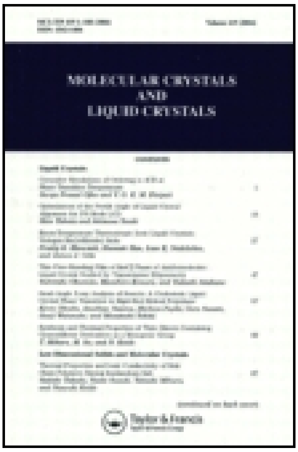

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Wavelength Dependence of Optical Reorientation in Dye-Doped Nematics

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WAVELENGTH DEPENDENCE OF OPTICAL REORIENTATION IN DYE-DOPED NEMATICS

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Abstract The wavelength dependence of the optical reorientation of nematic liquid crystals is investigated in the presence of two dyes, using the z-scan technique. A strong correlation is found between the magnitude of the dye-induced amplification of the optical torque and the dichroism of the system.

INTRODUCTION

In recent years, it was demonstrated that absorbing dyes have a dramatic influence on light-induced reorientation of nematic liquid crystals.[1,2] This effect was first discovered in a commercial guest-host system, containing a small amount of an anthraquinone dye; the reduction of the optical Freedericksz threshold by two orders of magnitude was observed. Later,[3] the influence of different dyes on optical reorientation was studied with the help of the z-scan technique,[4,5] using oblique incidence and extraordinary polarization of the irradiating beam. Under such conditions, reorientation occurs without threshold. This fact allows to carry out the measurements at relatively low input powers, hence strong thermal effcts (e.g. melting of the nematic) and light-induced degradation of the dye can be avoided. The low input intesities also guarantees the conditions under which a linearized theoretical model works accurately. Moreover, the z-scan technique has the advantage that both positive and negative Kerr-like nonlinearities can be investigated.

The effect of a dye can be characterized by an "amplification factor" η, which is defined as the ratio of the optical torques acting in the presence and in the absence of the dye respectively. The comparison of the nonlinear behaviour of the dye-doped and undoped samples gives a possibility to determine η quantitatively.

In Ref. 3. a simplified method was applied to deduce the amplification factor from the experimental data, using only the peak-valley amplitude of the z-scan curves. The first aim of the present paper is to improve the evaluation procedure in order to obtain more reliable values for η. We show that although optical reorientation of nematics is a nonlocal nonlinearity, the method worked out for local third-order nonlinearities and gaussian beams[5] can be applied in a good approximation in the present case too.

In former studies, the amplification factor was determined for a single wavelength only, namely for 633 nm. In the present paper, we report on measurements carried out for two anthraquinone dyes at various wavelengths. From the z-scan curves we determined the wavelength dependence of η and compared it with the corresponding variations of the absorption coefficients of the dyes. For one of the dyes, it was found that η is in a good approximation proportional to the dichroism of the system. For the other dye, although the general features of the wavelength dependence of η and the dicroism are similar, there are definite deviations from proportionality. We provide a theoretical discussion of these observation in the framework of a molecular model of the phenomenon.

In the final part of the paper, we give a preliminary account of our observations on reorientation effects in the presence of the non-anthraquinone dyes, methyl-red and para-red. With the former substance, a strong negative amplification of the optical torque was observed, while the latter one did not give a significant contribution to the optical reorientation. In both cases, however, a strong nonlinear bleaching was observed, which we attribute to the light-induced trans-cis conformational transitions in these dyes.

THE Z-SCAN TECHNIQUE FOR LIQUID CRYSTAL SAMPLES

The z-scan technique is a powerful tool for measuring both the nonlinear refractive index and nonlinear absorption coefficient of a wide variety of materials. A starting hypothesis of z-scan is that the distribution of the incident light beam and that of the phase delay at the sample output have the same profile. This hyphotesis holds for traditional Kerr optical media, in which the nonlinear Kerr coefficient n_2 is homogeneus in the whole system. In the case of liquid crystals, however, the molecular reorientation depends on the beam intensity distribution in the sample, so that the nonlinear response changes from point to point of the medium; this, in turn, requires a more careful analysis of beam propagation inside the sample even if the incident beam has a gaussian profile. In this section we focus our attention to the above mentioned problem and will derive an expression for the normalized z-scan transmittance which takes into account the response of the liquid crystal. For sake of simplicity, linear absorption of the sample will be assumed.

Let us consider a well defined geometry: a p-polarized gaussian beam incides on a liquid crystal sample in homeotropic configuration at an angle i. Then the phase delay through the sample is given by[6]

$$\Psi(x,y) = \Psi_0 + \delta\Psi(x,y) \tag{1}$$

with

$$\Psi_0 = \frac{2\pi L}{\lambda}\left[\frac{\epsilon_\perp\left(\epsilon_\parallel - \sin^2 i\right)}{\epsilon_\parallel}\right]^{\frac{1}{2}} + \frac{2\pi}{\lambda}\sin ix \tag{2}$$

and

$$\delta\Psi(x,y) = \frac{2\pi\sin i(\epsilon_\parallel - \epsilon_\perp)L}{\epsilon_\parallel\lambda}\langle\vartheta\rangle \tag{3}$$

where $\langle\vartheta\rangle$ is the director tilt angle averaged along the sample thickness L, λ is the incident light wavelength, $\epsilon_\parallel$ and $\epsilon_\perp$ are the dielectric costants parallel and perpendicular to the director axis, respectively.

In the stationary case, the linearized equation for ϑ can be written as (ϑ'' represents the second derivative of ϑ with respect to z)

$$\vartheta'' + K\,\nabla_\perp^2\,\vartheta - \left(\frac{\pi}{L}\right)^2 b\tilde{I} = 0 \tag{4}$$

where

$$\tilde{I} = \frac{I}{I_{th}}cos\gamma(x,z), \qquad b = \frac{\sin i}{\sqrt{\epsilon_\perp}}$$

and

$$K = (k_{11} + k_{22})/2$$

is the Frank's elastic costant in the single trasverse approximation. I_{th} is the threshold intensity for a pure sample at normal incidence of the beam, while $\gamma(x,z)$ is the angle between the Poynting vector inside the medium and the z-axis. For oblique incidence, the angle between the Poynting vector and z-axis depends from x and z. In the limit of small distorsions, however, we can suppose as a first approximation that γ does not depend from x and z.

Eq. (4) can be solved by Fourier transformation with respect to the x and y variables. The derived equation for $\hat{\vartheta}(k_x,k_y,z)$ (the Fourier trasform of ϑ) has the boundary conditions $\hat{\vartheta}(0)=\hat{\vartheta}(L)=0$. Taking the average of $\hat{\vartheta}(k_x.k_y,z)$ along the sample thickness, we obtain

$$\langle\hat{\vartheta}\rangle = \frac{(\pi/L)^2 b I_0}{\bar{\alpha}^2-k^2}\left\{\frac{[cosh(kL)-1]\left(e^{-\bar{\alpha}L}+1\right)}{kLsinh(kL)}+\frac{e^{-\bar{\alpha}L}-1}{\bar{\alpha}L}\right\}\hat{B}(k_x,k_y) \qquad (5)$$

where

$$\bar{\alpha} = \frac{\alpha}{cos\gamma} - ik_x tan\gamma,$$

I_0 being the incident intensity, α the linear absorption coefficient along the Poynting vector direction. Finally, $\hat{B}(k_x,k_y)$ is the transformed transverse profile of the incident beam intensity. The coefficient of $\hat{B}(k_x,k_y)$ in Eq. (5) can be regarded as a material response function accounting for the laser beam induced distortion in the medium. By retransforming Eq. (5) we obtain the output profile of the phase delay in the $\widehat{xy}$ space.

In order to determine the phase of the propagating beam behind the sample, it is necessary to solve the eikonal equation for free space:

$$\left(\vec{\nabla}\Psi\right)^2 = k_0^2 \qquad (6)$$

with $k_0 = \frac{\omega}{c} = \frac{2\pi}{\lambda}$. This equation has to be solved with the boundary condition on the plane $z=L$ given by

$$\Psi(x,y,L) = \Psi_0(x,y,L) + \delta\Psi(x,y,L). \qquad (7)$$

Up to this point, the calculation was general and it did not involve the hypothesis of a gaussian beam. In what follows, we consider a gaussian incident beam, which corresponds to our experimental conditions.

As shown previously, the output phase profile does not follow in general the intensity profile but it depends on the response function of the sample and, hence, on absorption and incidence angle. Moreover, the maximum of the phase profile is shifted with respect to the maximum of the intensity profile. Numerical calculations show, however, that for typical circumstances, the phase profil, normalized to its maximum, is very close to the intensity distribution and the shift of the position of its maximum is small. An example for a cell thickness of 35 μm and an initial beam waist of 30 μm is shown in Fig. 1. In view of this fact, a gaussian fit of the phase profile can be performed.

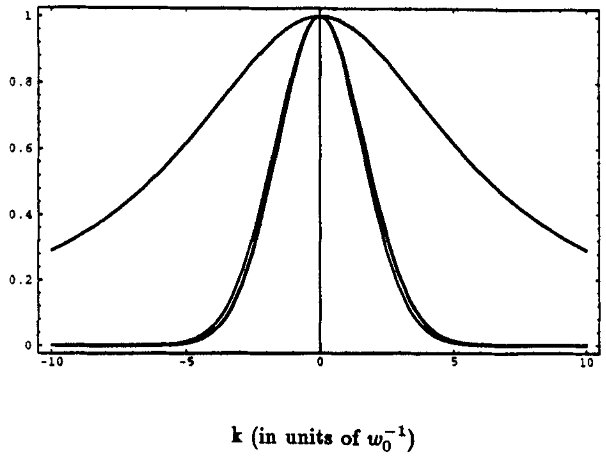

FIGURE 1. Response function of the material (outer curve), output phase profile (middle curve) and incident beam intensity (inner curve) in the k space. The curves are normalized to their maximum value.

The dependence of the maximum of the phase shift as a function of the absorbance of the sample is plotted in Fig. 2. The curve $f(\alpha L)$ is normalized with respect to the maximum phase shift at $\alpha L = 0$. For comparison, the dotted curve shows the function $\left[1 - e^{-\alpha L}\right]/\alpha L$ which corresponds to the correction for absorbance used in Ref. 3.

The complex electric field exiting the sample can then be expressed by the product of two terms: one accounts for the attenuated incident field and the other gives the phase pattern as obtained by the preceding calculations, i.e. $exp\left[i\delta\Psi(x,y,z)\right]$ where $\delta\Psi(x,y,z)$ is the fitted Gauss curve of waist $w/_0$. Using the gaussian decomposition at the first order[5] and under the hypothesis of far field investigation, small aperture and little phase distorsions we find the following formula for the normalized transmitted power

$$T(z,\Delta\phi_0) = 1 - \frac{4\Delta\phi_0 t e^{-\frac{c^2}{w'^2}}}{(t^2+1)(t^2+h)} \tag{8}$$

where $\Delta\phi_0$ is the phase delay amplitude, $t = z/z_0$ with z the sample position relative to the lens focus position and z_0 the characteristic diffraction length. $w' = w'_0(1 + z^2/z_0^2)$ is the propagating beam waist obtained by considering the fitting curve. Finally c represents the difference between the phase and intensity profile center positions, while h can be derived from the ratio w'_0/w_0; here w_0 is the beam waist at the focus of the incident beam.

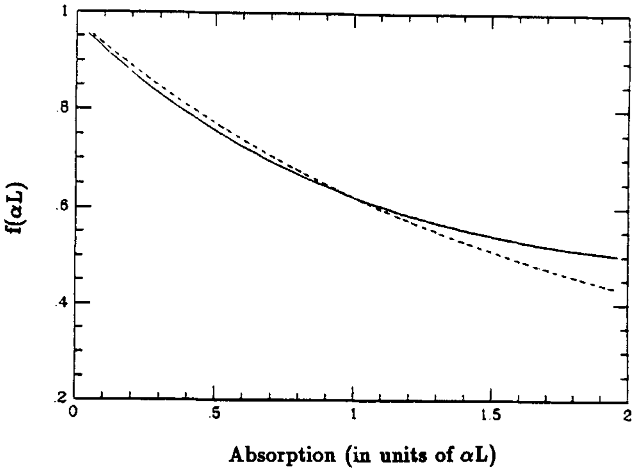

FIGURE 2. The function $f(\alpha L)$ vs. the sample absorption.

For a typical experimental situation, given α, L, w_0 and the other sample parameters involved, by means of the fitting procedure on the material response outlined before, w'_0, h and c can be estimated. After substitution of these calculated values in Eq. 8, a χ-square fitting of the normalized z-scan transmittance to the experimental data can be performed in order to get an estimation of the peak-valley amplitude of the curve. This, in turn, allows a determination of the amplification factor η. Indeed, following the approach of Ref. 3, we have for the phase delay amplitudes

$$\Delta\phi_{host} \propto P_{host}, \qquad \Delta\phi_{dye} \propto (\eta + 1) f(\alpha L) P_{dye} \tag{9}$$

where P_{host} and P_{dye} represent the incident power on a pure and dyed sample respectively. Finally, denoting by $\Delta\nu_{dye}$ and $\Delta\nu_{host}$ the peak-valley amplitudes of the z-scan curves, we get

$$\eta = \frac{\Delta\nu_{dye}P_{host}}{\Delta\nu_{host}P_{dye}} f(\alpha L)^{-1} - 1. \tag{10}$$

EXPERIMENTS

In the experiments we studied the dyes N,N'-(4 -methylphenyl)-1,4- diamino anthraquinone (D4) and 4,5-diamino 2,7-diisopentyl anthraquinone (AQ2), dissolved in the nematic mixture E63 from BDH. The concentration was 0.5% per weight, in both cases.

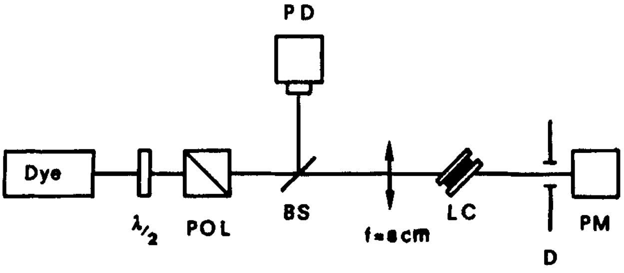

FIGURE 3. Experimental set-up. POL: polarizer; BS: beamsplitter; PD: photodiode; LC: liquid crystal sample; D: diaphragm; PM: photodetector.

The experimental set-up is shown in Fig. 3. A p-polarized dye laser beam is sent at 45° on the sample. The position of the liquid crystal cell with respect to the focus of the converging lens is varied by means of a micrometer screw. The thickness was 35μm for all the investigated samples. A typical z-scan curve for 630 nm is reported in Fig. 4. The triangles refer to experimental data taken with a 16 V a.c. bias voltage (1 KHz frequency) applied across the sample, while squares refer to data taken with no applied voltage. The former data represent refractive index modulation due to thermal effects only, since the strong electric voltage inhibits reorientation. The continuous curve was derived by the fitting procedure outlined in the previous sections.

The coefficient η was determined by comparing the z-scan curves for the pure host and the dye-doped materials. Results are shown in Figs. 5 and 6 for a wavelength range between 515 and 660 nm for D4 and AQ2 doped samples respectively. For comparison, the corresponding wavelength dependence of the dichroism ($\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$) is plotted also in the figures. It can be seen that there is a strong correlation between the variation of η and $\Delta\alpha$. A quantitative analysis follows in the next section.

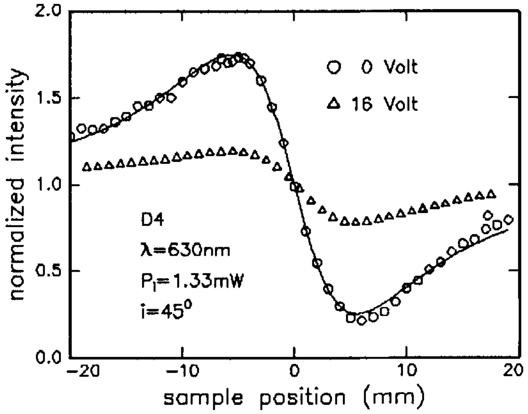

FIGURE 4. A typical z-scan curve.

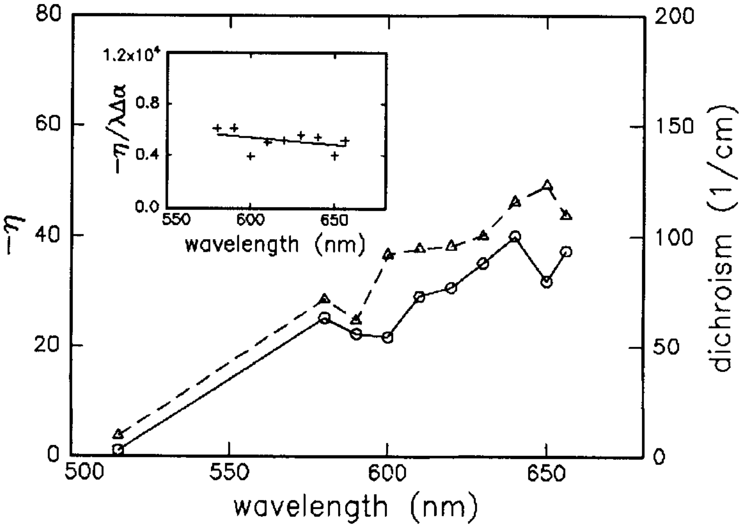

FIGURE 5. The amplification factor (o) and the dichroism ($\triangle$) as a function of the wavelength for 0.5% D4 in E63.

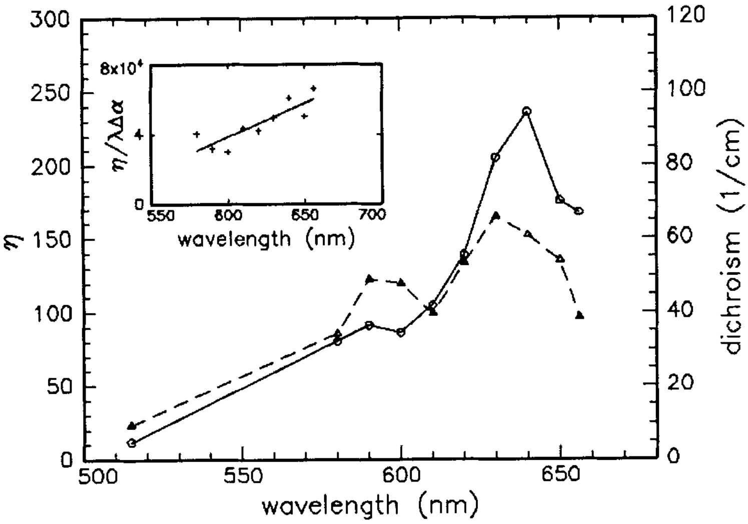

FIGURE 6. The amplification factor (o) and the dichroism (△) as a function of the wavelength for 0.5% AQ2 in E63.

THEORETICAL CONSIDERATIONS AND DISCUSSION

Very recently, a mean-field molecular model was proposed, which accounts for the dye-induced amplification of the optical torque in nematics[7]. A basic assumption of the model is that the dye molecules are strongly anisotropic, therefore the probability of the excitation of a molecule depends on its orientation relative to the polarization direction of the light wave. If, furthermore, the interaction energy of the dye molecules with the surrounding host molecules is different in the ground state and in the excited state, light absorption creates an internal angular momentum in the system. This internal motion is compensated by an appropriate rotation of the director, which can be described phenomenologically as an amplification of the optical torque.

In Ref. 7. rodlike molecules were considered with their transition dipole moment parallel to the rod direction, s. The probability of excitation of a molecule per unit time is

$$p = \Lambda(\mathbf{e}\cdot\mathbf{s})^2 E^2 \tag{11}$$

where e is a unit vector along the polarization, E is the effective value of the electric field and Λ is a parameter depending on the wavelength. In the limit of low intensities, the amplification factor is proportional to the quantity Λ. In turn, Λ is proportional to the average value of the imaginary part of the dielectric constants. Therefore

$$\eta \propto \bar{\epsilon}'' = (2\epsilon_\perp'' + \epsilon_\parallel'')/3 \propto \lambda(2n_e\alpha_\perp + n_o\alpha_\parallel)/3. \qquad (12)$$

Here we used the well-known relation between ϵ'' and the absorption coefficient:

$$\epsilon'' = \frac{\lambda n \alpha}{2\pi\epsilon_0}$$

In a more realistic description, one has to take into account the possibility that the transition dipole moment may have a component perpendicular to the rod axis too. Assuming that the dye molecules rotate freely around their long axis and averaging over the azimuthal angles, we find the more general form of Eq.(11):

$$p = (\Lambda_1(\mathbf{e}\cdot\mathbf{s})^2 + \Lambda_2)E^2 \qquad (13)$$

where both Λ_1 and Λ_2 are functions of the wavelength.

The importance of the Λ_2 term for a given dye can be checked experimentally by comparing the wavelength dependence of the average coefficient $\bar{\epsilon}''$ and that of the anisotropy of the imaginary part of the dielectric constants, defined as

$$\Delta\epsilon'' = \epsilon_\perp'' - \epsilon_\parallel'' \propto \lambda(n_e\alpha_\perp - n_o\alpha_\parallel). \qquad (14)$$

For $\Lambda_2 = 0$, the ratio $\Delta\epsilon''/\bar{\epsilon}''$ should be independent from the wavelength. In reality, for D4 we found that $\Delta\epsilon''/\bar{\epsilon}''$ varies by a factor of three within the wavelength-range investigated. This fact indicates a significant value of Λ_2.

A straightforward generalization of the considerations of Ref. 7. shows that η is proportional to Λ_1, which is proportional to the anisotropy of the imaginary parts of the dielectric constants. Hence, we expect:

$$\eta \propto \Delta\epsilon'' \propto \lambda(n_e\alpha_\parallel - n_o\alpha_\perp). \qquad (15)$$

If, as a first approximation, we neglect the birefringence and the dispersion of the refractive index, we find that the amplification factor is proportional to the product of the wavelength and the dicroism of the guest-host system:

$$\eta \propto \lambda\Delta\alpha. \qquad (16)$$

For D4, the experimental data presented in Fig. 5 are in satisfactory agreement with relation (16), as shown in the inset in the figure. On the other hand, for AQ2, there is a definite deviation from this rule (see the inset in Fig. 6); the $\eta/\lambda\Delta\alpha$ ratio increases with increasing wavelength. The discrepancy between our model and the experimental data in the case of AQ2 can be due to a more complex absorption mechanism which does not follow the simplified mean-field description.

OPTICAL REORIENTATION IN THE PRESENCE OF AZO-DYES

We carried out preliminary reorientation experiments with the nematic E63 doped with two azo-dyes: 4-dimethylaminoazobenzene-2'carboxylic acid (methylred) and 1-(4-nitrophenylazo)-2-naphthol. (parared). With methylred, a strong negative amplification of the optical torque was observed, similar to the case of D4.

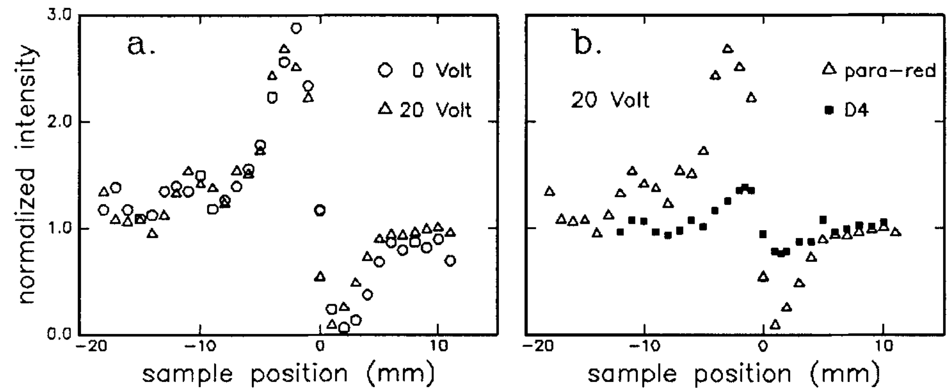

FIGURE 7. *a*: z-scan curves for 0.5% para-red in E63 with and without an applied field. *b*: comparison of the z-scan curves for para-red and D4 with the same absorbance in the presence of an applied field.

For para-red, the z-scan curves indicated again a strong defocusing nonlinearity, but this time, applied voltages up to 20 V had no effect on the measured points (Fig.7a). This observation shows that for para-red the observed nonlinearity is not of orientational character. The curves in Fig. 7b. prove that it cannot be a pure thermal effect neither. In this figure, we compare the z-scan curves for para-red and D4 dye at an applied voltage of 20 V d.c. The beam power is the same: 0.183 mW. The absorbance is $\alpha L = 0.590$ for D4 and 0.600 for para-red. The thermal effect therefore should be almost the same for the two samples, yet for para-red the modulation of thee z-scan curve is much larger than for D4.

We think that the nonlinearity in the case of the para-red dye is connected with the light-induced trans-cis conformational changes[8] of the molecules. Our assumption is supported by "open-aperture" mesurements[4], in which a strong maximum was observed around the focal point for both azo-dyes. This behaviour, which was not seen in the case of anthraquinone dyes, indicates a significant reversible bleaching of the system. Light-induced conformational changes of the azo-molecules provide a plausible explanation of this phenomenon.

Although further investigations are necessary in order to clarify the details of the nonlinear processes in the presence of azo-dyes, already these first observations prove that anomalous reorientation is not restricted to the anthraquinone class of dyes. (A similar result was obtained recently by Khoo *et. al.*[9]) Furthermore, the comparison of the influence of methylred and para-red dyes on optical reorientation shows once more the sensitivity of the amplification factor on the details of the molecular structure of the dye dopants.

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