

PHOTOISOMERIZATION OF AZO-DYES IN NEMATIC LIQUID CRYSTALS

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Received 27 January 1998

The photoisomerization of azo dyes in nematic liquid crystals is investigated. Using a pump-probe technique, the absorption coefficients of the trans and cis isomers are evaluated separately and the dye order parameters of both forms are determined. It is shown that as a consequence of the difference of the trans and cis orientational order, the trans-cis equilibrium can be controlled through the polarization direction of the pump beam.

1. Introduction

Light induced isomerization of azobenzene derivatives is a well-known phenomenon that has been studied in the past extensively.¹ Recently, interesting applications of this process have been proposed, such as data storage,² regulation of surface alignment of liquid crystals³ or material processing for second order non-linear optical effects.⁴ In these applications, the dye molecules are typically embedded in a solid matrix, where their orientational mobility is strongly restricted. Change of alignment becomes possible, however, during light-induced trans-cis or cis-trans transitions. Light irradiation can therefore generate a non-equilibrium orientational distribution of the dye molecules and a quadrupolar or even a polar order can be created in the sample.⁵

In the present paper, we describe photoisomerization of azo-dyes in bulk nematic liquid crystals. The general physical and optical properties of liquid crystals are discussed, e.g. in Ref. 6. Photoinduced conformational changes in liquid crystals has been studied earlier by a number of authors. Odulov *et al.*⁷ detected the refractive index change caused by conformers; Ikeda and Tsutsumi⁸ observed nematic-isotropic phase transition due to phototransformation of azo molecules; Chen and Brady⁹ reported self-diffraction effects in an azo-dye doped nematic; Folks *et al.*¹⁰ investigated photoinduced textural instabilities in a smectic liquid crystal containing an azobenzene derivative; Blinov *et al.*¹¹ studied the influence of liquid crystalline

order on the kinetics of photoisomerization. Here, we provide a systematic analysis of the polarization properties of the process and point out their possible use in dynamic holography.

In liquid crystals the situation is very different from that in solid films. The dye molecules have a high orientational mobility, a typical rotational relaxation time is of the order of nanoseconds. At the low light levels used for isomerization, the orientational distributions of both the trans and cis isomers basically correspond to a thermodynamic equilibrium. These equilibrium distributions are inherently anisotropic, the symmetry axis coincides with the nematic director. The extent of orientational order, however, may be different for the two isomers. In particular, one expects that the trans molecules, which have an elongated shape, are more effectively oriented along the liquid crystal host molecules than the V-shaped cis isomers. The former molecules should therefore give a significantly higher contribution to the dichroism of the liquid crystal than the latter ones. By light irradiation it is possible to change the cis concentration and, as a consequence, the magnitude of the anisotropy of the guest-host system. We verify the above expectation experimentally using a pump-probe technique and show that, performing measurements with different polarization combinations of the beams, the absorption coefficients of the two isomers can be determined separately. To characterize the difference between the order of the trans and cis isomers, we deduce from the data the dye order parameters, i.e., the order parameters associated with the transition dipole moments.

As a further step, we show that, due to the difference between the dye order parameters of the trans and cis forms, the steady state concentration of the cis isomer depends on the polarization direction of the exciting light. To understand this fact qualitatively, let us consider a dye that is perfectly aligned with its transition dipole moment along the nematic director in the trans form, but exhibit a significant orientational disorder in the cis form. For a light beam propagating perpendicularly to the director, at *ordinary* polarization (electric vector perpendicular to the director) the trans molecules are not excited at all, therefore trans-cis transitions do not take place and in steady state the cis concentration vanishes. If the light is switched to *extraordinary* polarization (electric vector parallel to the director), trans-cis transitions become possible, and a new equilibrium develops with a finite cis concentration. The process is reversible; when returning to ordinary polarization, the initial equilibrium is restored, partly through thermal but more importantly through light-induced cis-trans transitions. Although in reality the trans molecules are not perfectly aligned, the above consideration illustrates the fact that in liquid crystals the trans-cis equilibrium can be controlled through the polarization direction of the pump beam.

In Sec. 2, we analyze the rate equations of the problem and show how can one evaluate the relevant material parameters from pump-probe measurements. In Sec. 3, the results of steady-state measurements are presented and discussed. In Sec. 4, we deal with transient processes. Finally, in Sec. 5, the polarization dependence of the trans-cis equilibrium is analyzed in detail.

2. Theoretical Considerations

Azo dyes contain a central azo group to which two aromatic rings are attached. The *trans* and *cis* configurations differ first of all in the directions of the central bonds; in the energetically more stable *trans* state the two bonds linking the azo group to the aromatic rings are parallel, while in the metastable *cis* state the angle between these two bonds is 120 degrees.

The mechanism of the *trans-cis* isomerization is illustrated schematically in Fig. 1. The configurational coordinate may correspond e.g. to a rotation of one of the central bonds about the double nitrogen bond. *Trans-cis* transitions involve electronic excitation, followed by a relaxation of the nuclear coordinates towards the energy minimum of the excited state. After de-excitation, a further relaxation process takes place, which can lead, with a certain probability, to the stabilization of the *cis* form. In a similar way, light-induced *cis-trans* transitions can occur too. Thermal *cis-trans* transitions are taken into account also, but the effect of thermal transitions in the other direction is neglected.

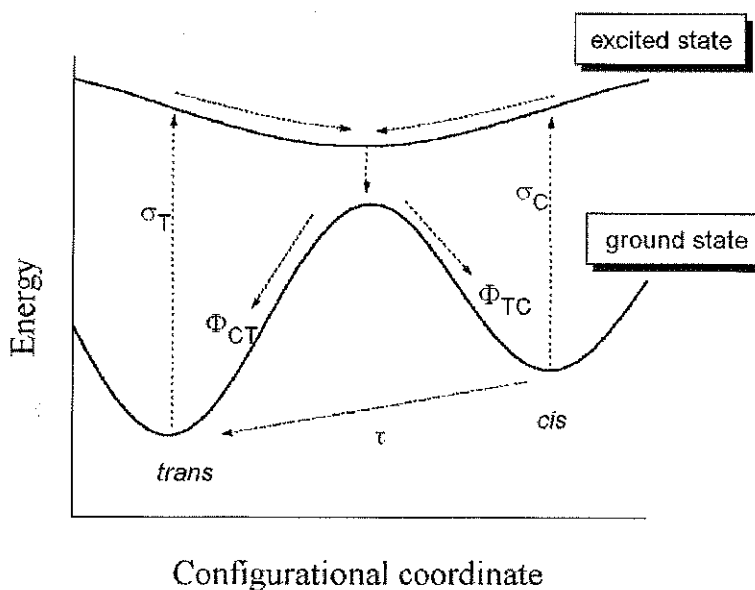


Fig. 1. Schematic representation of the *trans-cis* isomerization. σ_T and σ_C are the molecular cross sections for photon absorption, Φ_{TC} and Φ_{CT} are the quantum efficiencies for the transitions, τ is the thermal relaxation time for *cis-trans* transitions. In reality, more than one excited state can play role in the transitions and the nuclear motions cannot be represented with a single configurational coordinate.

We consider low light intensity levels, at which the number of excited molecules is negligible compared to that of the ground-state molecules, furthermore the orientational distribution of the isomers can be regarded to be in thermodynamic equilibrium. For low dye concentrations, the orientational distribution functions

of the trans and cis isomers are independent, they are determined by the guest-host interaction between the nematic molecules and the particular isomer.

In the presence of a pump beam, the concentration of the cis molecules (N_C) obeys the rate equation

$$\frac{dN_C}{dt} = (N_T\sigma_T^i\Phi_{TC} - N_C\sigma_C^i\Phi_{CT})I/h\nu - N_C/\tau. \quad (1)$$

The first term on the right-hand-side of the equation describes light-induced transitions. Φ_{TC} and Φ_{CT} is the quantum efficiency of the trans-cis and cis-trans transition respectively, N_T is the concentration of the trans isomers; I is the light intensity. σ_T^i and σ_C^i denotes the cross section of absorption of a photon with energy $h\nu$ for a trans and a cis isomer respectively, averaged over the orientational distribution function of the relevant isomer. The index i refers to the polarization direction of the pump beam; it can correspond to the extraordinary (e) or ordinary (o) ray. For the extraordinary ray, the averaged cross sections depend on the angle between the wave vector of the light beam and the director. The second term in Eq. (1) represents thermal cis-trans transitions, with a relaxation time of τ .

In order to connect the microscopic quantities σ_T^i and σ_C^i to the macroscopic absorption coefficients that can be measured in an experiment, we introduce the trans and cis absorption coefficients through the definitions

$$\alpha_T^i = N\sigma_T^i, \quad \alpha_C^i = N\sigma_C^i, \quad (2)$$

$N = N_T + N_C$ is the total number of dye molecules per unit volume. In a system containing a fraction $X = N_C/N$ of cis isomers, the attenuation of a weak probe beam, polarized along the m direction, can be described by an absorption coefficient that is a linear superposition of the contributions from the trans and cis isomers

$$\alpha^m = (1 - X)\alpha_T^m + X\alpha_C^m. \quad (3)$$

In the following, we show that from pump-probe measurements the trans and cis absorption coefficients and the dye order parameters can be determined experimentally. Under the influence of a pump beam with intensity I and polarized along i , in steady-state conditions ($dN_C/dt = 0$) the equilibrium cis fraction, $X = X_{eq}^i$ is

$$X_{eq}^i = \frac{X_S^i}{1 + I_S^i/I}, \quad (4)$$

where I_S^i is an intensity parameter and X_S^i is the saturation value of the cis fraction at intensities much higher than I_S . From the rate equation (Eq. (1)) one finds that they are related to the parameters of the model as

$$I_S^i = \frac{\sigma_C^i\Phi_{CT} + \sigma_T^i\Phi_{TC}}{\tau h\nu}, \quad (5)$$

$$X_S^i = \frac{\sigma_T^i A}{\sigma_C^i + A\sigma_T^i} = \frac{\alpha_T^i A}{\alpha_C^i + A\alpha_T^i} \quad \text{with} \quad A = \Phi_{TC}/\Phi_{CT}. \quad (6)$$

Consider a probe beam polarized in the m direction and propagating in the same direction as the pump beam. We denote the probe absorption coefficient, belonging to steady-state conditions, by α_{im} . According to Eq. (3),

$$\alpha_{im} = (1 - X_{eq}^i)\alpha_T^m + X_{eq}^i\alpha_C^m. \quad (7)$$

By measuring α_{im} as a function of the pump intensity at the four possible combinations of the pump and probe polarizations ($i = e, o$, $m = e, o$), the parameters involved in the model can be determined. The following procedure can be used. First, measurements at $I = 0$ (no pump beam) are performed. Without illumination $X_{eq}^i = 0$, therefore one can obtain directly α_T^e and α_T^o . Next, pump intensities significantly higher than I_S^i are used, at which the cis concentration saturates. In this case, applying different combinations of the polarization direction of the pump and probe beams, four limiting α_{im} values can be measured, corresponding to $X_{eq}^i = X_S^i$. Combining Eqs. (6) and (7), one finds that from these experimental data, the parameter A can be calculated in two independent ways, using either α_{oe} or α_{eo}

$$A = \frac{\alpha_T^e - \alpha_{ee}}{\alpha_{ee} - \alpha_{oe}} \left(\frac{\alpha_{oe}}{\alpha_T^e} - \frac{\alpha_{oe}}{\alpha_T^o} \right) \quad \text{or} \quad A = \frac{\alpha_T^o - \alpha_{oo}}{\alpha_{oo} - \alpha_{eo}} \left(\frac{\alpha_{eo}}{\alpha_T^e} - \frac{\alpha_{ee}}{\alpha_T^o} \right). \quad (8)$$

The cis absorption coefficients are given as

$$\alpha_C^e = \frac{\alpha_{ee}\alpha_T^e A}{\alpha_T^e(A+1) - \alpha_{ee}}, \quad \alpha_C^o = \frac{\alpha_{oo}\alpha_T^o A}{\alpha_T^o(A+1) - \alpha_{oo}}. \quad (9)$$

The above procedure has the advantage that it does not require an accurate determination of the pump intensity within the sample; it is only necessary to apply a sufficiently strong light beam at the second set of measurements, so that the cis concentration should saturate. On the other hand, from these data it is only possible to evaluate that ratio of the quantum efficiencies, but not their absolute values. To obtain separate informations on Φ_{TC} and Φ_{CT} , steady-state measurements at low intensities or transient measurements are needed. In both cases, the intensity has to be determined within the absorbing layer, which is a difficult task, especially because the intensity is non-uniform in the sample. In this work, although experimental results on transient phenomena are presented, we do not attempt to evaluate the absolute values of the quantum efficiencies.

3. Experimental Results — Steady-State

In the experiments, the azo dyes Disperse Orange 3 (DO3), Disperse Red 13 (DR13) (both from Aldrich) and a di-azo dye 4'-dimethylaminophenyl-[1,4-phenylenebis(azo)]-3-chloro-4-heptyloxy benzene (R4 from Hoffman La Roche) were investigated. 0.5 weight percent of the dyes were added to the nematic mixture E63 (supplied by British Drug House). These guest-host systems exhibit an absorption peak in the visible range due to the $n \rightarrow \pi^*$ electronic transition¹; the absorption

maxima are at 440nm (DO3), 525nm (DR13) and 490nm (R4). The experiments were carried out at room temperature; the nematic-isotropic phase transition point of the systems is at 82°C.

The samples were 50 μ m thick homeotropic layers. During the experiments a stabilizing voltage (10V) was applied to the cell to prevent the effect of light-induced bulk or eventual surface reorientation of the director.³ This field is sufficient to secure the homeotropic alignment while its influence on the orientational order is completely negligible.⁶ The light source was a Spectra Physics Ar laser. The angle of incidence of the pump and probe beam was 45° and -45° respectively, so that the two beams were perpendicular. (We note that in this geometry the angle between the polarization and the nematic director is identical for the pump and the probe beams, therefore the theoretical analysis presented in the previous section can be applied.) The probe beam was focused to the center of the unfocused pump beam (spot radius 1mm).

To avoid the influence of the recording procedure on the effect itself, the probe beam consisted of 10 msec pulses with a repetition time of 250 msec. The transmitted intensity behind the sample was measured synchronously with the probe beam pulses using a digital voltmeter. A typical experimental recording is shown in Fig. 2.

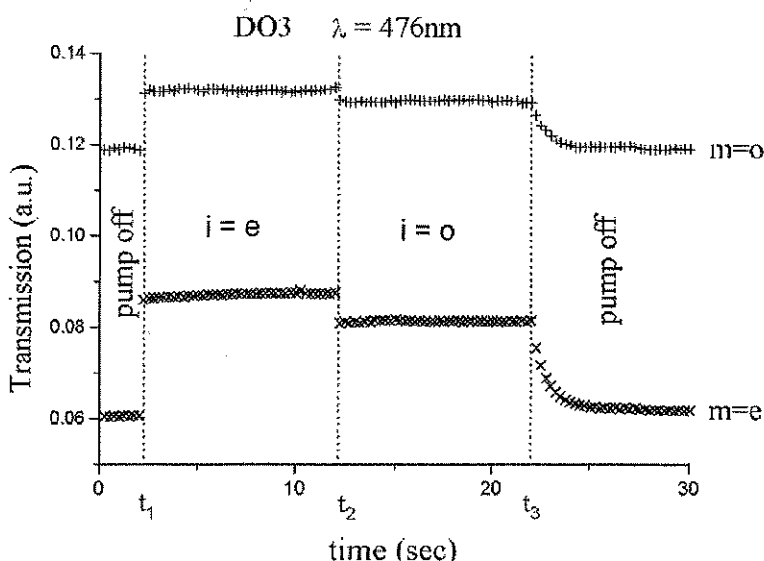


Fig. 2. Probe transmission as a function of time. The pump beam was switched on at t_1 with extraordinary polarization, at t_2 it was turned to ordinary polarization, at t_3 it was switched off.

The α_{im} absorption coefficients were evaluated from the transmitted probe intensities, using the relation $T_o \exp(-\alpha_{im}d) = I_{im}/I_o$ where I_{im} is the transmitted, I_o is the incident probe intensity, d is the pathlength of the beam in the nematic. T_o represents the correction for reflections and losses not originating from the dye.

(In order to determine T_o , the transmission coefficient of an undoped sample was measured under circumstances identical to that used for the dyed cells.) From the α_{im} data A , α_T^e , α_T^o , α_C^e and α_C^o , were calculated along the lines described above. These α values refer to an angle of incidence of 45° ; the principal values of the absorption coefficients α^{par} and α^{perp} (polarization direction parallel and perpendicular to the director) were determined using the standard laws of crystal optics.¹² The calculation requires the knowledge of the refractive indices of the system, which were assumed to be equal to those of the host material ($n_e = 1.75$, $n_o = 1.52$).

For DO3 and R4, complete saturation of the transmission changes were observed already at few mW pump input powers. We note that the temperature rise due to laser heating at such power levels, with a spot radius of 1 mm, is less than 1°C .¹³ As the measurements were performed about 60 degrees below the clearing point, the change of orientational order caused by this amount of heating is insignificant,⁶ thus the observed transmission changes can be attributed to the photoisomerization process alone.

The thermal relaxation time, τ , was 0.75 sec for DO3 (see Fig. 2) and around 10 sec for R4. The ratio of the quantum efficiencies (A) were found to change from 0.45 to 0.33 (DO3) and from 0.30 to 0.35 (R4) as the wavelength was changed from 458 nm to 514 nm. The absorption coefficients are shown in Figs. 3(a) and 4(a). The calculations were based on the first relation in Eq. (8) using the α_{oe} values; in most cases the $\alpha_{oo} - \alpha_{eo}$ values were too small to use α_{eo} for reliable evaluation of A .

The above results show that — in agreement with our expectation — the trans form possesses a much higher dichroism than the cis one for both dyes. To elucidate the physical content behind this fact, we plot in Figs. 3(b) and 4(b) the dye order parameters, calculated according to the usual definition¹⁴ as

$$S_D = \frac{\alpha^{\text{par}} - \alpha^{\text{perp}}}{2\alpha^{\text{perp}} + \alpha^{\text{par}}} \quad (10)$$

On a molecular level, the dye order parameter basically reflects the degree of order of the transition dipole moment of the dye molecules; if the transition dipole moments are perfectly oriented along the director, its value is 1, in the isotropic phase it is zero. (For a detailed discussion of the relation between dichroism and the order parameter, see Ref. 15). The large decrease of the dye order parameter upon isomerization can be a result of several contributions. First, the disorder of the "long axis" of the molecules (defined e.g. as the axis for which the moment of inertia is the smallest) can be much more important for the cis form than for the trans one. This effect can be attributed to the difference in the shape of the two conformers; the elongated trans molecules are more effectively oriented parallel to the host liquid crystal molecules than the cis ones, which have a less pronounced shape anisotropy. Second, the angle between the transition dipole moment and the long

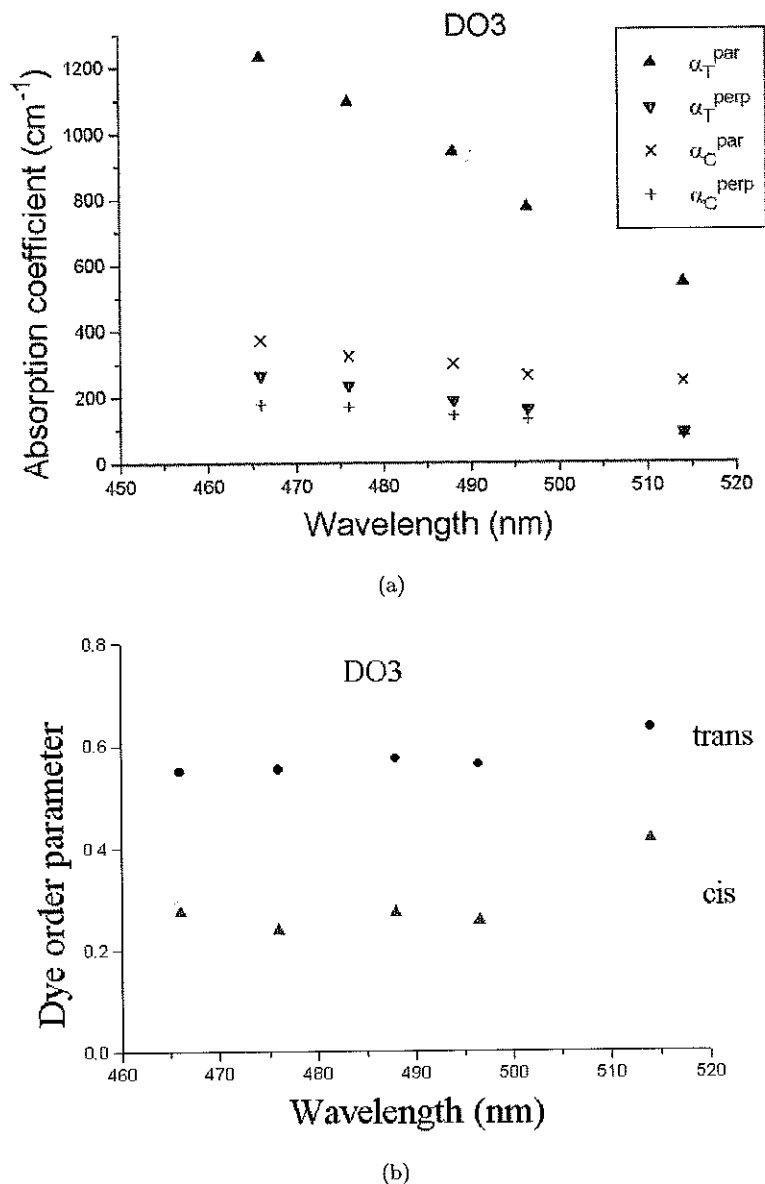


Fig. 3. Results for DO3. (a) Trans and cis absorption coefficients. (b) Trans and cis orientational dye order parameters.

axis may be different for the two isomers, leading to a further difference in the dye order parameters. A further complication is that the cis molecules may not rotate freely about their long axis. From the present measurements alone it is not possible to estimate the relative significance of these contributions; other methods, like NMR combined with quantum-chemical calculation of the molecular structures could help to solve this problem.

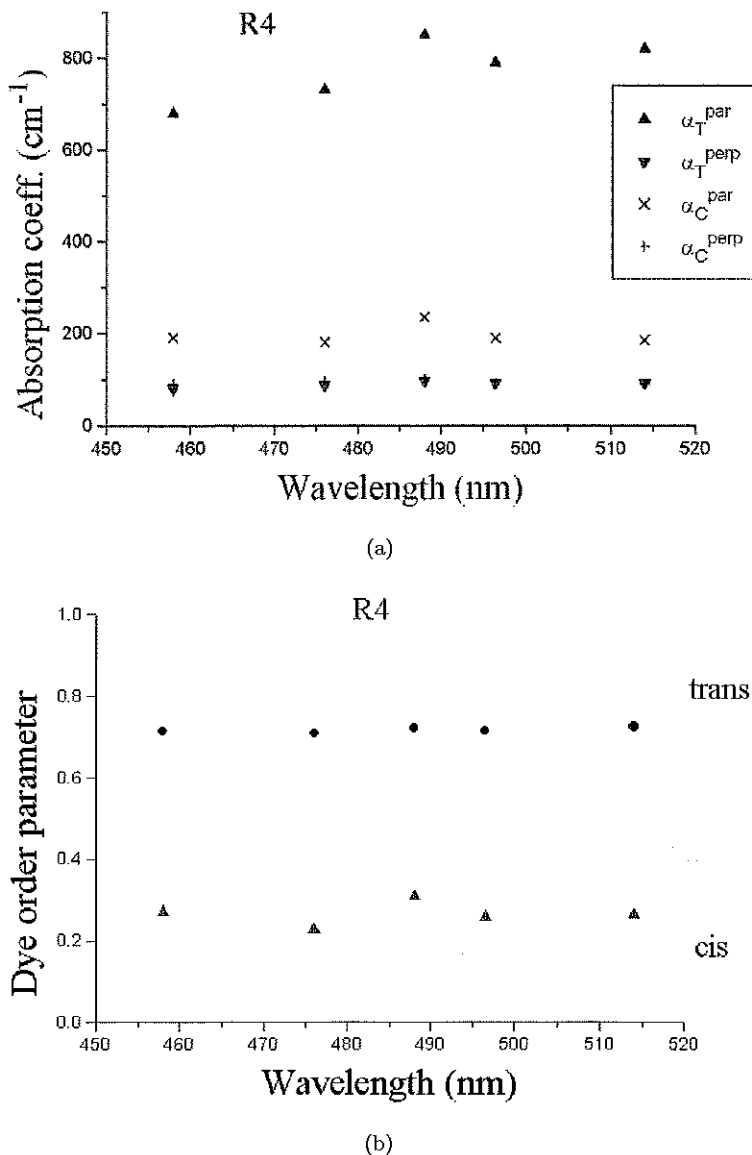


Fig. 4. Results for R4. (a) Trans and cis absorption coefficients. (b) Trans and cis orientational dye order parameters.

The data show that the cis molecules still exhibit a nonzero orientational order. It is interesting to note that although the trans molecules show a much higher orientational order in the case of the R4 dye than in the case of DO3, the cis order parameters are close to each other for the two dyes.

In the case of DR13, no transmittance change was observed, indicating either a zero quantum efficiency for the trans-cis transition in the wavelength region investigated, or a very short relaxation time for the thermal cis-trans transitions.

4. Transient Phenomena

In the transient measurements a very weak, continuous probe beam was applied. The signal was monitored by a photomultiplier and recorded with a storage oscilloscope. This setup allowed a fast but less accurate detection than the one used for steady-state investigations. The transient transmission curves could be fitted with simple exponential kinetics. An example of the dependence of the transient time on the input light power, for extraordinary pump beam, is shown in Fig. 5.

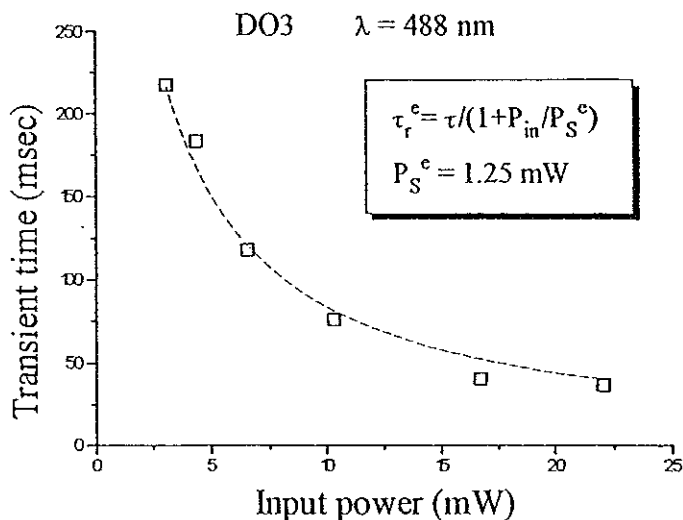


Fig. 5. Transient time, τ_r^e , as a function of the input power, P_{in} for extraordinary polarized pump beam. Dotted line: fitted curve with $\tau = 750$ msec.

In order to interpret the results, we note that from the rate equation, presented in the theoretical part, one finds that at constant intensity the cis concentration changes according to an exponential kinetics, with a time constant τ_r^i

$$\tau_r^i = \frac{\tau}{1 + I/I_S^i} \quad (11)$$

The application of the above formula to the experimental curves is not straightforward, because during transient processes the intensity is not constant neither in time nor in space. Nevertheless, as a rough approximation, one can replace the intensity in Eq. (11) with an average value

$$I \approx \bar{I} = \frac{P_{in}}{r^2\pi} \frac{1 - \exp(-\bar{\alpha}d)}{\bar{\alpha}d} T_o,$$

where P_{in} is the input power, r is the spot radius of the pump beam. The second factor in the expression is a result of averaging over the intensity along the path of the light beam within the nematic layer, with an $\bar{\alpha}$ value that is between the initial

and final value of the absorption coefficient. T_0 accounts for reflection losses. In this approximation,

$$\tau_r^i \approx \frac{\tau}{1 + P_{in}/P_S^i} \quad \text{with} \quad P_S^i = \frac{I_S^i r^2 \pi}{T_0} \frac{\bar{\alpha} d}{1 - \exp(-\bar{\alpha} d)}$$

As indicated in Fig. 5, the above relation gives a good fit of the experimental curve. From the value of P_S^e one obtains the order-of-magnitude estimation $I_S^e \approx 20 \text{ mW/cm}^2$. Measurements with ordinary pump beam yielded a value about 20% higher for I_S^o .

We note that the characteristic times for photoisomerization in the intensity range used in our experiments is several orders of magnitude larger than the typical rotational diffusion times for molecules in the nematic phase (nanoseconds). This fact justifies the assumption made in our model, i.e., that the orientational distributions of the trans and cis isomers are constantly in thermodynamic equilibrium, even during the photoisomerization process.

5. Polarization Dependence of the Trans-Cis Equilibrium

It is known that the trans-cis equilibrium can be controlled through the wavelength of the irradiating light.¹ As we pointed out earlier, in nematics the steady-state cis concentration can be controlled, at a fixed wavelength, through the polarization direction of the pump beam too. An inspection of the equations presented in Sec. 2, shows that the saturation cis concentrations for $i = o$ and $i = e$ are different from zero whenever the dye order parameters of the trans and cis forms are not equal. This fact underlines the argument presented in the Introduction: the polarization dependence of the trans-cis equilibrium is connected with the difference of the dye order parameters of the two isomers.

The experimental verification of the effect can be seen in Fig. 2; when the pump polarization direction is rotated, a fast change occurs in the transmission of the probe beam. The possibility to control the probe transmission through the pump polarization is demonstrated more explicitly in Fig. 6. In this experiment, the pump consisted of 5 msec long pulses, polarized alternatively in the ordinary and extraordinary direction. The repetition time was 140 msec. As it can be seen from the figure, subsequent pump pulses switched the probe intensity between two well-defined values.

It should be noted that the above switching procedure is governed by light-induced transitions, thermal cis-trans transitions play only a secondary role in it. The transient time of the process can be estimated by τ_r^i (Eq. (11)), where i denotes the final polarization direction of the pump beam. For $I \gg I_S^i$, τ_r^i is inversely proportional to I , thus increasing the light intensity the transient time can be decreased. Experimentally, we found that the pulse length necessary to switch the probe transmission could be indeed further reduced by focusing the pump beam on the sample, but this possibility was restricted by laser heating. Above a threshold

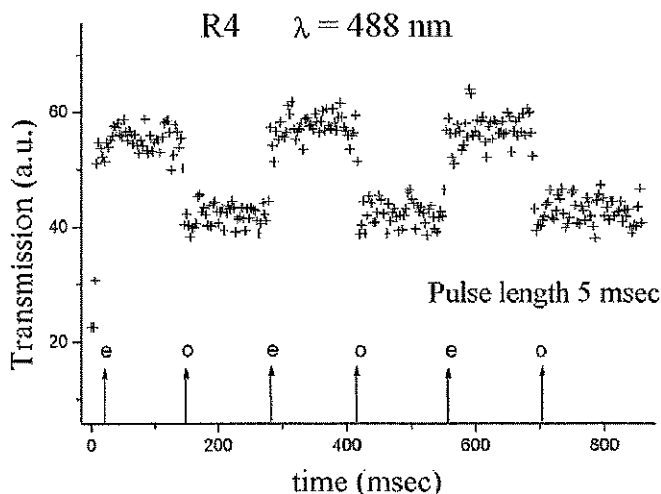


Fig. 6. Probe transmission as a function of time. The arrows indicate the times at which the pump pulses were applied, the corresponding letters indicate the polarization direction. Input power 12.5 mW, spot radius around $100\mu\text{m}$.

intensity, melting to the isotropic phase took place in the illuminated area and the polarization dependence of the equilibrium cis concentration disappeared.

Regarding applications in dynamic holography, there may be some advantages to use bulk effects in nematics instead of solid films. In the former case, much lower number of absorbed photons is needed to produce a given anisotropy change than in the latter one. In addition, saturation is easily achieved in nematics while it is hardly observable in solids. Finally we note that although photoisomerization of azo-dyes in liquids or liquid crystals is not suitable for data storage, because of the thermal cis-trans relaxation, the lifetime of the cis isomers is still long enough for real time processes.

Acknowledgments

Discussions with Drs. N. Éber, A. Jákli and T. Kósa are highly appreciated. This work was supported by the Hungarian National Science Foundation, OTKA, under Contract No. T 024098.

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