiphenyles, all containing a the strong polar cyano group. We may then argue that the dye-nematic interaction energy is made of the sum of a polar contribution u_p and a van der Waals (or steric) contribution u_W and that the polar contribution is dominant in the case of nematic host containing the cyano group in their side chains. In the case of MBBA host the weaker van der Waals forces prevail.

This interpretation is also supported by some recent measurements of the order parameter of anthraquinone dyes in nematic hosts as a function of the length-to-width ratio l/d of the dye molecule¹⁴. In the case of nematic host with no cyano group, the dye order parameter was found to be an increasing function of l/d , ranging from 0.3 to 0.65, as expected for steric van der Waals forces. For cyano-nematic hosts, the dye order parameter was found to be almost independent on l/d and generally much higher, ranging from 0.5 to 0.8. Such effect is not observed in azo dyes, confirming that u_p is much larger than u_W . The occurrence of some peculiar interaction between cyano-nematics and anthraquinone dyes is also suggested by the anomalous decreasing of the order parameter as a function of the dye anisotropic

polarizability¹⁵. It should be stressed, however, that our measurements are more sensitive to the change Δu of the interaction energy, rather than u itself. Then, we may infer that, when present, also Δu_p is much larger than Δu_w . As final point, we may exclude, at least for anthraquinone dyes, that conformational changes in the dye molecule may play any role. If this were the case, in fact, we would expect a strong dependence of the effect on the material constants of the nematic host as viscosity, and the dye order parameter should be strongly dependent on the geometrical ratio l/d of the dye molecule. We ascribe therefore the effect to some redistribution of the (electronic or protonic) charge inside the dye molecule. These conclusions may be not true for azo dyes.

CONCLUSIONS

A comparative study was carried out on the enhancement of the optical torque in dye-nematic mixtures, first observed by Jánossy et al.⁶. The interest was motivated by the fact that such effect, unlike other nonlinear optical effects in liquid crystals, seems to be very sensitive to the molecular structure of the guest-host system. A simple model is presented that, although neglecting the molecular diffusion and the dye saturation, is enough to understand the main features of the molecular mechanism underlying the phenomenon. A merit figure, characteristic of the guest-host molecular interaction only, was then devised. The model presented here can be seen as the low diffusion limit of a much more complicated statistical model already appeared in the literature⁹. The key point of the model is keeping a finite difference Δu in the interaction energy with the host between the dye molecules in their excited and ground state. The dye-assisted amplification of the optical torque may be both positive and negative, and it is observed in the large majority of dye-nematic mixtures. We found only one dye (our dye 9) leading to no enhancement effect. The enhancement effect was found to be strongly dependent on the host, and it is very large when the liquid crystal host has strong polar groups, as CN, in its side chain. The corresponding change of Δu is to be ascribed to the (electronic or protonic) intramolecular charge redistribution and not to a conformational transitions, at least for anthraquinone dye. Some aspects of the phenomenon, as for example the wavelength dependence of the merit figure of AQ2 in E63 host, is not yet well understood. We hope however that the results presented here may be of some help in suggesting a way to make guest-host systems exhibiting a very high amplification of the optical torque. Having such materials could be very interesting

for nonlinear optics applications, because the increase of the nonlinear response is not accompanied here by a corresponding decreasing in the response time.

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