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Effect of *cis/trans*-Isomerisation on Photoalignment of Azo Dyes

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Abstract—Using potassium 5-[{4'-[(5'-carboxy-4'-hydroxy-2'-methylphenyl)diazenyl]biphenyl-4-yl}diazenyl]-2-hydroxy-4-methylbenzoate and potassium 3-[{4'-[(3-carboxy-2,4-dihydroxyphenyl)diazenyl]biphenyl-4-yl}-diazenyl]-2,6-dihydroxybenzoate as examples, *cis*/*trans*-isomerization of azo dyes in solutions and dynamics of their photoalignment in thin film under irradiation with polarized light were studied.

Keywords: azo dyes, intramolecular hydrogen bonds, photoalignment, polarized absorption spectroscopy

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Liquid crystals (LC) find wide application in various devices of information display: monitors, TV sets, watches, etc. [1–5]. The alignment layers are a necessary part of any LC device since they form the required structure of LC [2–4]. In the present time the rubbed thin films of imide polymers are used as alignment layer for LCs [2], however noncontact methods of anisotropic layers formation are required because of some drawbacks of the grating technology. Photo-orientation of azo dyes layers is the promising method [6, 7]; for this thin film after exposure to the polarized light high values of anchoring energy with LC are typical and also thermo- and photostability [8–11]. Under irradiation of thin films, reorientation of the molecules of azo dye perpendicularly to the polarization plane of the incident light occurred that led to the formation of anisotropic distribution in the thin film, which contributes to the liquid crystal orientation [12]. The photoalignment of dyes makes it possible to produce rasters in 3D-dispalys, phase retarders; also they can be applied in various integral devices of photonics, optoelectronics, organic electronics, etc.

Now a number of azo dyes are known which are applied for photoalignment of liquid crystals, and the models were proposed which describe the process of reorientation as statistic macroscopic phenomenon of *cis/trans*-isomerization [13], rotation diffusion [6], intermolecular binding [14].

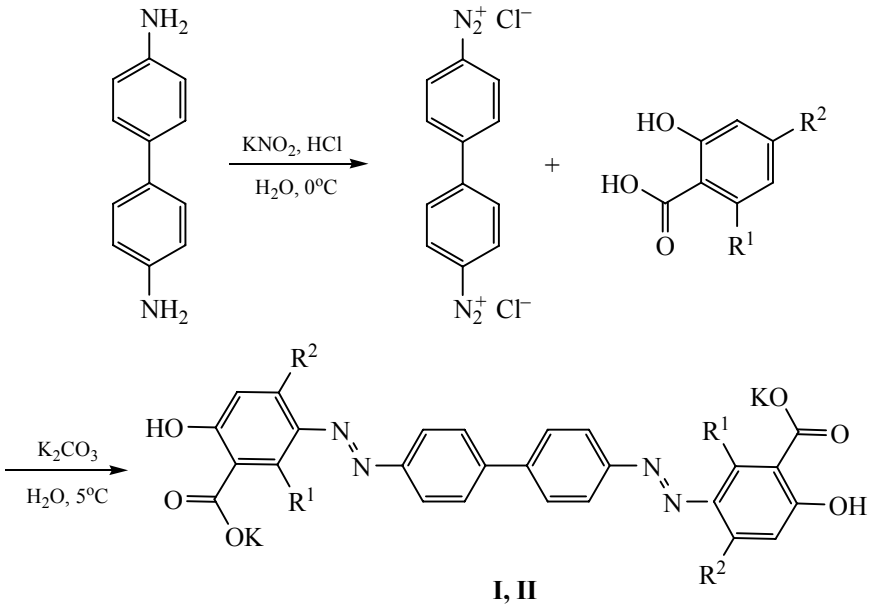
The key elements characterizing the structure of photoaligned dyes according to the existing theories are rigid symmetrical linear structure [15], intramolecular coordination bond whose energy is less than photon energy [16, 17], and free volume [18].

The role of *cis/trans*-isomerization for reorientation of azo dye is insufficiently studied. In order to study azo-group isomerisation and its impact on photo-alignment of the molecules two model dyes were synthesized: potassium 5-[{4'-[(5'-carboxy-4'-hydroxy-2'-methyl-phenyl)diazenyl]biphenyl-4-yl}-diazenyl]-2-hydroxy-4-methylbenzoate **I** and potassium 3-[{4'-[(3-carboxy-2,4-dihydroxyphenyl)-diazenyl]biphenyl-4-yl}-diazenyl]-2,6-dihydroxy-benzoate **II**.

In structure **II** there is phenol hydroxyl moiety, *ortho*-position with respect to the azo bond, which is known [19–22] to be able to form intramolecular hydrogen bond with the azo group that impedes the *cis/trans*-isomerization [22]. The structural difference of azo dye **I** is the presence of *ortho*-position methyl substituent, therefore the azo group in the molecule remains free.

The structures of prepared azo dyes **I** and **II** were confirmed by IR and NMR spectroscopy. Thus, in the ^{1}H NMR spectrum of **I**, the OH group resonated at a very low field (17.8 ppm) that may be due to the formation of a hydrogen bond with C=O group of the

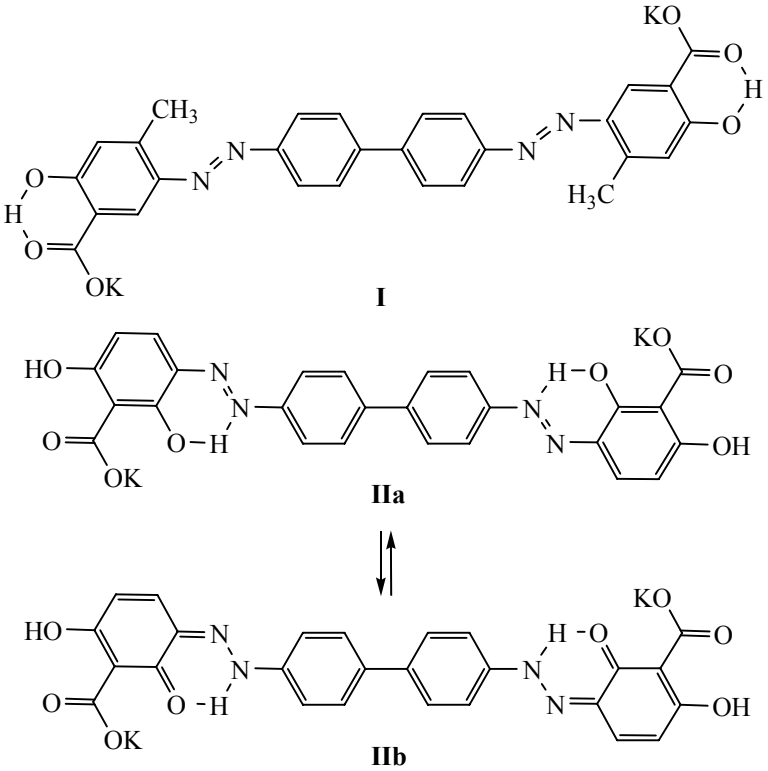
Scheme 1.



I, II

R^1 = H, R^2 = CH_3 (**I**); R^1 = OH, R^2 = H (**II**).

Scheme 2.



I

IIa

IIb

carboxy fragment [23]. In the IR spectrum of azo dye **I** there was a strong absorption band at 3424.7 cm^{-1} (O–H) that additionally confirmed the presence of the intramolecular hydrogen bond (Scheme 1).

In the ^1H NMR spectrum of azo dye **II**, the signal of one of the phenol hydroxyls *ortho*-position relative to the azo group appeared at 16.34 ppm that indicated the formation of intramolecular hydrogen bond with

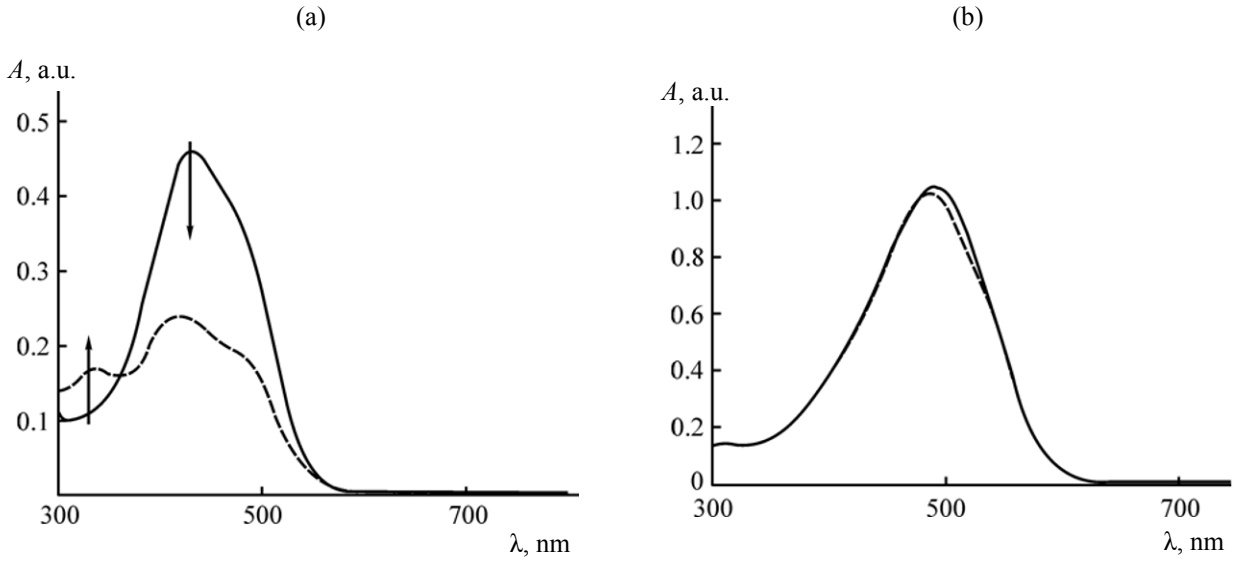


Fig. 1. Isomerism of the azo dyes **I** (a) and **II** (b) in DMF solution before (solid line) and after irradiation (dotted line).

the azo group [24]. In this case the formation of the hydrazone structure may happen [25–27] that would be registered by the appearance of the signals at 14–16 ppm in the ^{1}H NMR spectra [28–30]. An additional confirmation of the formation of the hydrazone structure **IIb** was the presence of the signal of the carbon atom at 180 ppm in the ^{13}C NMR spectrum [31] (Scheme 2).

According to the data of electronic spectroscopy, in DMF solution of compound **I** (λ_{max} 430 nm) a distinct phenomenon of *cis/trans*-isomerization was observed (Fig. 1a) with the appearance of an isobestic point at 360 nm [32, 33]. In the case of azo dye **II** (λ_{max} 487 nm) the isomerism was absent (Fig. 1b) that evidenced the formation of the hydrazone structure which is characterized by low probability of *cis/trans*-isomerization or its absence in similar compounds [34].

The irradiation of thin films of azo dye **I** induced the appearance of anisotropy that was proven by increase in absorption at perpendicular and its reduction at parallel position of probing irradiation relative to the exposing one (Fig. 2a) [11]. The irradiation of dye **I** in thin film caused an increase in the dichroic ratio (*DR*) (Fig. 2b) that achieved value of 3.38 after 40 min of exposure to the polarized light (8 mW cm^{-2}), but in the case of compound **II** only insignificant dichroic ratio was induced (*DR* 1.2). However, a decrease in light absorption in thin films of the second azo dye was found both at perpendicular and parallel orientation with respect to the polarization of the exposing irradiation (Fig. 2c). The obtained dependences indicated discoloration of the dye (its oxidation) at irradiation, but not its reorientation.

The formation of the strong hydrogen bond with the azo group led to restructuring the molecule with the formation of the hydrazone fragment, which causes a decrease in the ability of the compound to *cis/trans*-isomerization and the absence of azo dyes photoalignment. Therefore photoalignment capability of azo dyes is determined by their ability to *cis/trans*-isomerization.

EXPERIMENTAL

Benzidine (Vekton, Russia), 4-methylsalicylic and 2,6-dihydroxybenzoic acids (Sigma Aldrich, Germany) were used without further purification.

^{1}H and ^{13}C NMR spectra were recorded from DMSO-d_6 solutions on a Bruker Avance 500 spectrometer operating at 500 MHz. IR spectra were registered on a Fourier spectrometer Bruker Tenzor 27 from KBr pellets. Electron absorption spectra were recorded on an Ocean Optics Maya2000Pro spectrometer.

Preparation of the film carriers and the samples. Purification of the glass substrate (float alkali glass, thickness 2 mm, size 20 × 25 mm) was done successively in ultrasonic bath with distilled water with surfactant, with water, and with isopropanol. The

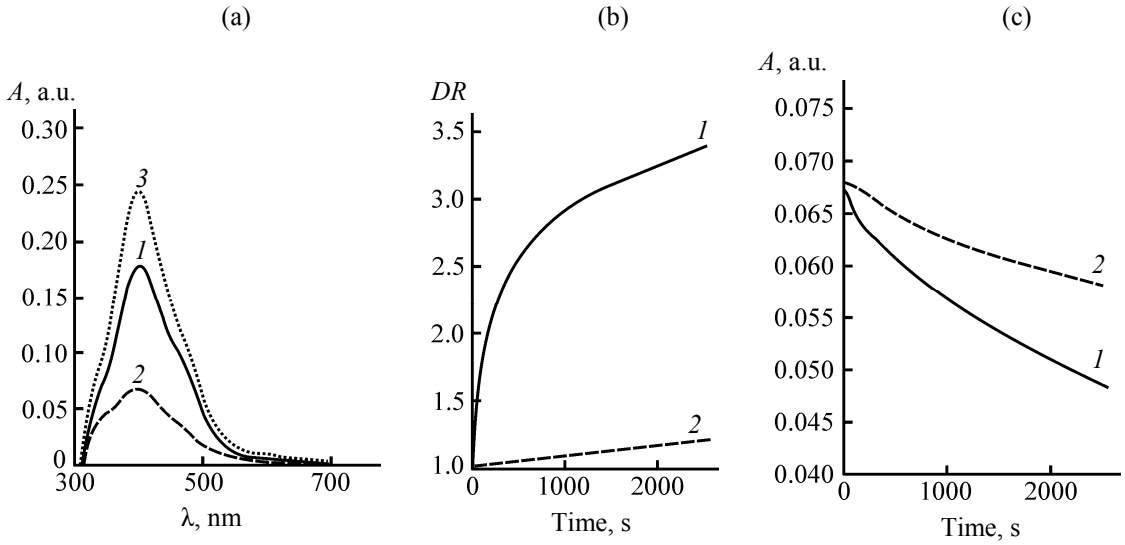


Fig. 2. Variation of the dichroic ratio and absorption of the dyes in thin film. (a) polarized absorption spectra of the thin film of aza dye **I** before (*1*) and after irradiation at coincidence of the probing and exposing irradiation (*2*) and at the perpendicular direction of the probing and exposing irradiation (*3*); (b) dynamics of photoalignment of aza dyes **I** (*1*) and **II** (*2*); (c) change of absorption in the thin film of aza dye **II** in time at irradiation for *S*- (*1*) and *P*-polarization (*2*).

glass substrates were dried at 110°C for 5 min followed by additional UV purification on a Photo Surface processor PL 16-110D (SEN Lights Corp., Japan). Spin-coating of film on top of the glass substrates was performed with the use of 1% solutions of the dyes in DMF applying a VTC-100 centrifuge (MTI Corp., USA) at 600 rpm for 3 s and then at 2500 rpm for 60 s. The prepared samples were dried at 100°C for 5 min.

Potassium 5-[{4'-[(5'-carboxy-4'-hydroxy-2'-methylphenyl)diazenyl]biphenyl-4-yl}diazenyl]-2-hydroxy-4-methylbenzoate (I) [35]. A mixture of 1.84 g (0.01 mol) of benzidine, 4.8 mL (0.06 mol) of hydrochloric acid, and 10 mL of distilled water was stirred for 20 min to get homogeneous suspension. Then 45 mL of boiling water was added at vigorous stirring to achieve complete dissolution of benzidine. After cooling to 0°C, a solution of potassium nitrite [1.75 g (0.021 mol) in 5 mL of water] was added within 20 sec. The obtained mixture was stirred for 1 h at 5°C. Next, the prepared diazo solution was added dropwise within 45 min to a solution of 2.9 g (0.021 mol) of 4-methylsalicylic acid in 50 mL of water and 9.66 g (0.07 mol) of potassium carbonate cooled to 5°C. The reaction mixture was stirred for 3 h and left overnight. The prepared dye was salted out with potassium chloride, filtered off, washed with 17% solution of potassium chloride, dried at room temperature, and chromatographed eluting with ethanol–water mixture (4 : 1). The obtained powder-like substance was dissolved in 50 mL of DMF and re-precipitated by adding 300 mL of diethyl ether. The precipitate formed was filtered off, washed with diethyl ether and dried in a vacuum at 40°C. Yield 53.2%. IR spectrum (KBr): ν, cm^{-1}: 3424.7, 2923.91, 1637.35, 1586.02, 1492.25 1460.46, 1427.75, 1378.74, 1265.33, 1173.96, 1064.42, 1002.8, 920.1, 852.35, 739.1, 626.55, 525.85. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 8.17 s (2H), 7.94 d.d (8H, $J^1 = J^2$ = 90 Hz), 6.64 s (2H), 2.63 s (6H), 17.80 s (OH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 17.45, 116.77, 117.9, 122.59, 127.50, 140.14, 140.82, 143.41, 152.16, 162.25, 168.51, 170.97.

Potassium 3-[{4'-[(3-carboxy-2,4-dihydroxyphenyl)-diazenyl]biphenyl-4-yl}diazenyl]-2,6-dihydroxy-benzoate (II) was prepared similarly. Yield 26%. IR spectrum (KBr): ν, cm^{-1}: 3422.5, 1616.77, 1576.7, 1538.9, 1479.4, 1386.9, 1335, 1280.1, 1235.2, 1163.5, 1123.5, 1003.37, 954, 817, 731.4, 628.3. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 16.34 s (OH), 7.67 d (4H, *J* 8.5 Hz), 7.43 d (4H, *J* 8.5 Hz), 6.9 d (2H, *J* 9.5 Hz), 5.96 d.d (2H, J^1 2.5, *J* 9.5 Hz), 5.32 s (2H). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 180.81, 169.07, 146.29, 135.35, 133.73, 133.54, 127.48, 122.66, 117.41, 104.84.

Dynamics of azo dyes photoalignment was studied on a computerized setup which allowed

exposure of the sample for a specified period of time followed by measurement of the polarized absorption spectra for *S*- and *P*-polarization [36]. The process of irradiation and recording of the absorption spectra was repeated to achieve the designated irradiation dose. The setup was used to reduce an error of the experiment since a number of the successive measurements were always done in the same investigated area of the sample.

The dichroic ratio for each instant was determined according to the equation:

$$DR = A\perp/A_{||},$$

where $A_{||}$ and $A\perp$. are absorption of the linearly polarized light of the probing irradiation in parallel and perpendicular direction relative to the polarization of the exposing irradiation respectively.

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