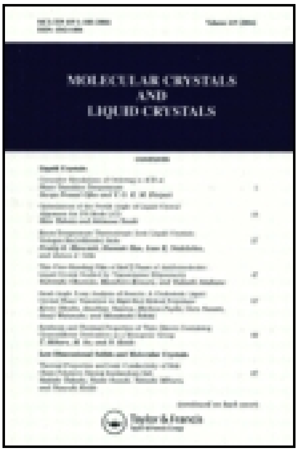

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Experimental Study of the Photoisomerization of Azo Dye in Nematic Liquid Crystal Host

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The photoisomerization of azo dye molecules in two different nematic liquid crystal host is investigated. The absorption coefficients of trans and cis isomers are determined using a pump-probe technique. The absorption coefficients of trans isomers were measured in the absence of the pump beam. Although, the absorption coefficients of the cis isomers were calculated in the presence of the pump beam using the rate equation of cis isomers in the steady state and under saturation condition. The investigation of beams polarization effects indicates dichroism of trans and cis forms of azo dye molecules. Using the experimentally obtained results, the ratio of quantum efficiency of the trans-cis transition to that of the cis-trans transition was calculated. Then results were used to obtain the value of the fraction of cis isomers and also the order parameters of the dye molecules in the host liquid crystal medium.

Keywords Liquid crystal, dye molecules, photoisomerization, absorption coefficients, pump-probe technique, quantum efficiency

1. Introduction

Recently azo dye doped nematic liquid crystals, as a guest-host system, have been investigated widely [1–3], because of their interesting optical properties and applications. Photoisomerizaton of azo dyes in nematic liquid crystals (NLC) can cause change in orientational order parameter [4], nematic- isotropic phase transition [5] and refractive index change [4,6,7]. So azo dyes has been investigated as an active component for a variety applications such as all optical switches [8], data storage [9], surface alignment of liquid crystal [10,11] and real time holography [12].

Trans isomers have elongated molecular conformation and it can be considered that they are perfectly aligned (with their transition dipole moment) along the nematic director. If the electric field of the irradiating light, with wavelength within the absorption spectrum of dye molecules, has a component along the director, trans isomers absorb the light energy and become stimulated and change their conformation to the cis form. In the presence of the irradiating light, the thermal relaxation of cis isomers begins and in the steady state when saturation occurs, the rate of cis-trans transitions equals to the rate of trans-cis transition and so fraction of the cis isomers remains constant. In this experimental work, absorption coefficients of the trans and cis isomers in the guest- host systems with two liquid crystalline host E7 and the new liquid crystal 1294-1b are determined and compared.

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2. Theory

The rate equation for the number of the cis isomers per unit volume, N_C, is expressed as [1]:

$$\frac{dN_C}{dt} = \left(N_T\sigma_T^i\phi_{CT} - N_C\sigma_C^i\phi_{CT}\right)I/h\upsilon - N_C/\tau \tag{1}$$

in which the first term on the right-hand corresponds to the light induced transition, N_T is the concentration of the trans isomers; ϕ_{TC} and ϕ_{CT} are the quantum efficiency of the trans-cis and cis-trans transitions, respectively. σ_T^i and σ_C^i denote the cross section of absorption of a photon with energy $h\upsilon$ for a trans and cis isomers, respectively. The second term represents the thermal cis-trans transitions, with a relaxation time of τ. Figure 1 illustrates the mechanism of the trans-cis isomerization schematically.

The index "i" refers to the polarization of irradiated light in all the text and can correspond to the extraordinary (e) or ordinary (o) ray.

In the steady state ($\frac{dN_C}{dt} = 0$), it can be possible to obtain the saturation value of the cis fraction ($X_s^i = N_c/N$) with respect to the cross section of absorption of trans and cis isomers. It should be noted that the cross sections of absorption are microscopic parameters and it is not possible to obtain them experimentally. On the other hand, they can be connected to the absorption coefficients using the relation, $\alpha_{T,C}^i = N\sigma_{T,C}^i$, in which N is the number of dye molecules in unit volume, so it is possible to write the X_s^i as [1]:

$$X_s^i = \frac{\alpha_T^i\,A}{\alpha_C^i + A\alpha_T^i}. \tag{2}$$

In this equation α_T^i and α_C^i are absorption coefficients for trans and cis isomers, respectively, which are macroscopic quantities and can be measured experimentally. Also the parameter A is the ratio of quantum efficiency of the trans-cis transition to that of the cis-trans transition ($A = \phi_{TC}/\phi_{CT}$). If the used light intensity as pump beam satisfies the saturation condition, so in a system with saturation value of cis fraction, X_s^i, a weak probe beam

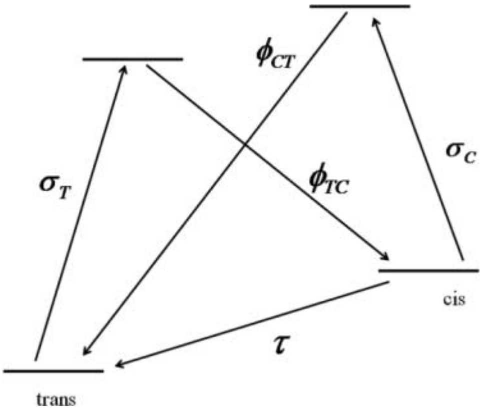

Figure 1. Schematic representation of the trans- cis isomerization.

becomes attenuated with absorption coefficient α_{im}, in which index "i" and "m" represent the polarization of the pump and probe beam, respectively, which is given by:

$$\alpha_{im} = \left(1 - \chi_s^i\right)\alpha_T^m + \chi_s^i\,\alpha_C^m \quad (i = e, o, \quad m = e, o) \tag{3}$$

α_{im} can be measured for four possible combinations of the pump and probe polarizations, using the relation below:

$$I_{im} = I_0 T_0 \exp(-\alpha_{im} d), \tag{4}$$

where I_{im} and I_0 are transmitted and incident probe intensities, respectively, d is the path length of the beam in the sample, which is not equal to the sample gap (L), and T_0 is a coefficient that represents the correction for reflections and losses not originating from dye.

For a homeotropic cell, the ordinary and extraordinary rays are shown in Fig. 2.

Absorption coefficients of trans isomers (α_T^e, α_T^o) can be measured using the equation 4, in the absence of the pump beam. Then in the presence of the pump beam, according to the equation 3, four absorption coefficients ($\alpha_{ee}, \alpha_{eo}, \alpha_{oe}, \alpha_{oo}$) can be measured. So, using these coefficients the quantity A and absorption coefficients of cis isomers can be calculated according to the following equations [1].

$$A = \frac{\alpha_T^e - \alpha_{ee}}{\alpha_{ee} - \alpha_{oe}}\left(\frac{\alpha_{oe}}{\alpha_T^e} - \frac{\alpha_{oe}}{\alpha_T^o}\right) \tag{5}$$

$$\alpha_C^e = \frac{\alpha_{ee}\,\alpha_T^e A}{\alpha_T^e(A+1) - \alpha_{ee}} \tag{6}$$

$$\alpha_C^o = \frac{\alpha_{oo}\,\alpha_T^o\,A}{\alpha_T^o(A+1) - \alpha_{oo}} \tag{7}$$

Using the obtained values, fraction of the cis isomers can be calculated via equation 2.

Order parameters for two isomers can be obtained separately, using the relation below:

$$S_1 = \frac{\alpha^{par} - \alpha^{perp}}{\alpha^{par} + 2\alpha^{perp}} \tag{8}$$

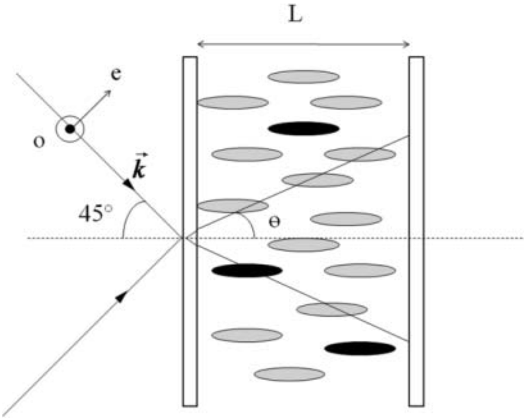

Figure 2. Ordinary and extraordinary rays for a homeotropic cell. θ is the refraction angle inside the sample.

α^{par} and α^{perp} are absorption coefficients for polarization directions parallel and perpendicular to the director.

3. Experiment

In this experimental study homeotropic aligned cells with thickness L = 20 μm were used. The NLC mixtures (1294-1b) and E7 and the cells were purchased from AWAT PPW Company (Poland). The dye doped NLC mixtures were prepared by dissolving about 0.5% weight of 2-(ethyl(4-((4-nitrophenyl) azo) phenyl) amino) ethanol. (C.I. disperse red 1, DR1) from Aldrich. Azo dye doped liquid crystals were filled to the cells using the capillary forces.

Experimental setup to measure the absorption coefficients is illustrated in Fig. 3. Laser beam with wavelength 514 nm from an Ar^+ laser was divided into two beams using a beam splitter. One beam having the power of 4 mw was used as pump beam and the other was attenuated using a filter and was used as probe beam. Difference of the path length of the probe and pump beams after beam splitter must be larger than the coherence length of the Ar^+ laser to avoid interference of the beams.

The angle of incidence of the pump and probe beam was 45° and −45°with respect to the normal direction to the cell surface, respectively.

To avoid the light-induced bulk reorientation a stabilizing AC voltage (5 v, 10 kHz) was applied to the sample. Thus, the dye molecules are fixed homeotropically and the angle between the long axis of the dye molecules and the polarization direction is specified. To determine the coefficient T_0, the transmission coefficient of an undoped sample was measured under the same circumstances in which the absorption coefficients were measured.

In the room temperature trans isomers are stable and in the absence of the pump beam we can consider fraction of the cis isomers negligible. So, absorption coefficients measured using probe beam with polarizations "e" and "o" gave the coefficients α_T^e and α_T^o. Then four absorption coefficients (α_{ee}, α_{eo}, α_{oo}, α_{oe}) were measured in presence of the pump beam. From the obtained values, α_C^e, α_C^o and A were calculated using the equations 4, 5, 6. Since α values obtained for e polarization refer to an angle of incidence 45° on the air and an angle θ within the sample, as shown in Fig. 2, the values of absorption coefficients α^{par},

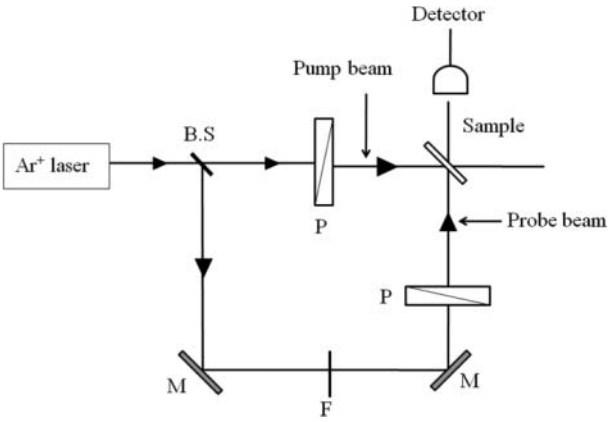

Figure 3. Experimental setup to investigate the photoisomerization of azo dyes in nematic liquid crystal host. B.S, beam splitter; P, polarizer; M, mirror; F, filter.

Table 1. The average value of the transmission intensity of the probe beam for samples containing DR1 doped E7 and 1294-1b NLCs

	DR1 doped E7		DR1 doped 1294-1b	
	$\bar{T}$ (m = e)	$\bar{T}$ (m = o)	$\bar{T}$ (m = e)	$\bar{T}$ (m = o)
In the absence of the pump beam	0.714	1.439	0.885	1.797
In the presence of the pump beam (i = e)	0.854	1.542	1.014	1.869
In the presence of the pump beam (i = o)	0.797	1.505	0.9709	1.831

can be determined using [13]:

$$k v_e^2(\theta) = k_o v_o^2 \cos^2(\theta) + k_e v_e^2 \sin^2(\theta) \tag{9}$$

in which $v_e^2(\theta) = v_o^2 \cos^2(\theta) + v_e^2 \sin^2(\theta)$ and k for all polarizations is related to the corresponding absorption coefficients via the relation below

$$k = \alpha v/2\omega \ , \ \ v = c/n \tag{10}$$

4. Results and Discussion

The average value of the transmission intensity of the probe beam for different polarizations of the pump and probe beams for samples containing DR1 doped E7 and 1294-1b nematic liquid crystals are illustrated in Table 1.

According to the alignment of dye molecules in the direction of the director, in the absence of the pump beam transmission intensity of the probe beam with "o" polarization is more than that of the probe beam with "e" polarization, due to the dichroic absorption of the azo dye molecules. In the presence of the pump beam with "e" polarization, the average transmission intensity of the probe beams (either "e" or "o" polarizations) is more with respect to the presence of pump beam with "o" polarization. This clears that the dye molecules absorb more when the pump polarization is "e". The absorption coefficients of the trans isomers are measured to be $\alpha_T^e = 388\,\text{cm}^{-1}$, $\alpha_T^o = 244.5\,\text{cm}^{-1}$ in the E7 NLC and $\alpha_T^e = 393.8\,\text{cm}^{-1}$, $\alpha_T^o = 205.05\,\text{cm}^{-1}$ in the 1294-1b NLC. Absorption coefficients in the presence of the pump beam, measured for DR1 doped E7 and 1294-1b are listed in Table 2.

Table 2. Absorption coefficients measured for four possible combinations of the pump and probe polarizations, in DR1 doped E7 and 1294-1b

	DR1 doped E7		DR1 doped 1294-1b	
α_{im} (cm^{-1})	m = e	m = o	m = e	m = o
i = e	337.5	226.6	355.6	194.7
i = o	359.3	232.5	374.3	199.8

Table 3. List of the calculated parameters for two samples

	A	$\alpha_c^e(\text{cm}^{-1})$	$\alpha_c^o(\text{cm}^{-1})$	X_s^e	X_s^o
DR1 doped 1294-1b	1.78	337.2	196.9	0.675	0.64
DR1 doped E7	1.26	305.8	223.7	0.615	0.57

Using the obtained data, the ratio of the quantum efficiencies, A, absorption coefficients of the cis isomers, α_C^e, α_C^o, and fraction of the cis isomers, X_s^e, X_s^o are calculated and listed in Table 3.

Using the absorption coefficients of the trans and cis isomers for both "e" and "o" polarizations, the coefficient α^{par} for these isomers were calculated using the equations 8 and 9. So, the order parameter of trans and cis isomers were calculated, using the equation 7, to be 0.56 and 0.44 in the E7 NLC host and 0.77 and 0.63 in the 1294-1b NLC host.

The obtained results clear that the difference of absorption coefficients of the trans isomers for the e and o polarizations is larger than that of the cis isomers. These differences and also X (fraction of the cis isomers) in the 1294-1b nematic liquid crystal were enhanced with respect to the E7 nematic liquid crystal.

5. Conclusion

Absorption coefficients of the trans and cis isomers are measured in two different nematic liquid crystal host E7 and 1294-1b. Absorption coefficients of trans isomers are more than that of the cis isomers in both host materials. Also difference of absorption coefficients for polarizations parallel and perpendicular to the director is more for the trans isomers in both NLCs. This result shows that the trans isomers have a higher dichroism than the cis isomers. Also, these differences are more in the 1294-1b NLC compared to the E7 NLC, which can be due to the higher orientational order of the isomers in the former NLC. The quantity A is larger in the DR1 doped 1294-1b and consequently fraction of cis isomers is larger in this sample compared to the sample containing DR1 doped E7 NLC. Order parameter of the cis isomers is smaller with respect to the trans isomers in both NLC host. This fact is related to the difference in the shape of the two isomers, so that trans isomers with elongated conformation orient more effectively parallel to the host liquid crystal molecules.

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