

# Role of dye structure in photoinduced reorientation of dye-doped liquid crystals

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The giant optical nonlinearity associated with photoinduced molecular reorientation of dye-doped nematic liquid crystals has been measured for a homologous set of dyes belonging to the anthraquinone family, dissolved both in a polar and in a nonpolar liquid crystal host. We found a strong sensitivity of the nonlinearity merit figure to the detailed structure of the dye substituent groups. Our results provide some insight into the molecular mechanisms underlying this phenomenon, whose full understanding will finally require a detailed picture of guest–host intermolecular interactions and their dependence on the molecule electronic state. © 2000 American Institute of Physics. [S0021-9606(00)50546-7]

## I. INTRODUCTION

Nematic liquid crystals (NLCs) exhibit a very large optical nonlinearity associated with collective molecular reorientation driven by the “optical torque”  $\tau_o$ .<sup>1</sup> In the case of transparent materials this torque is well understood in connection with the anisotropy of optical polarizability, which makes it energetically favorable for the molecules to align parallel to the electric field. Its expression in terms of the optical field  $\mathbf{E}$  and molecular director  $\mathbf{n}$  is  $\tau_o = \tau_{em} = \epsilon_a \langle (\mathbf{n} \times \mathbf{E})(\mathbf{n} \cdot \mathbf{E}) \rangle / (4\pi)$ , where  $\epsilon_a = n_e^2 - n_o^2$  is the dielectric anisotropy in the optical domain,  $n_e$  and  $n_o$  being the extraordinary and ordinary refractive indices, respectively, and the angular brackets denote the average over an optical cycle.

In contrast, the case of light-absorbing materials has been the subject of intensive research in the last decade.<sup>2–13</sup> In most cases, visible-light absorbing NLCs are obtained by dissolving a small amount of organic dye in a transparent liquid crystal host. In 1990, Jánossy *et al.* discovered that the strength of the optical torque acting in dye-doped materials can be completely different from that of the corresponding pure (transparent) hosts, despite the small difference observed in the dielectric anisotropy  $\epsilon_a$ .<sup>2</sup> For certain dyes the optical torque was found to be enhanced by more than two orders of magnitude for dye fractions below 1%.<sup>3</sup> For other kinds of dye the torque is sign reversed, so as to reorient molecules away from the electric field direction.<sup>5</sup> Still other dyes are instead ineffective, i.e., they leave the optical torque approximately unaltered. These strong torque variations are reflected into equally strong variations of the optical nonlinearity. In some dye-NLC mixtures the optical Kerr-like nonlinearity is among the highest ever observed. Moreover, it is worth mentioning that a similar enhancement of optical nonlinearity has been recently observed in the ordinary

isotropic-liquid phase of dye-doped materials.<sup>14–16</sup>

As discussed in Ref. 10, the effect of light absorption is actually to introduce an additional “photoinduced” torque  $\tau_{ph}$ , so that the overall optical torque is now  $\tau_o = \tau_{em} + \tau_{ph}$ , where  $\tau_{em}$  is the ordinary dielectric anisotropy torque, which is almost unchanged by the presence of dye. Symmetry considerations show that, in the limit of small light intensity,  $\tau_{ph} = \zeta \langle (\mathbf{n} \times \mathbf{E})(\mathbf{n} \cdot \mathbf{E}) \rangle / (4\pi)$ , i.e., the photoinduced torque has exactly the same functional form as the dielectric torque.<sup>10</sup> This explains why the overall effect of dye appears phenomenologically as a multiplicative enhancement, by a factor  $\eta = 1 + \zeta / \epsilon_a$ , of the optical torque. The new constant  $\zeta$  must be related to the presence of dye, to its interaction with the NLC host, and to light absorption.

A fundamental theory of the photoinduced torque  $\tau_{ph}$ , predicting for example the value of  $\zeta$  of a given dye-NLC mixture, must be based on a molecular kinetic approach, the light absorption process being a nonequilibrium one. Recently proposed molecular models are based on the hypothesis that a strong reversible variation of guest–host intermolecular interactions may occur during photoinduced electronic excitation of the dye molecule.<sup>7,10,11</sup> To test these models, one can study how the torque changes when the molecular structures of both dye and host are varied, possibly in a systematic way. Some studies of this kind have already appeared in the literature,<sup>3,5,8,11</sup> but in all of them the dye structures were too varied and complex, not allowing an easy identification of the critical structural factors. Motivated by these considerations, in this work we measured the optical torque in dye-doped NLCs, using a set of dyes selected for having relatively simple molecular structures and small structural variations from one dye to the next. For the time being we limited our interest to the family of anthraquinone derivatives. Moreover, we used two different NLC hosts, one

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composed of polar molecules and the other essentially non-polar.

When comparing the effect of different dyes, aiming at extracting the important molecular features, the strength of the optical torque  $\zeta$  is not a good merit figure, for example, because it depends on dye concentration  $c$ . In general, for sufficiently small dye concentrations, the torque strength  $\zeta$  is expected (and found)<sup>16</sup> to be proportional to  $c$ . Moreover, it is reasonable to assume that  $\zeta$  is proportional to the dye absorption cross-section  $\sigma$ , that controls the number of absorption events per dye molecule. Therefore, to focus on all other less-obvious molecular dependencies we introduced the merit figure  $\mu = \zeta / [(n_e \alpha_e + 2n_o \alpha_o) \lambda S]$ ,<sup>11</sup> where  $\alpha_e$  and  $\alpha_o$  are the absorption coefficients for the extraordinary and ordinary wave, respectively,  $\lambda$  is light wavelength, and  $S$  is the NLC order parameter. In plain English,  $\mu$  gauges the ability of a single dye molecule to contribute to the torque *provided* that it has absorbed a photon. Moreover, in the limit of small concentration  $c$ ,  $\mu$  is independent of both  $c$  and  $\sigma$ , because  $(n_e \alpha_e + 2n_o \alpha_o) \lambda \propto c \sigma$ . The discussion on our results will be based mainly on the merit figure  $\mu$ .

## II. EXPERIMENT

Our measurements of optical nonlinearity are based on the pump-and-probe laser interferometric technique described elsewhere.<sup>11</sup> Briefly, the pump-laser optical torque induces a molecular reorientation in the sample, resulting in a phase shift  $\Delta\phi$  of the probe beam. This phase shift was measured by letting the emerging probe light interfere with a plane-wave reference beam and observing the interference fringe deformation. For such measurements, the samples were prepared in the homeotropic film geometry, i.e., with the molecular director perpendicular to the containing glasses. This geometry was chosen because it reduces the effect of absorption thermal indexing. The residual thermal contribution to  $\Delta\phi$  was separated from the orientational contribution by exploiting the large difference in their response times (of the order of 1 ms for the former and 0.1 s for the latter). To measure the absorption spectra we used instead the planar geometry, in order to obtain both  $\alpha_e$  and  $\alpha_o$ . The pump beam was either from a He-Ne laser, having  $\lambda = 633$  nm, or from a frequency-doubled Nd:YAG continuous-wave laser, having  $\lambda = 532$  nm. For each sample, we chose the pump wavelength that is within the absorption band. In one case (dye A1) we used both wavelengths, as they were both within the band and we could thus check the possible wavelength dependence.<sup>11</sup> The pump beam was focused to the same spot size  $w_0 = 43 \pm 2$   $\mu\text{m}$  in all cases. The incidence angles of pump and probe lasers were  $\beta_0 = 28^\circ$  and  $\beta_1 = 47^\circ$ , respectively. The film thickness was  $L = 55 \pm 1$   $\mu\text{m}$  in all samples. For each sample the nonlinearity factor  $\Delta\phi/P$  was obtained from the slope of the measured phase shift  $\Delta\phi$  versus pump power  $P$ . The factor  $\zeta$  was then obtained from the ratio of the dye-doped and pure NLC nonlinearity by means of the enhancement factor expression

$$\eta = 1 + \frac{\zeta}{\epsilon_a} = \frac{1 (\Delta\phi/P)_{\text{dye doped}}}{f (\Delta\phi/P)_{\text{pure host}}}, \quad (1)$$

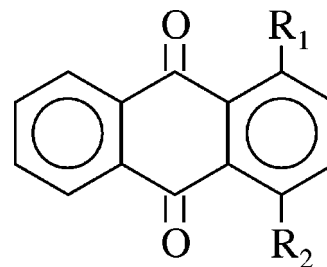


FIG. 1. General molecular structure of the dyes employed in this study. The group substituents  $R_1$  and  $R_2$  are listed in Table I.

where  $f$  is a factor taking into account absorption losses in the dye-doped sample. As shown in Ref. 11,

$$f = \frac{12}{(\alpha_x L)^2} \left[ 1 - \left( \frac{1}{2} + \frac{1}{\alpha_x L} \right) (1 - e^{-\alpha_x L}) \right], \quad (2)$$

where

$$\alpha_x = \frac{n_e \alpha_o - n_o / n_e [(\alpha_o / n_o) - (\alpha_e / n_e)] \sin^2 \beta_0}{\sqrt{n_e^2 - \sin^2 \beta_0}} \quad (3)$$

is the effective absorption constant along the normal to the NLC film (for the homeotropic alignment). In Eq. (1), one must take care of using the dye-doped and pure host nonlinearities as measured at the same wavelength. For laser power limitations we could measure  $(\Delta\phi/P)_{\text{pure host}}$  only at  $\lambda = 532$  nm, but this value can be converted to the corresponding one at  $\lambda = 633$  nm just by multiplying it by the wavelength ratio 532/633 (neglecting dispersion).<sup>1</sup>

The basic structure of the dyes labeled A1–A6 is shown in Fig. 1. They are all anthraquinone derivatives, with the substituent groups  $R_1$  and  $R_2$  located at positions 1 and 4 of the core. The list of group pairs  $R_1$  and  $R_2$  for the different dyes is given in Table I. Dyes A1–A3 and A5–A6 have been bought from Aldrich; dye A4 was provided by Nematel (Darmstadt, Germany). Their purity is 98%–99%. The dye labeled AD1 in Table I has a different structure (i.e., not that shown in Fig. 1) and was included only as a reference for comparison with previous works. It is 1,8-dihydroxy-4,5-diamino-2,7-diisopentylanthraquinone (see Ref. 11 for a drawing) and was provided by the Liq. Cryst. Soc. “Sodruzhestvo,” Moscow, Russia. The employed NLC hosts are the commercial mixtures E7 and ZLI3086, both from Merck KGaA (Darmstadt, Germany), whose components are shown in Fig. 2.<sup>17</sup> E7 is a eutectic mixture of 51% 4'-*n*-pentyl-4-cyanobiphenyl (5CB), 25% 4'-*n*-heptyl-4-cyanobiphenyl, 16% 4'-*n*-octyloxy-4-cyanobiphenyl, and 8% 4'-*n*-pentyl-4-cyano-*p*-terphenyl, exhibiting a stable nematic phase over the range  $-10$  to  $60$   $^\circ\text{C}$ .<sup>17</sup> ZLI3086 is nematic in the similar range  $-20$  to  $72$   $^\circ\text{C}$ . The detailed proportions of its components are confidential information and cannot be reported here. However, for our purposes, the main difference between E7 and ZLI3086 is that the former is composed of polar molecules (owing to the cyano substituent CN) while the molecules of the latter are almost perfectly nonpolar. The large difference of polarity of these two hosts is evidenced, for example, by the dielectric constants at 1

TABLE I. Measured properties of dye-liquid crystal mixtures for pump light wavelength  $\lambda$  at room temperature.  $\alpha_e$  and  $\alpha_o$  are given at wavelength  $\lambda$ .  $\mu$  denotes the nonlinearity merit figure as defined in the text. Where the dye is not indicated, data refer to the pure transparent host. The label ZLI is a short notation for ZLI3086, by Merck. Dye AD1 did not have the structure shown in Fig. 1 (see the text and Ref. 11).

Dye label	R <sub>1</sub>	R <sub>2</sub>	NLC	$\lambda$ (nm)	$\alpha_e$ (cm <sup>-1</sup> )	$\alpha_o$ (cm <sup>-1</sup> )	$\Delta\phi/P$ (rad/mW)	$\zeta$	$\mu$
...	...	...	E7	532	0	0	0.067±0.004	0	0
A1	NH <sub>2</sub>	NH <sub>2</sub>	E7	532	235	55	1.21±1	15±2	650±80
A1	NH <sub>2</sub>	NH <sub>2</sub>	E7	633	36	12	0.21±0.01	2.1±0.3	450±60
A2	OH	OH	E7	532	166	48	$ \Delta\phi/P  < 0.07$	$-1.5 < \zeta < 0.7$	$-90 < \mu < 10$
A3	NHCH <sub>3</sub>	NHCH <sub>3</sub>	E7	633	66	29	-0.28±0.01	-4.7±0.4	-490±50
...	...	...	ZLI	532	0	0	0.027±0.001	0	0
A1	NH <sub>2</sub>	NH <sub>2</sub>	ZLI	532	20	15	0.048±0.008	0.3±0.1	100±30
A2	OH	OH	ZLI	532	33	17	$ \Delta\phi/P  < 0.03$	$-0.7 < \zeta < 0.1$	$-150 < \mu < 20$
A3	NHCH <sub>3</sub>	NHCH <sub>3</sub>	ZLI	633	84	60	$ \Delta\phi/P  < 0.06$	$-1.5 < \zeta < 0.7$	$-100 < \mu < 50$
A4	NH <sub>2</sub>	H	E7	532	53	19	1.7±0.1	19±2	3200±300
A5	NHC <sub>2</sub> H <sub>5</sub>	NHC <sub>2</sub> H <sub>5</sub>	E7	633	42	41	-0.50±0.02	-8±1	-850±90
A6	NHC <sub>5</sub> H <sub>11</sub>	NHC <sub>5</sub> H <sub>11</sub>	E7	633	36	48	-0.54±0.02	-9±1	-880±90
AD1			E63	633	189	29	7.5±0.2	87±8	4400±400
AD1			E63	532	64	15	2.2±0.1	20±2	3100±300

kHz, which are, respectively,  $\varepsilon_{\parallel}=19.0, \varepsilon_{\perp}=5.2$  in E7 and  $\varepsilon_{\parallel}=2.9, \varepsilon_{\perp}=2.8$  in ZLI3086 (both at 20 °C).<sup>17</sup> The reference dye AD1 was dissolved in the nematic E63, also from Merck, which is a cyanophenyl mixture quite similar to E7 (see Ref. 18 for a list of its components).

The solubility of all our dyes in ZLI3086 resulted lower than in E7, probably because of the different degree of polarity. For this reason, we made solutions in ZLI3086 only of the three dyes A1, A2, and A3, which are the most interesting ones for a comparison. The measured optical nonlinearity  $\Delta\phi/P$ , torque constant  $\zeta$ , and absorption coefficients  $\alpha_e, \alpha_o$  at the pump wavelength, and the resulting calculated merit figure  $\mu$  for all guest-host combinations are reported in Table I. In the calculations, we used  $n_e=1.746$  and  $n_o=1.522$  for E7 and  $n_e=1.617$  and  $n_o=1.504$  for ZLI3086 (20 °C, 589 nm).<sup>17</sup> Moreover, we took a nominal value of  $S=0.75$  for both hosts. By trying samples of different concentration (as measured by the absorption coefficient), we verified that the photoinduced nonlinearity is indeed proportional to concentration (i.e., to absorption coefficient). For those mixtures for which the orientational nonlinearity was too small to be measured, we report the experimental bounds on all quantities. In particular, the bounds on  $|\Delta\phi/P|$  were

determined by dividing the phase-shift sensitivity of our apparatus by the maximum light power  $P$  that did not cause permanent or long-lived thermal effects disturbing our measurements.

### III. DISCUSSION

Let us focus first on the three anthraquinone derivatives labeled as A1, A2, and A3 in Table I. As shown in the same table, for these dyes dissolved in E7 we have measured, respectively, a positive, vanishing (within our experimental sensitivity), and negative value of  $\mu$ . When using the nonpolar host ZLI3086, we observed a small positive  $\mu$  with A1, and a vanishing  $\mu$  with A2 and A3. These differences must somehow be related with the different substituent groups R<sub>1</sub> and R<sub>2</sub>. In the three dyes A1, A2, and A3 they are equal, i.e., R<sub>1</sub>=R<sub>2</sub>, and are, respectively, the amino NH<sub>3</sub>, hydroxyl OH, and methylamino NHCH<sub>3</sub>.

Actually, the structures of these three substituent groups are quite similar, as highlighted in Fig. 3. First, they all have a filled  $p_{\pi}$  atomic orbital on the central electronegative atom (i.e., the nitrogen in A1 and A3, the oxygen in A2) which, after hybridization with  $\pi$  orbitals of the anthraquinone core, gives the main contribution to the highest occupied molecular  $\pi$  orbital (HOMO) of the substituted molecule.<sup>19,20</sup> Second, all three substituent groups have at least one hydrogen atom that is capable of medium-strength hydrogen bonding with suitable proton acceptors.<sup>21,22</sup> In particular, when the substituent group is properly oriented it may get hydrogen bonded with the oxygen of the carbonyl CO group, within the dye molecule itself, as shown in Fig. 3. Or, for a different orientation [see Fig. 4(b)], the group may be involved in intermolecular hydrogen bonding with one of the host molecules, if the host is polar. In particular, all components of E7 have a cyano CN group that can act as a proton acceptor, as shown in Fig. 4.<sup>21</sup> No such acceptor group is instead present in ZLI3086. In general, intermolecular hydrogen bonding between anthraquinone proton-donor substituent groups and proton-accepting solvents has already been

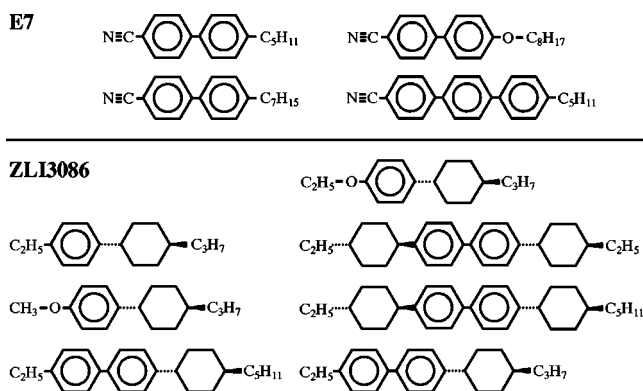


FIG. 2. Components of the two nematic mixtures E7 and ZLI3086 used as hosts (Ref. 17).

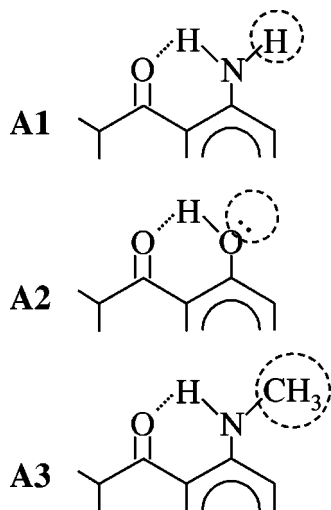


FIG. 3. Comparison between the three substituent groups in A1, A2, and A3 dyes, showing similarities and differences. The dotted line indicates a possible intramolecular hydrogen bond with the CO group of the anthraquinone core. The dashed circle highlights the main structural difference between the three groups.

reported.<sup>23–26</sup> In our case, the actual establishing of such intermolecular hydrogen bonds is suggested by several observations. First, we found a greater solubility of all dyes in the polar hosts (E7 in this work, E63 and 5CB in Ref. 11) than in the nonpolar ones (ZLI3086 in this work, MBBA in Ref. 11). Second, there is evidence that polar interactions may enhance the orientational order of dissolved dye molecules of low aspect ratio, i.e., when steric orientational effects are not so important (see the data reported in Ref. 27 and their reinterpretation given in Ref. 11). Third, for some of our dyes we observed significant solvatochromic shifts when passing from ZLI3086 to E7, similar to those observed for the same dyes in standard solvents of increasing polarity.<sup>23,28,29</sup>

Besides these common properties of all three substituent groups, there are a couple of important features that do distinguish them and that must somehow be related with the completely different torque observed. One such feature is obviously the electronegative atom that is a nitrogen for A1 and A3 and an oxygen for A2. The second main distinguish-

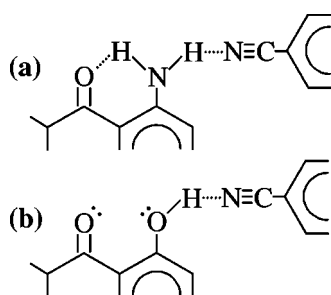


FIG. 4. Examples of hydrogen-bond intermolecular interactions between the dye substituent group  $R_1$  and the host cyano group of E7. (a) The case of the amino group (present in dyes A1 and A4), capable of simultaneous internal and external hydrogen bonds. (b) The case of the hydroxyl group oriented so as to be involved in an external hydrogen bond, thus breaking the internal bond with the carbonyl group shown in Fig. 3.

ing feature is the moiety of the group highlighted in Fig. 3 by a circle: the second hydrogen atom in the amino (dye A1), the electron lone pair in the hydroxyl (dye A2), and the methyl group in the methylamino (dye A3). Totally different electrostatic and hydrogen-bonding properties must be expected here. In the case of A1 there is a positive charge excess and proton-donating ability; in the case of A2 there is a negative charge excess and proton-accepting ability; in the case of A3 there is approximate neutrality and no hydrogen-bonding capability. In particular, this implies that only for the dye A1 dissolved in E7 can the internal and external hydrogen bonds discussed previously take place simultaneously, as shown in Fig. 4(a). In the case of A2 and A3 in E7, on the contrary, intra- and intermolecular bonds are in competition, and at equilibrium we may expect that both kinds of bonds will exist, each with a nonvanishing probability.

It is not obvious why these structural features lead to the observed striking differences in  $\mu$ . A full answer to this problem will probably require a detailed theoretical analysis of the dye molecules and of their interactions with the host, which is beyond the scope of this work. Here we limit ourselves to a qualitative discussion based on the ideas presented in Refs. 11 and 12 and on the models reported in Refs. 7, 10, and 11. These models relate the value of  $\mu$  to the variation of intermolecular interactions between dye and host molecules occurring because of the dye being electronically excited by light. An increase of the average intermolecular interaction strength in the excited state should be associated with a positive  $\mu$ , while a decrease should yield a negative  $\mu$ .<sup>11</sup> We emphasize, however, that this link between the change of intermolecular interactions and the photoinduced torque is not straightforward, being the result of a nontrivial model of dye orientational kinetics. In particular, to obtain a torque it is not necessary that the involved dye–host interaction be anisotropic. A variation of an isotropic force of attraction can be effective too, via the ensuing variation of rotational diffusion constant of the excited dye molecules.<sup>10,11</sup> It is only necessary that the probability of light-induced excitation be anisotropic.

In our case, we believe that the main contribution to the variation of guest–host interactions must come from polar interactions and more specifically hydrogen bonding of the dye with host molecules. This hypothesis is naturally suggested by the observation that the nonpolar host ZLI3086 is either ineffective or significantly less effective than the polar host E7 in all cases (see also Ref. 11 for similar results obtained with other materials, including the pure compounds 5CB and MBBA). All other intermolecular forces such as steric, dispersive, and quadrupolar ( $\pi$ – $\pi$ ) ones cannot easily account for such large difference. Moreover, our hypothesis is independently confirmed by solvatochromic shifts in the absorption spectra observed for solvents of different polarity, as we will discuss in the following. Besides the dependence on host polarity, the intermolecular interaction involved in the photoinduced effect must satisfy two additional conditions. The first is that it must undergo a significant variation due to light-induced electronic excitation, as required by the above-mentioned models. The second is that

this variation must be drastically different for the three dyes A1, A2, and A3 to account for our observations. Steric interactions, for example, can hardly satisfy the first condition. In our anthraquinone derivatives large photoinduced conformational transformations do not occur. Only a small adjustment of the nuclei positions in the excited states may be expected, as verified for example by the small Stokes shift found between the absorption and fluorescence bands.<sup>11</sup> Dispersive and maybe quadrupolar interactions could instead be slightly modified by electronic excitation. However, these interactions are dominated by the dye core, with only a small contribution coming from the substituent groups. Both the ground and excited electronic states of the three dyes A1, A2, and A3 are very similar (in particular the dyes A1 and A3 are almost perfectly iso-electronic, as the only difference in the  $\pi$  orbitals should arise from the different inductive effects of the proton and the methyl groups in the substituent group of A1 and A3, respectively). Therefore, all photoinduced variations of dispersive and quadrupolar interactions are expected to be very similar for the three dyes, contradicting our observations.

Let us now see how polar interactions could satisfy the two above-mentioned conditions. We focus mainly on hydrogen bonding, although other forms of polar interactions might also play some role. When the dye is electronically excited, some electron charge is displaced from the substituent group to the anthraquinone core (intramolecular charge transfer).<sup>19,20,30</sup> This may lead to an increase of the acidity and proton-donating properties of the group. In the case of A1 in E7, this increase will in turn strengthen both the internal and external hydrogen bonds and, by effect of the latter, will give rise to a positive  $\mu$ , in agreement with the observations. For A1 in ZLI3086 there might still be an increase of the weaker polar (or "weak" hydrogen bonds)<sup>21</sup> interactions between the amino group and, for example, the aromatic moieties or the oxygens of the host, explaining the small positive  $\mu$  measured. The strength increase of intermolecular hydrogen bonds in the excited state of A1 is confirmed by reported solvatochromic data, indicating a significant redshift of the absorption peak for increasing solvent polarity.<sup>28,29</sup> Also in our absorption spectra there is a redshift of about 12 nm of the main absorption peak when passing from ZLI3086 to E7 as a solvent. Moreover, an excited-state variation of intermolecular hydrogen bonding is discussed also in Refs. 31 and 32, in connection with the radiationless deactivation of aminoanthraquinones in polar solvents.

The case of A2 and A3 is instead less straightforward, due to the role possibly played by the competition between intra- and intermolecular hydrogen bonding. If the intramolecular bond dominates both in the ground and excited states, there should be little variation of intermolecular interactions on excitation and therefore  $\mu$  should vanish. This is certainly the case when A2 and A3 are dissolved in ZLI3086, which is not capable of medium or strong hydrogen bonding. Indeed, the merit figure of A2 and A3 in ZLI3086 is below our experimental sensitivity. Moreover, this explanation could apply also to the case of A2 in E7. Here the intramolecular hydrogen bond could be favored due, for example, to the electrostatic repulsion between the lone pairs of hydroxyl

and carbonyl. However, the ineffectiveness of A2 might be explained also by the larger electronegativity of oxygen as compared to nitrogen, which could lead to a smaller charge transfer upon excitation. A relatively small charge transfer is indeed predicted theoretically in Ref. 20 for this dye. Moreover, the vanishing variation of the intermolecular-interaction strength in the excited A2 is again directly confirmed by solvatochromic data that show only a very small blueshift with increasing solvent polarity.<sup>28,29</sup> We also observed a redshift of only 1–2 nm in the absorption spectra when passing from ZLI3086 to E7. Finally, if in the dye ground state there is a balanced equilibrium between internal and external hydrogen bonds, electronic excitation is likely to shift it in favor of intramolecular bonding (because the carbonyl acquires some extra electronic charge).<sup>19,20,30</sup> This would lead to a reduction of the time-averaged strength of intermolecular interactions and therefore to a negative  $\mu$ . We ascribe to this effect the behavior of A3 in E7. In this case there is no straightforward correlation with solvatochromic observations, as the dye A3 actually exhibits a small redshift with increasing solvent polarity.<sup>29</sup> We also observed a redshift of about 4 nm in the absorption spectra when passing from ZLI3086 to E7. However, this lack of correlation is not surprising in this case, as a blueshift would result only from a reduced strength of external hydrogen bonds in the excited molecules and not from an increased strength of internal bonds. In fact, solvatochromic shifts in absorption spectra give information only on the variation of solvation energy occurring immediately after the molecule excitation (on a coherent-electronic femtosecond time scale), thus not reflecting time-averaged effects that would eventually result from a subsequent switching to the internal bond.

Let us now discuss the other mixtures. 1-aminoanthraquinone A4 is similar to A1, except for having only one substituent group instead of two symmetrically placed groups. This leads to a much larger  $\mu$ , implying a much larger increase of interaction energy during electronic excitation in dye A4 with respect to A1. This interpretation is again well supported by solvatochromic data, as a much larger redshift in the absorption peak with increasing solvent polarity is observed for dye A4 than for dye A1.<sup>29</sup> A possible explanation of the difference between A4 and A1 is that intramolecular charge transfer is more effective for a single-amino substituted dye than for a doubly substituted one. This is plausible for two reasons: First, in the doubly substituted dye the HOMO will have symmetrical contributions from both substituent groups, each contributing with roughly half atomic orbital instead of one; second the charge transfer could be quenched for electrostatic reasons as the two amino groups are on opposite sides of the anthraquinone core. The calculations reported in Ref. 19 qualitatively confirm a trend of decreasing charge transfer with increasing number of substituent groups. Dye A4 has roughly the same  $\mu$  as the AD1-E63 mixture of Ref. 11 (we measured again  $\mu$  of AD1 in E63 and found  $\mu = 4400 \pm 500$ ; we do not know the cause of the discrepancy between our last result and our previous measurement  $\mu = 2500$  reported in Ref. 11; a possibility is the different degree of dye purity in the two experiments). Dyes A4 and AD1 are the most effective positive- $\mu$  dyes found so

far. The two dyes A5 and A6 are similar to A3 but have longer alkyl chains in the place of the methyl group on the substituent group. They also exhibit a negative  $\mu$  and are slightly more effective than A3. This could result from a slightly different balance between intra- and intermolecular hydrogen bonding, in connection with steric interactions.

#### IV. CONCLUSIONS

By studying the anomalous optical torque in dye-doped liquid crystals for several molecular structures of dye and host, we are trying to shed light on the underlying photoinduced molecular phenomena. We were actually able to propose a qualitative explanation for all the strong variations of dye efficiency observed with different structures, based on the hypothesis that a significant change of guest–host polar interactions occurs in the excited dye molecules. We also discussed briefly the reasons that led us to favor this hypothesis against other possibilities related to other kinds of intermolecular interactions. However, we emphasize that our explanation has been found largely *a posteriori*, so that its predictive power remains to be proven. At this stage it must be regarded essentially as a plausible “working hypothesis.” A final understanding will require developing a detailed model of the dye electronic structure and of its intermolecular interactions both in the ground and excited states, a work which is currently under way. Besides trying to achieve a basic understanding of the anomalous torque effect, we envision the possibility of exploiting its strong sensitivity to the variation of intermolecular interactions following electronic excitation as a new tool to study intermolecular interactions in the excited states in condensed phases.

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<sup>1</sup>For a review see, e.g., L. Marrucci and Y. R. Shen, in *The Optics of Thermotropic Liquid Crystals*, edited by R. Sambles and S. Elston (Taylor and Francis, London, 1998).

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