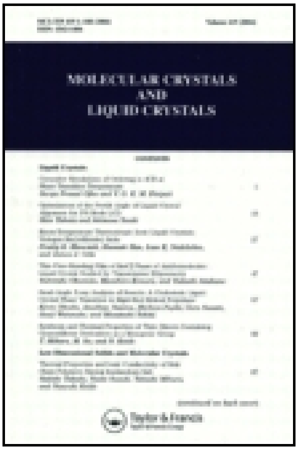

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Optical Nonlinearity by Photoinduced Variation of Intermolecular Forces in Liquids and Liquid Crystals

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Optical nonlinearity by photoinduced variation of intermolecular forces in liquids and liquid crystals

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Recent experimental and theoretical results on the optical nonlinearity associated with molecular reorientation in dye-doped liquids and liquid crystals are reviewed. The variation of intermolecular forces experienced by a photo-excited dye molecule and the resulting change of molecular-statistical parameters such as rotational friction and orientational energy appear to be at the core of this effect. Photoinduced intramolecular charge transfer could be the cause of such variation. The angular momentum conservation is also discussed.

Keywords: nonlinear optics; liquid crystals; dye; intermolecular forces

INTRODUCTION

In 1990, I. Jánossy *et. al.* reported the first observation of a surprising phenomenon: a small amount of a dye dissolved in a nematic liquid crystal (LC) to make it light-absorbing can greatly enhance the orientational optical nonlinearity of the material[1]. The enhancement is of the order of 10-100 for dye-LC weight fractions of the order of 0.1%. In that paper and in subsequent works, the phenomenology of this effect was studied in detail[2–10]. It was proved that what is actually enhanced is the effective optical torque $\boldsymbol{\tau}_o$ that light exerts on the molecular director $\boldsymbol{n}$. In transparent LCs, this torque is due to the material optical polarizability and has the following expression:

$$\boldsymbol{\tau}_o = \boldsymbol{\tau}_{em} = \frac{\varepsilon_a}{4\pi}\langle(\boldsymbol{n}\cdot\boldsymbol{E})(\boldsymbol{n}\times\boldsymbol{E})\rangle, \tag{1}$$

where the angle brackets denote average over the optical cycle, $\boldsymbol{E}$ is the optical electric field and ε_a is the dielectric anisotropy. In dye-doped absorbing LCs, the effective optical torque becomes $\boldsymbol{\tau}_o = \eta\boldsymbol{\tau}_{em}$, where η is the enhancement factor. Note that the dielectric anisotropy ε_a is not changed significantly in the dye-doped materials. The enhancement η is strongly dependent on the kind of dye, not being just proportional to its absorbance, and in some cases it can even be negative, thus reversing the torque effect. The enhancement was observed using many different dyes, mainly belonging to the families of anthraquinone and azo derivatives.

Rather than an actual enhancement of the ordinary torque mechanism, the effective optical torque is the result of the simultaneous action of the ordinary electromagnetic torque $\boldsymbol{\tau}_{em}$ and of an additional photoinduced torque $\boldsymbol{\tau}_{ph}$ due to a new mechanism related to light absorption:

$$\boldsymbol{\tau}_o = \boldsymbol{\tau}_{em} + \boldsymbol{\tau}_{ph}. \tag{2}$$

To appear as an enhancement, however, the new torque must have the same dependence on $\boldsymbol{E}$ and $\boldsymbol{n}$ as $\boldsymbol{\tau}_{em}$, i.e.,

$$\boldsymbol{\tau}_{ph} = \frac{\zeta}{4\pi}\langle(\boldsymbol{n}\cdot\boldsymbol{E})(\boldsymbol{n}\times\boldsymbol{E})\rangle. \tag{3}$$

The constant ε_a is replaced by a new material constant ζ, proportional to dye concentration, whose physical interpretation cannot be determined phenomenologically. That the expression of the new torque is exactly equal to that of the electromagnetic torque is not a coincidence: it is the only symmetry-allowed expression to the lowest order in $\boldsymbol{E}$, assuming that the new mechanism be local (i.e., independent of material and optical gradients), nonmagnetic, and history independent. Note that the local-response assumption, consistent with the observed phenomenology, suffices to exclude several hypothetical mechanisms based on heating, thermal gradients, flow, photorefractive phenomena, surface photoinduced effects, etc.

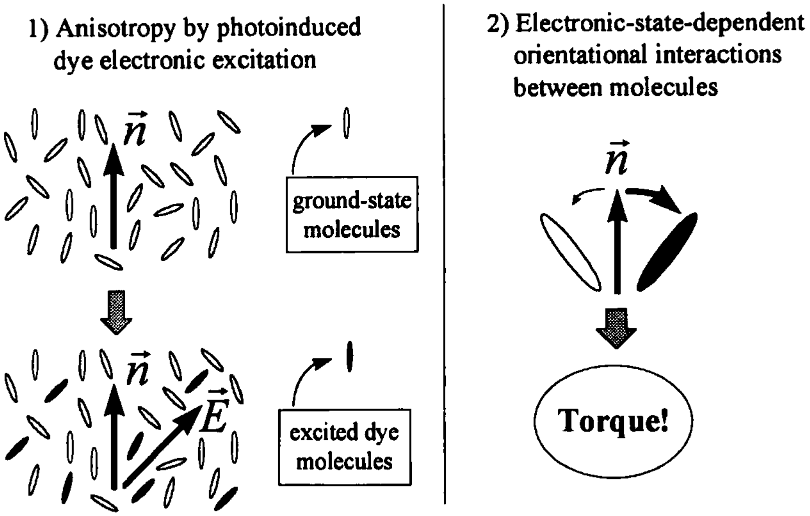

FIGURE 1 Basic idea of Jánossy's model to explain the dye photoinduced torque.

In 1994, Jánossy proposed a model of the new photoinduced effect[11], whose basic idea is schematically illustrated in Fig. 1. The process can be divided in two steps: first, light absorption preferentially excites those dye molecules which are oriented closer to the optical field $\boldsymbol{E}$, since the absorption probability is $p \propto \cos^2\theta$, where θ is the angle between the dye molecule transition dipole (parallel to the molecule long axis for dyes having positive dichroism) and the local field $\boldsymbol{E}$; second, the two anisotropic populations of ground- and excited-state dye molecules interact differently with host molecules, thus inducing an effective mean-field which breaks the azimuthal anisotropy around $\boldsymbol{n}$. In particular, if excited dye molecules "attract" the host molecule orientation stronger than ground-state dye molecules, a net torque acting on the molecular director and pulling toward the electric field $\boldsymbol{E}$ should be generated. This idea was translated in a detailed model, and the resulting calculated values of ζ are of the right order of magnitude. However, a strict quantitative comparison between theory and experiment was not possible due to decisive role played in the theory by a set of unknown molecular parameters.

In 1995, the following questions had still no clear answer: (i) The orientational optical nonlinearity of nematic LCs is analogous to the orientational optical Kerr effect of isotropic liquids, as both are due to the dipole torque arising because of the molecule anisotropic polarizability; does such analogy extend to the new photoinduced torque? In other words, is there a dye-induced enhancement of the optical Kerr effect in isotropic liquids? (ii) Does the model proposed by Jánossy work quantitatively, i.e., can it predict the value of ζ with reasonable accuracy? (iii) Why do intermolecular forces change when a dye molecule is excited? What happens inside a dye molecule? (iv) The enhanced optical torque should correspond to a larger amount of angular momentum exchanged by the molecular director; however, this angular momentum cannot be exchanged with light, since it can be shown that absorption by itself transfers a negligible amount of angular momentum; therefore, what is the "source" of this additional angular momentum?

In this paper, a tentative answer to these questions is proposed, in view of recent experimental and theoretical results[12–15]. The article is divided in four sections, corresponding to each of the four questions above.

ISOTROPIC PHASE

It is easy to think of a mechanism analogous to that proposed by Janossy for the nematic phase but applied to the isotropic liquid phase of a material made of anisotropic molecules (either a liquid-crystalline material in its isotropic phase or just a liquid), as illustrated in Fig. 2. It is a simple idea, but that the effect is actually observable is far from obvious. However, recently its observation has been reported independently by two groups[13, 16]. The experimental technique employed in both these works is based on a pump and probe geometry to measure the nonlinear birefringence, as for the ordinary optical Kerr effect. The pump was a laser pulse about 20 nanoseconds long at a wavelength within the absorption band of

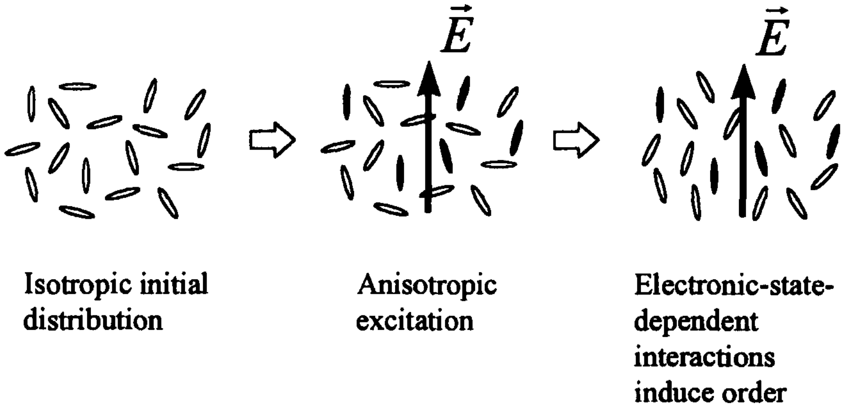

FIGURE 2 Possible mechanism of dye-induced optical Kerr effect in isotropic liquids.

the dye. The probe wavelength was instead outside the absorption band, in order to minimize the optical effects related to saturated absorption. The experiments reported in Refs. [13] and [16] differ for the range of pulse energies investigated. In the former, pulse energy was of the order of 1 mJ, large enough for observing the absorption saturation effects with ordinary focusing, as shown in Fig. 3[13]. In the latter experiment[16], the energy per unit area was hundreds of times smaller, not allowing a study of the saturation behavior, but useful to minimize secondary effects related to absorption and heating. In both cases the dyes were anthraquinone derivatives. The observed enhancement in the two works is approximately the same, for equal values of the absorption coefficient.

What indicates that the observed nonlinear birefringence is indeed due to the proposed mechanism, and not for example to flow, thermal-lensing, or direct electronic nonlinearity of dye molecules? Our interpretation is supported by the following observations. (a) The nonlinear birefringence axis was checked to be determined by the optical electric field E of the pump: if the pump polarization was rotated by 90 degrees, the birefrin-

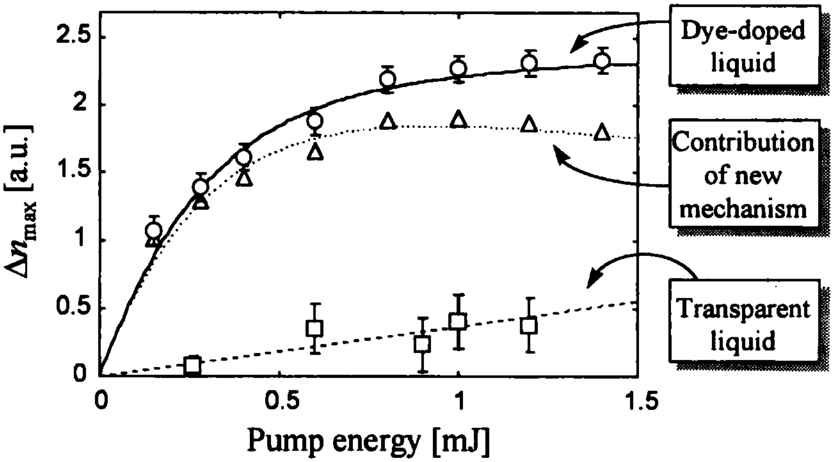

FIGURE 3 Peak nonlinear birefringence induced in isotropic liquid by a 20 ns laser pulse.

gence changed sign accordingly[13]. (b) The temperature behavior of the nonlinearity shows the signature of a molecular orientation response: when a liquid-crystalline material was used, a pretransitional enhancement of the birefringence was observed when approaching the isotropic-to-nematic transition temperature T_c (see Fig. 4). It show the expected power law $(T - T^*)^{-1}$, where T^* is a material characteristic temperature slightly below T_c[13, 16]. This law has actually been verified in two different dynamical regimes: in Ref. [13], the peak instantaneous nonlinearity Δn_{max} was measured for a material response time smaller than pulse duration; in Ref. [16], the time-integrated squared birefringence was measured, for a material response time longer than the pump pulse duration. (c) The nonlinearity enhancement in the isotropic phase of a liquid-crystalline material is only slightly larger than that observed in the nematic phase, and this would be a strange coincidence if the involved mechanism were not the same.

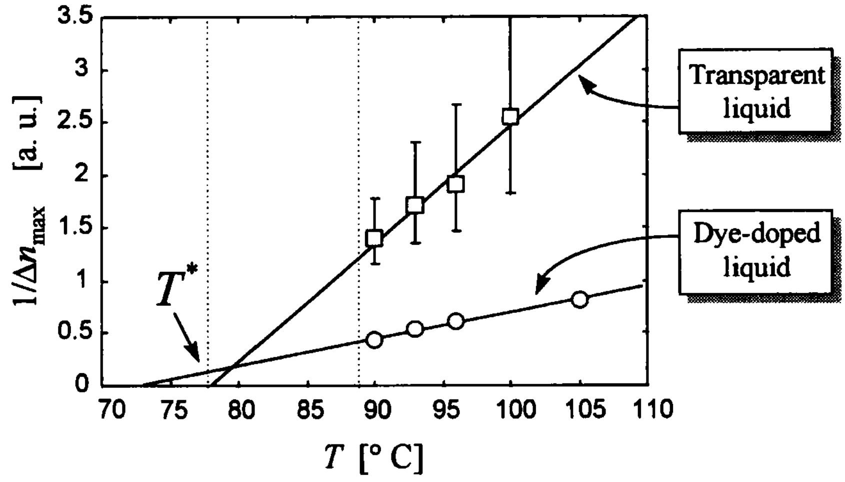

FIGURE 4 Temperature behavior of optical Kerr effect close to isotropic-to-nematic transition.

QUANTITATIVE CHECK OF THE MODEL

Rather than on the enhancement factor η or the torque constant ζ, it is useful to base all comparisons on the merit figure μ, defined as[15]

$$\mu = \frac{\zeta}{(n_e\alpha_e + 2n_o\alpha_o)\lambda S} = \frac{\eta}{(n_e\alpha_e + 2n_o\alpha_o)\lambda}\frac{\varepsilon_a}{S}, \qquad (4)$$

where n_o and n_e are the ordinary and extraordinary refractive indices, α_o and α_e the absorption coefficients, and S the order parameter. The main advantage of this quantity is that it is independent of dye concentration and absorbing efficiency. Moreover, its definition can be extended also to the isotropic phase, by replacing $(n_e\alpha_e + 2n_o\alpha_o)$ with $3n\alpha$ and the ratio ε_a/S with its isotropic limit given approximately by $\eta_a N$, where η_a is the anisotropy of single molecule polarizability, corrected for local-field-effects, and N is the (host) molecule number-density. Typically $\varepsilon_a/S \approx \eta_a N \approx 1$. In the nematic phase, μ has roughly the physical meaning of "angular momentum transferred to the host per absorbed photon", in units of Planck constant $h = 2\pi\hbar$.

The models reported in Ref. [11] for the nematic phase and Ref. [13] for the isotropic phase require numerical calculations for an "exact" solution. However, in both cases an analytical solution is possible within a simple approximation, valid in a limit which can be roughly defined as "of small dye anisotropy"[13, 14]. This approximation is very good in the isotropic case for not too high light intensities (compared to dye saturation intensity), but it is often poor in the nematic case. The expression obtained within the hypotheses introduced in Jánossy's model[11] is the following:

$$\mu \simeq \frac{2}{15h}\frac{\tau_e}{1+6D\tau_e}\left(u_e - u_g\right). \tag{5}$$

In this expression, τ_e is the dye excited-state lifetime, D is the dye rotational diffusion constant, u_g and u_e are the ground- and excited-state energy coefficients describing the orientational interaction between dye molecules and host. The precise definition of u_α, with $\alpha = g, e$, is given in terms of the mean-field orientational potentials U_α acting on dye molecules, which are taken in the form $U_\alpha = -\frac{1}{2}u_\alpha S\cos^2\theta$, where S is the host order parameter and θ is the angle between the dye molecule and the host director $\boldsymbol{n}$.

The main obstacle to a quantitative check of the theory is that the molecular parameters τ_e, D, u_g, u_e are not easily known (moreover their definition relies somewhat on model idealizations; for example, a fully precise definition of D requires that the diffusional approximation be valid). The constants τ_e and D can be obtained from measurements of time-resolved fluorescence. This has been done for the dye 1,8-dihydroxy 4,5-diamino 2,7-diisopentyl-anthraquinone (AD1) dissolved in the commercial nematic cyanophenyl mixture E63, obtaining $\tau_e \simeq 1$ ns and $D \simeq 0.1$ ns^{-1} at $T = 25°$C[12]. For mixtures of AD1 in other cyanophenyl hosts, such as 5CB, we expect these numbers not to change very much. Therefore, while waiting for additional measurements, we used the AD1-E63 values of τ_e and D also in the analysis of AD1-5CB. The constant u_g can be obtained from measurements of dichroism: in the mixture AD1-E63, $u_g \simeq 0.6$ eV;

in AD1-5CB, $u_g \simeq 0.4$ eV[15]. The excited-state energy u_e has not been measured yet. Perhaps also this parameter could be obtained from measurements of time-resolved fluorescence, but it is not an easy task. For the time being, therefore, we cannot perform a strict check of Janossy's model. We must content ourselves with using the experimental values of μ to estimate u_e and verify if the results are reasonable.

In the isotropic phase, the nonlinearity enhancement reported in Ref. [13] corresponds to $\mu \approx 3700$. From Eq. (5), we obtain $\Delta u = u_e - u_g \simeq 0.15$ eV or $\Delta u/u_g = 25\%$. However, the employed pump wavelength $\lambda = 532$ nm is not in the main absorption band of the dye AD1, but in a vibronic replica. The wavelength behavior, studied in the nematic phase, shows that vibrational excitation reduces the dye efficiency[6, 9, 15]. If the value of μ in the isotropic phase is extrapolated using the nematic wavelength behavior to $\lambda = 640$ nm, in the main band of AD1, we obtain $\mu \approx 6800$, corresponding to $\Delta u/u_g \approx 50\%$. Such energy variation is too large to be accepted with no doubts.

In the nematic phase, the calculation (based on numerical methods) of the predicted merit figure μ as a function of relevant parameters is reported in Fig. 5, together with the experimental values found in AD1-E63 and AD1-5CB[15]. It is seen that, in order to reach the measured values of μ regardless of u_g, the ratio u_e/u_g must be larger than 2. If we try to match also the value of u_g, the agreement is possible in the case of AD1-5CB only if $u_e/u_g \simeq 2.7$, and it is not possible at all in the case of AD1-E63. It is clear that the model in its most basic version does not work quantitatively.

A straightforward generalization of Janossy's model is obtained by allowing also the dye rotational diffusion constant D to depend on the electronic state[14, 15]. This corresponds to introducing two different constants D_e and D_g for the dye molecule in the excited- and ground-state, respectively. The one actually measured with time-resolved fluorescence is D_e. Note that the diffusion constant D is related to the molecular friction coefficient β by Einstein relation $\beta = kT/D$.

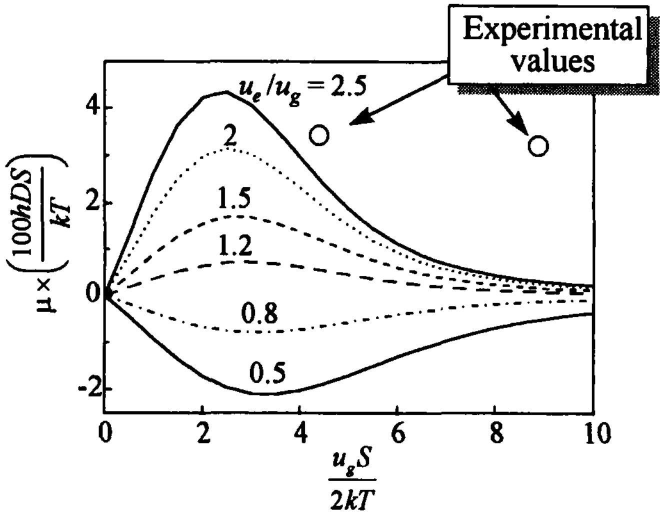

FIGURE 5 Merit figure μ calculated in the hypothesis of single diffusion constant D for different energy ratios u_e/u_g and for $D\tau_e = 0.1$. The experimental points refer to the dye AD1 dissolved in 5CB (left) and E63 (right), respectively.

Why does the change in diffusion constant contribute to the dye torque? The reason is described pictorially in Fig. 6. Including this effect, Eq. (5) is generalized to[14]:

$$\mu \simeq \frac{2}{15h}\frac{\tau_e D_e}{1+6D\tau_e}\left(\frac{u_e}{D_e} - \frac{u_g}{D_g}\right). \tag{6}$$

It is now possible to reinterpret the experimental values of μ using two unknown parameters: u_e and D_g. In the isotropic phase of AD1-E63, if we make the hypothesis $u_e = u_g$, we obtain $D_g/D_e \approx 2$ in the vibronic band, and $D_g/D_e \approx 2.6$ in the main band. In the nematic phase, the results of numerical calculations for $u_e = u_g$ are reported in Fig. 7. Agreement can be obtained with $D_g/D_e \approx 2$ both in AD1-5CB and AD1-E63.

A factor $D_g/D_e = 2$ may be considered too large to be realistic. However, there are reasons to believe that the constant D (contrary to u) may be very sensitive to small changes of the interaction between dye molecules and host. The temperature dependence of D as measured from

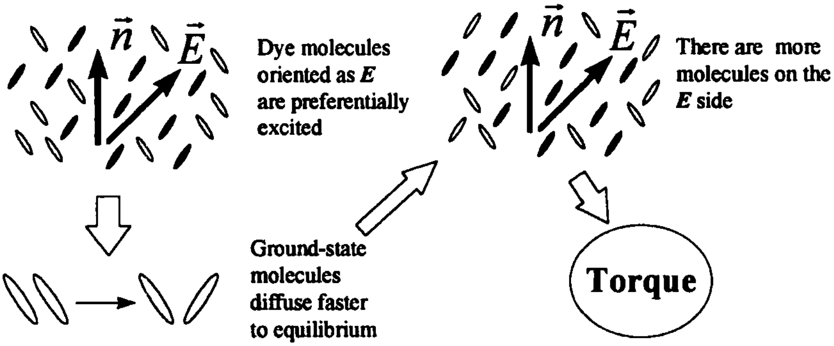

FIGURE 6 Photoinduced torque resulting from $D_g > D_e$.

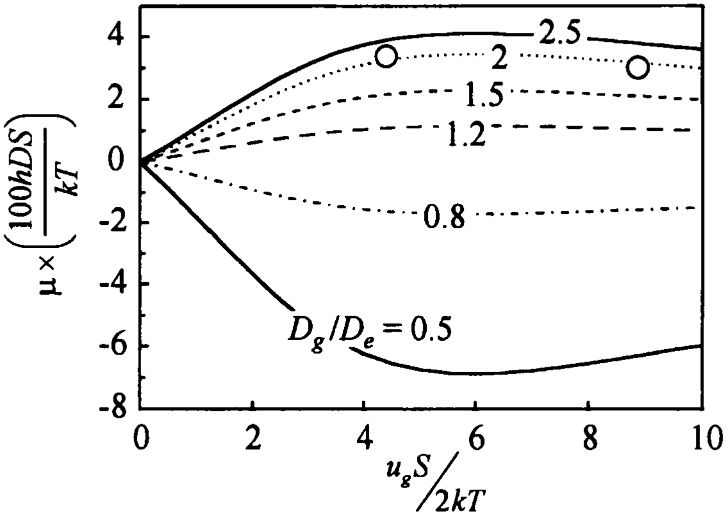

FIGURE 7 Merit figure μ calculated for different values of the diffusion constant ratio D_g/D_e, for $u_e = u_g$ and $D_e \tau_e = 0.1$. The circles are the experimental values, as in Fig. 5.

time-resolved fluorescence often shows an activation-energy-like exponential behavior. On the other hand, an "ab initio" statistical theory of D (i.e., of the friction coefficient β) yields the following expression[17]:

$$D = D_0 e^{-\frac{E_0+E_1}{kT}}, \tag{7}$$

where D_0 is a preexponential factor, and E_0 and E_1 are two different contributions to the activation energy. In particular, E_1 is an energy related to the anisotropic interaction, i.e., to the orientational mean-field U. E_0 is instead an energy characterizing the isotropic interactions, i.e., molecular cohesion. According to Ref. [17], E_0/kT is typically of the order of 10, while E_1/kT is of the order of 1. Therefore, D is very sensitive to small changes of E_0. A fractional change of 10% in E_0 yields a change in the exponential by a factor close to 3. However, this variation can be partly compensated by the change of D_0, which may also depend on E_0, although less strongly. We used the law $D_0 \propto E_0^3$ reported in Ref. [17], although probably this result is more critically model-dependent (in Ref. [17] only Van der Waals forces are considered). At any rate, after including this contribution, an increase of E_0 by 10%, when passing from ground-state to excited state, still yields a ratio $D_g/D_e \approx 2$.

A fit of the observed temperature behavior of μ based on Eq. (7), assuming a temperature independent ratio u_e/u_g and employing the measured temperature behavior of D_e and τ_e[12] leads to the following results[15]: $u_e/u_g \simeq 1.3$, $\Delta E_0 = 4.5$ kJ/mol $= 20\% E_0$, and $D_g/D_e = 1.4$ at a temperature $T = 20$°C. These results are reasonable enough. However, it is clear that a final test of the model will be possible only after measuring the ratios u_e/u_g and D_g/D_e independently of μ.

INSIDE A DYE MOLECULE

Anthraquinone derivatives such as AD1 are large molecules, with hundreds of electrons. The visible-band excitation is mainly (by more than 90%) a $\pi - \pi^*$ transition involving a single electron. Such a transition usu-

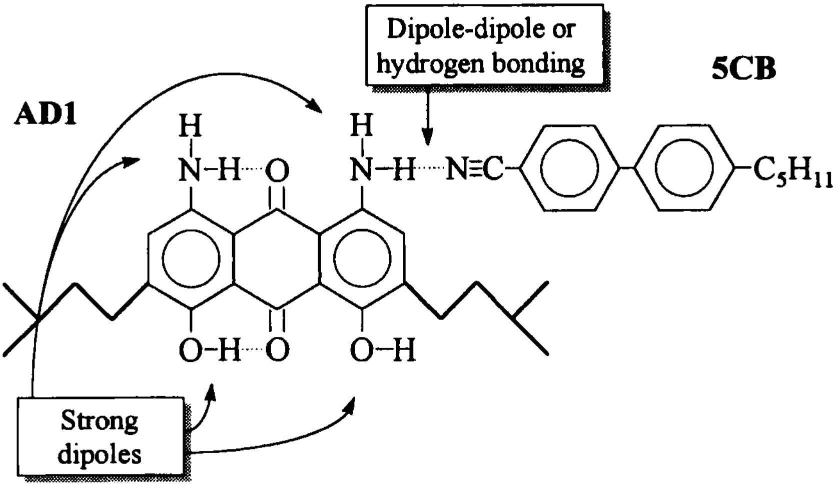

FIGURE 8 Structure of the anthraquinone dye denoted as AD1 and scheme of its polar interaction with a LC host such as 5CB.

ally does not lead to large rearrangement of the molecule conformation. Therefore it may be considered surprising and unlikely that intermolecular forces change by 20% or more.

For this reason, it would be useful to understand a little more of the photoinduced transformations occurring in such dyes (in particular in AD1), and of their possible effects on intermolecular forces. Due to scarcity of direct information, however, the considerations presented here rest to a high degree on speculation.

The structure of AD1 is shown in Fig. 8. We call attention on the four polar side-groups, two NH_2 and two OH. These groups are capable of strong dipole-dipole or even hydrogen-bond interactions, of both *intra*molecular (with the C=O group of the anthraquinone) and *inter*molecular nature. When the dye is dissolved in the LC host, these polar groups may easily couple with the CN groups of the cyanophenyls (see Fig. 8). The role of such polar interactions compared to that of steric and dispersive forces is not known. However, there is at least an indication that it may be very important: the measured dye order parameter in LC

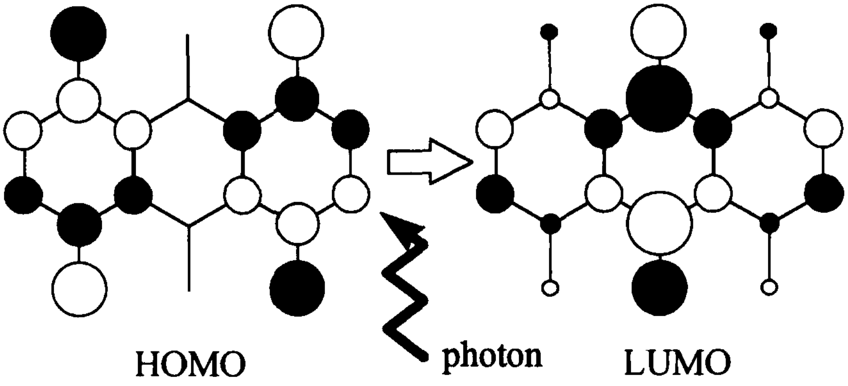

FIGURE 9 Scheme of HOMO-LUMO π orbitals involved in the visible transition of 1,4,5,8-tetraamino-anthraquinone, a dye with a structure very similar to AD1 (but more symmetrical), as resulting from LCAO calculations.[19]

host is strongly dependent on the polarity of the host, as can be observed in the measurements reported in Ref. [18] (see also Ref. [15]).

Molecular orbital calculations on molecules quite similar to AD1 have been reported[19, 20]. They show that the visible dye transition, composed for more than 90% of HOMO-LUMO, is accompanied by a considerable intramolecular electron charge transfer from the substituent side-groups (NH_2 or OH) to the anthraquinone main body, as illustrated in Fig. 9. In other words the π electron charge on the nitrogen or oxygen atoms of the side-groups is reduced in the excited molecule. What consequence can this have on polar interactions? Again we do not know. However, there are reports of experiments indicating a significant enhancement of hydrogen bonds in excited molecules undergoing internal charge transfer processes[21–23]. A qualitative explanation could be that the proton H^+ is more weakly bound to the more positively-charged nitrogen or oxygen atoms and it is therefore more easily "donated" in a hydrogen bond.

There are two direct experimental results supporting this picture[15]:

(i) The merit figure μ of AD1 is strongly dependent on the host polarity; indeed, at room temperature we obtained $\mu = 3400$ for AD1 in 5CB and $\mu = 2500$ for AD1 in E63, but only $\mu = 740$ for AD1 dissolved in MBBA, which has no strong polar groups; similar results have been obtained for another dye having a positive value of ζ, while another dye having a negative ζ did not show analogous behavior. (ii) The main absorption band of AD1 is red-shifted by about 5 nm when it is dissolved in 5CB and E63 (polar hosts) with respect to when it is dissolved in MBBA (nonpolar host). The shift is even larger in the vibronic bands. This shift is a direct indication of a larger interaction energy in the excited state than in the ground-state. It corresponds to $\Delta E \approx 1.5$ kJ/mol. This figure obtained from the absorption spectra must be considered as a lower bound to the overall energy change occurring after the excited molecule and the "solvation shell" have had time to relax. Such result is therefore fully consistent with the change $\Delta E_0 = 4.5$ kJ/mol estimated from the temperature dependence of μ.

ANGULAR MOMENTUM

Two points of view can be adopted[14]: (i) a macroscopic one, based on continuum theory; (ii) a microscopic one, based on Jánossy's model.

According to continuum theory of liquid crystals, every torque acting on the molecular director $\boldsymbol{n}$ can be written as

$$(\boldsymbol{\tau})_i = \frac{\partial}{\partial x_j}(\epsilon_{ihk} n_h s_{jk}) + \epsilon_{ihk} t_{hk}, \tag{8}$$

where t_{hk} is a stress-tensor (defined for fluid displacement with no director rotation), s_{hk} is a surface torque tensor (the torque applied from one side to an imaginary surface element which rotates rigidly with the director), ϵ_{ihk} is the antisymmetric Levi-Civita tensor, and x_j is the space coordinate. The two terms on the right-hand-side of Eq. (8) can be interpreted respectively as an exchange of angular momentum with the director field in the surroundings and an exchange of angular momentum with degrees of freedom other than the molecular director within the same volume element.

In the ordinary constitutive equations of nematic LCs, only the elastic torque has both kinds of contributions. Other torques such as the viscous and the electromagnetic ones have only the second contribution. And the new photoinduced torque? Since spatial gradients do not enter its expression, given in Eq. (3), also this torque must have only the second contribution. Therefore a photoinduced stress-tensor associated with light absorption must exist. Its antisymmetric part is given by

$$t_{ij}^{ph} = \frac{\zeta}{8\pi}\langle(\boldsymbol{n}\cdot\boldsymbol{E})(n_iE_j - n_jE_i)\rangle, \tag{9}$$

while its symmetric part is unrelated to the torque, and it is currently unknown. The momentum of the force resulting from the gradient of this new antisymmetric stress-tensor accounts for the angular momentum exchanged by other degrees of freedom (fluid flow and sample-boundaries), thus closing the angular momentum balance.

From the microscopic point of view, each torque acting on the molecular director is the average of molecular torques acting on the orientational degrees of freedom of all molecules within the volume element. We call "system" the set of all molecule orientational degrees of freedom. The system therefore should include also the orientational degrees of freedom of dye molecules. Note that the choice of the system is somewhat arbitrary, but ours is the most natural one if we want our description to be valid in the limit of large dye-LC fractions, or even of a pure absorbing LC (i.e., a LC made of dye molecules). If dye could be considered as external to the system, we would write down the following expression of the photoinduced dye torque:

$$\boldsymbol{\tau}_{\mathrm{dye}} = N_g\langle\boldsymbol{s}_g \times \nabla U_g\rangle + N_e\langle\boldsymbol{s}_e \times \nabla U_e\rangle, \tag{10}$$

where $\boldsymbol{s}_g$ and $\boldsymbol{s}_e$ are unit vectors giving the orientation of a ground- or excited-state dye molecule, respectively, U_g and U_e are the mean-field potentials describing the dye-host orientational interaction, N_g and N_e are the number of dye-molecules per unit volume, and $\langle\rangle$ here denotes average over the corresponding orientational distribution. However, if dye molecules are not considered external to the system, Eq. (10) is just an "internal" torque which cannot be immediately identified with the photoinduced torque. The solution to this problem lies in the dye molecule dynamics. Indeed, it can be proved that, due to the continuous photoinduced electronic transitions and to the different intermolecular forces they experience in different electronic states, the dye molecules possess a nonzero average angular velocity $\langle\boldsymbol{\omega}\rangle \neq 0$, even if the molecular director and the light intensity are constant in time[11, 14]. The physical meaning of this surprising result can perhaps be grasped with the help of Fig. 10, where the limit case $u_e \gg kT \gg u_g$ is considered: a dye molecule in its ground-state performs an almost free random-walk with vanishing angular velocity; after a photon absorption event, occurring preferentially when its orientation is closer to $\boldsymbol{E}$, the excited molecule drifts toward $\boldsymbol{n}$ with nonzero velocity, under the effect of the mean-field U_e; once at $\boldsymbol{n}$, it decays and then starts another cycle. Now, a nonzero average angular velocity implies a nonzero average friction torque experienced by dye molecules $\boldsymbol{\tau}_f = -\beta\boldsymbol{\omega}$, where $\beta = kT/D$. This friction torque corresponds to an angular momentum exchange of dye orientational degrees of freedom with the center-of-mass degrees of freedom of surrounding molecules, which are "external to the system". This exchange can be identified with the photoinduced torque, which is therefore given by

$$\boldsymbol{\tau}_{ph} = -N_g\frac{kT}{D_g}\langle\boldsymbol{\omega}_g\rangle - N_e\frac{kT}{D_e}\langle\boldsymbol{\omega}_e\rangle. \qquad (11)$$

Actually, for small dye concentration or light intensity, it can be proved that this expression is approximately equivalent to Eq. (10)[14].

CONCLUSIONS

State-of-the-art and possible future developments can be summarized in the following points: (i) the "dye" photoinduced effect proved to be very

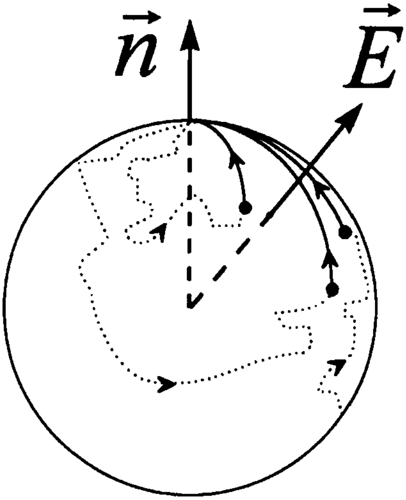

FIGURE 10 Examples of dye molecule orientation dynamics depicted as a trajectory of a point on a sphere, for the case $u_e \gg kT \gg u_g$. Dotted lines: random-walk of a ground-state molecule. Circles: photon absorption events. Solid lines: excited molecule rotational drift.

general, having been observed in liquid crystals, Langmuir films[24], and isotropic liquids; we may wonder whether other materials could exhibit similar effects, perhaps still based on photoinduced variation of intermolecular forces but not necessarily on the orientational response; (ii) the model proposed by Jánossy, somewhat generalized, seems to work well; but for a final test we need independent measurements of the parameters u_e and D_g; (iii) we are finding the first clues of what molecular features make a dye effective or not in orienting the host; perhaps the best way to improve our understanding is to try designing more and more effective dyes. How far can this go?

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