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Photoinduced anchoring transitions in a nematic doped with azo dyes

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Recently, we reported on a light-induced anchoring transition of an azobenzene nematic from planar to homeotropic alignment. In the proposed model of the transition, the changes in shape of the liquid crystal molecules and of their net dipole moment, due to the photoisomerization, were considered to play a vital role in the occurrence of the transition. In order to assess the validity of this model, a study of the anchoring behaviour of nematic guest–host liquid crystal mixtures containing two photochromic dyes, 3,3′- and 4,4′-substituted azobenzenes, was carried out. The dyes have very similar molecular structures to that of the azobenzene nematic previously studied, and their molecules, having a linear shape in the *trans*-form, maintained this shape after photoisomerization in the case of the 3,3′-azo dye, and changed it to bent in the case of the 4,4′-azo dye. The dyes possessed similar net dipole moments that increased substantially after photoisomerization, resulting in a preferential adsorption of their *cis*-isomers on the solid substrate. However, only the mixture containing the 4,4′-azo dye exhibited an anchoring transition from planar to homeotropic alignment upon illumination with unpolarized UV light, a behaviour in excellent agreement with the prediction of the model for the light-induced anchoring transition. An anchoring transition from random planar to uniform planar alignment was found to take place in the mixtures when linearly polarized UV light was used, requiring, however, a different exposure time for the two dyes.

1. Introduction

The alignment of liquid crystals, which originates from liquid crystal/solid surface interactions, is of vital significance for liquid crystal displays and devices. Therefore, the study of these interactions is very important for their understanding and for tailoring them properly to achieve desirable liquid crystal device performances.

It is known that, in the absence of external factors such as electric or magnetic fields, the alignment of liquid crystals confined between two solid substrates depends on the anchoring of the liquid crystal molecules to the solid surface. Hence, this surface dictates the preferred direction of alignment in the volume. Recently, a fast switching of liquid crystals by control of command surfaces has been demonstrated [1].

The anchoring of the liquid crystal is characterized by two quantities, the polar W_θ and azimuthal W_φ anchoring energies. In general, these energies depend on dipole–dipole, van der Waals and steric interactions, as well as on hydrogen bonding. The alignment of liquid crystals by solid substrates covered with surface-active agents is a classical example of the role of steric interactions between the liquid crystal molecules and those of the surface-active agent [2].

There are different methods for achieving a desirable alignment. Rubbed polymer films are the most widely used layers for obtaining uniform planar or tilted alignment. However, the rubbing technique has certain disadvantages. Mechanical defects and surface charges are generated during the rubbing process and, in the case of ferroelectric liquid crystals, these may have a crucial effect on the operation and the quality of the devices. Recently, a new alignment method was introduced, the so-called light buffing method. According to this method, the substrate surface, which is chemically modified or coated with a photoresponsive material, is illuminated by linearly polarized UV light [3]. In this way, the preferred direction of alignment is fixed to be normal to the light polarization.

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Light-induced alignment can also be a dynamical process. Photoregulation of surface-assisted alignment, using the so-called 'command surface effect', provides an effective way to control liquid crystal alignment reversibly. There are two categories of command surfaces classified on the basis of the changes in the liquid crystal alignment. The first type involves a change in the preferred direction of alignment (in the position of the liquid crystal director) through light illumination from homeotropic to planar [4] or the reverse [5] (out-of-plane reorientation) (figure 1). The switching of the alignment in these cases resembles that in conventional electrically driven liquid crystal cells with negative and positive dielectric anisotropy, respectively. The second type is realized by the action of linearly polarized light on photoresponsive molecules that, in the case of initial planar alignment, results in an azimuthal reorientation of the preferred direction of alignment (in-plane reorientation) [3]. The in-plane reorientation by light causes a transition from initial random planar (with no preferred direction of alignment) to uniform planar alignment (with unique director orientation) (see figure 2). The photoisomerization of the dyes plays a very important role in these anchoring transitions.

In certain organic materials, reversible transformations between different isomers can be induced by light [6]. In some of these materials, *trans-cis* photoisomerization may result in drastic changes in the molecular shape, as well as in the distribution of permanent dipole moments in the molecular structure. Such photoinduced structural alternations, however, have a substantial impact on the liquid crystalline bulk and surface properties [7]. Recently, we reported on the photoinduced anchoring transition in an azobenzene nematic and on photoinduced changes in the flexoelectric polarization of a nematic doped with azo dye [5, 8]. The changes in both molecular shape and net dipole moment were considered to be of importance for the observed phenomena. In order to evaluate the role of each of these parameters, and thus to assess the suggested model of the light-induced anchoring transition from planar to homeotropic alignment in the nematic azobenzene, we have studied the influence of the photoisomerization of two azo dyes, 3,3′- and 4,4′-substituted azobenzenes, on the anchoring behaviour of their mixtures with a nematic host. As we shall see, the photoisomerization behaviour of the dyes has a strong impact on the anchoring of the guest–host mixtures to the solid substrates.

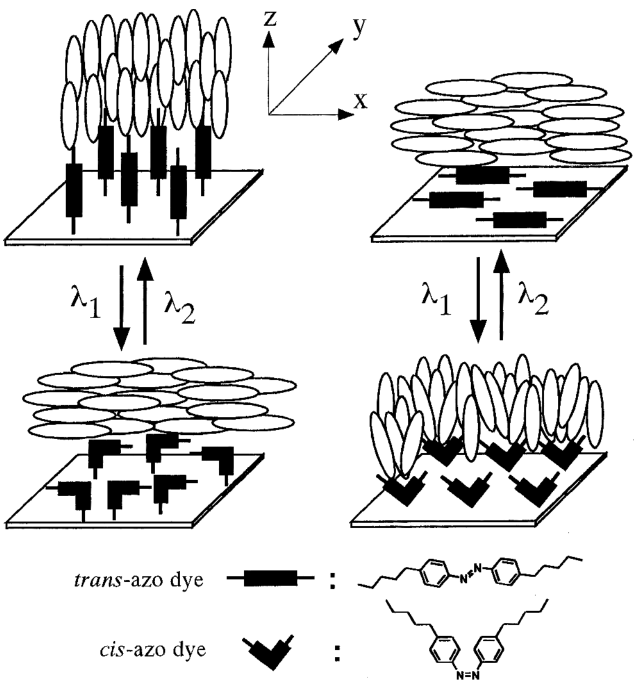

Figure 1. Schematic representation of light-induced transitions of liquid crystal alignment (out-of-plane anchoring transitions) in liquid crystal cells with initial homeotropic (left) and planar (right), anchoring conditions.

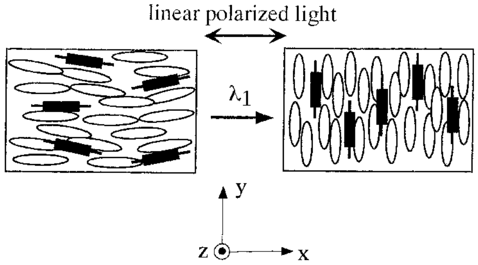

Figure 2. Schematic presentation of light-induced in-plane reorientation of the liquid crystal molecules from random planar to uniform planar alignment under illumination with linearly polarized light (in-plane anchoring transition).

2. Experimental

2.1. *Materials*

The structures and phase sequences of the azo dyes, 4,4′-dihexyloxyazobenzene (4,4′-azo) and 3,3′-dihexyloxy-2,2′-dimethylazobenzene (3,3′-azo), are shown in figure 3. Their structures, as can be seen, are quite similar, and they are also similar to the azobenzene nematic studied in [5]. Therefore, a comparison of these three compounds, concerning their photoisomerization behaviour and anchoring properties, is expected to give important information necessary for the assessment of the model for the light-induced anchoring transition. The synthesis of the azo dyes has been reported previously [9]. A nematic liquid crystal, DON-103 (LODIC) with nematic–isotropic transition temperature $T_{NI} = 74°C$ was used as the host liquid crystal material (see also figure 3). Azo dyes were dissolved in the nematic host at a concentration of approximately 9 wt %.

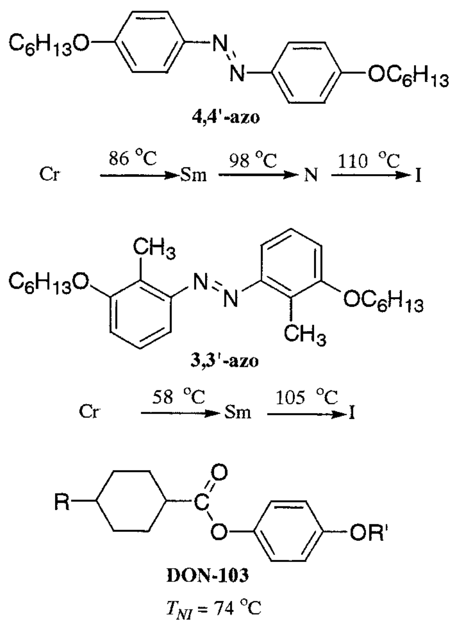

Figure 3. Molecular structures and phase sequences for 4,4′-dihexyloxyazobenzene (4,4′-azo), 3,3′-dihexyloxy-2,2′-dimethylazobenzene (3,3′-azo), and of the nematic host, DON-103.

The experimental cells were prepared in the following way. Two glass plates ($1 \times 3\,\mathrm{cm}^2$) were ultrasonically cleaned with acetone/sodium hydroxide solution, concentrated sulfuric acid and copious amounts of distilled water, successively, and dried at 100°C. The glass surfaces were not subjected to any chemical or physical alignment treatment. The plates were then used as substrates to fabricate conventional sandwich liquid crystal cells where the cell gap was controlled using colloidal silica (5 μm). The guest–host mixtures were fed into the cells at 80°C by capillary action.

2.2. *Experimental procedures*

The alignment of a cell was evaluated by optical microscopy (Olympus BH-2) using crossed polarizers. The guest–host liquid crystal cells were exposed to unpolarized UV light from a high pressure mercury arc lamp USH-500D (Ushio) through a combination of glass filters, UV35 and UVD36 (Toshiba). The intensity of the transmitted light was $0.5\,\mathrm{mW\,cm^{-2}}$. To obtain linearly polarized light, a Glan–Thomson polarizer was used.

3. Results and discussion

After the filling process of the cells was completed, the liquid crystal was found to adopt a random planar alignment, i.e. without any preferred direction. However, in some regions of the cells, the liquid crystal appeared to be partially aligned by the liquid crystal flow during cell fabrication. Part of each cell was masked and the open sides were subjected to UV light exposure. The experiments were carried out with unpolarized or linearly polarized light.

After illumination of the samples with unpolarized UV light, only the cell containing 4,4′-azo exhibited an anchoring transition from random planar to homeotropic that occurred after an exposure time of 5 min (see figure 4). A longer exposure time did not result in any further changes. In contrast, the random planar alignment in the cell with 3,3′-azo was unaffected by UV light, even on exposing the cell for a much longer time (30 min). The temperature of the N–I phase transition (T_{NI}) of the guest–host mixtures was found to decrease by a few degrees due to the photoisomerization of the dyes. In order to understand the difference in the anchoring behaviour of the dyes under illumination, first we should consider their photoisomerization behaviour, i.e. the changes that take place in their molecular shape and net dipole moment, and then try to relate these photoinduced changes to the changes in the anchoring of the guest–host mixtures to the solid surface.

The photoisomerization behaviour of the 4,4′-azo and 3,3′-azo was reported previously [9]. Exposure of the photostationary state to UV light gave more than 90% of *cis*-isomer in solvents and 80% in nematic liquid crystals. The half-life times of the *cis*-isomers of 4,4′-azo and 3,3′-azo in hexane solution at 25°C were determined to be *c.* 8.7 h and 140.5 h, respectively. It has also been indicated that the *cis*-isomers of 3,3′-disubstituted azobenzenes may prefer a rod-like structure in contrast to the bent structures of the 4,4′-disubstituted azobenzenes [9, 10].

Based on the most stable conformations of both *trans*- and *cis*-isomers obtained using molecular orbital calculations (the semi-empirical MOPAC with PM3 parameter), the net dipole moments of the molecules were estimated for the model compounds illustrated in figure 5. As shown, due to the photoisomerization, the net dipole moments of the *cis*-isomers of both dyes become larger than those of the corresponding *trans*-isomers and so are more polar compared with them. The net dipole moment increases during photoisomerization by 40 and 50 times for 3,3′- and 4,4′-azo dyes, respectively. Although there is no substantial difference between the net dipole moments of the *cis*-isomers of the dyes, i.e. they are more or less equally polar, there is however a significant difference in their molecular shape. The *cis*-isomer of the 4,4′-azo dye has a bent shape, whereas that of the 3,3′-azo dye maintains the linear form of its *trans*-isomer. It should be stressed here that, after being absorbed on a solid surface, such a difference in the

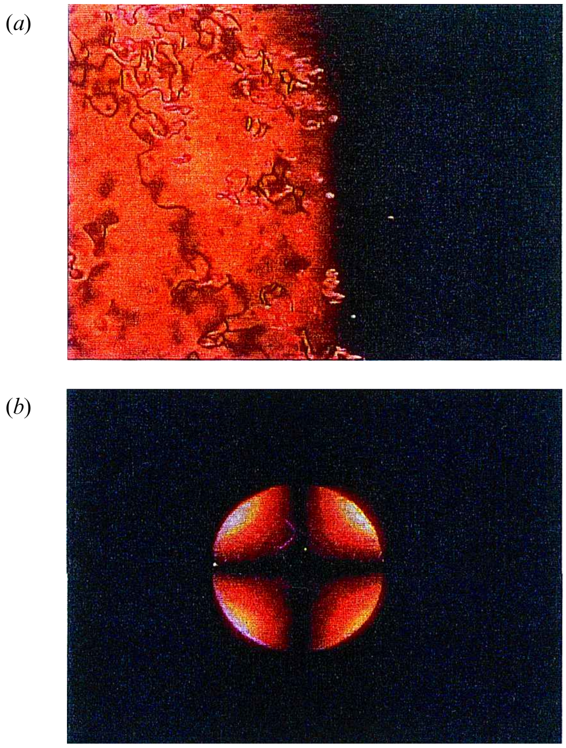

Figure 4. Photomicrographs of the out-of-plane anchoring transition in a guest–host mixture containing 4,4′-azo dye after illumination for 5 min with non-polarized UV light at normal incidence. The left half of the sample was protected from the light. Anchoring transition from random planar to homeotropic alignment occurred in the illuminated part of the sample (*a*); the conoscopic image of this part is shown in (*b*).

molecular shapes of the *cis*-isomers of these two compounds can result in a substantial difference in the anchoring conditions at the solid surface and strongly influence the liquid crystal alignment in the cells.

The adsorption of the *cis*-isomers on the solid surface, so modifying the anchoring conditions of this surface, is of vital importance for the anchoring transitions induced by light. In order to obtain some information concerning the adsorption of the *cis*-isomeric molecules on the solid substrate, π-A isotherms of monolayers of the *cis*-isomers of both azobenzenes were investigated. The results of this study will be published elsewhere [11]. Here, we will outline only some of the most important results and conclusions from this study that are closely related to the subject of the present paper. No distinct π-A isotherms were observed for the *trans*-isomers of either compound because monolayer formation is totally inhibited for the *trans*-isomers due to the hydrophobic character of the molecules, leading to the formation of droplets on a water surface. On the other hand, a rise in the π-A curve was observed at an area per molecule of *c.* 8 nm^2 for both *cis*-isomers, suggesting that each *cis*-isomer possesses a polar site at the azo-group which interacts directly with the water surface to form floating monolayers (see figure 6). It should be noticed that there is a significant difference in the monolayer collapse pressures for the two isomers. Whereas the floating monolayer of *cis*-3,3′-azo is very unstable, the collapse pressure of the monolayer of 4,4′-azo was relatively large, at about 15 $\mathrm{mN\,m^{-1}}$. The enhanced stability of the monolayer of the latter is

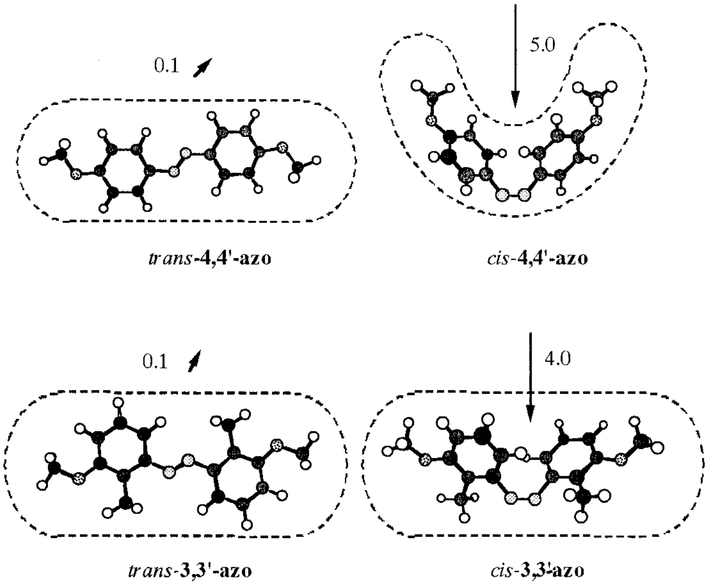

Figure 5. Conformational structures and net dipole moments of geometrical isomers of the model compounds 4,4′-azo and 3,3′-azo estimated by semi-empirical molecular orbital calculations.

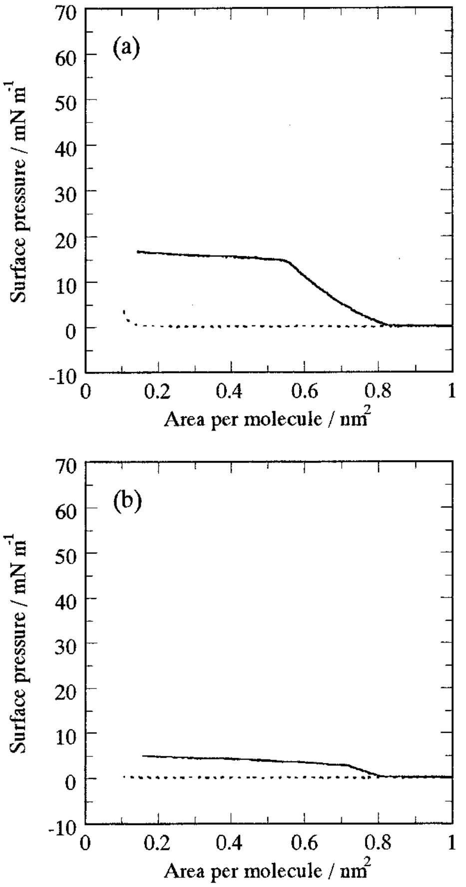

Figure 6. π-A isotherms of *trans*- (dashed line) and *cis*- (full line) isomers of (*a*) 4,4′-azo and (*b*) 3,3′-azo at 20°C.

evidently due to the azo group acting as a polar head which interacts efficiently with the water surface. On the other hand, the presence of two methyl groups at the *ortho*-positions of *cis*-3,3′-azo sterically inhibit the direct interaction of the polar azo group with the water surface.

Now, relating these results to our case of a confined liquid crystal in a sandwich cell with substrates whose surface is hydrophilic (polar), it follows that it is very likely that the molecules of the *cis*-isomer of 4,4′-azo are adsorbed on the polar substrate surface in a manner quite similar to that on the water surface, resulting in a highly tilted orientation of their hexyloxy chains. As found, such a positioning of *cis*-isomer molecules has a crucial impact on the alignment of the liquid crystal mixture containing 4,4′-azo dye. This kind of surface adsorption of the *cis*-isomer of 3,3′-azo is however suppressed by the presence of hydrophobic methyl groups at the *ortho*-positions.

In the model proposed to explain the light-induced anchoring transition in an azobenzene nematic [5], it has been pointed out that the concentration of *cis*-isomer in the nematic volume increases with UV exposure time. Due to the higher polarity, however, the concentration of *cis*-isomer molecules on the solid surface increases more rapidly than in the bulk. The surface concentrations of *cis*-isomer in both dye-doped mixtures have quite a similar behaviour with exposure time, since the *cis*-forms of both dyes possess a larger transverse net dipole moment compared with their *trans*-forms, and therefore are preferentially adsorbed on the solid surface. Due to differences in their molecular structures, however, there is a substantial difference in the surface packing of the *cis*-isomers of 3,3′- and 4,4′-azo and thus in the surface anchoring conditions after their adsorption on the solid substrate (figure 7).

The molecules of the 3,3′-azo dye retain their linear form during the photoisomerization process, so preserving the initial planar alignment imposed by the surface. On the contrary, the 4,4′-azo dye drastically changes its shape during the photoisomerization, becoming strongly bent in its *cis*-form. As already argued in [5], such a form does not favour in-plane orientation of the *cis*-isomer on the solid surface. Therefore, it is more likely that the polar azo-group of the *cis*-isomer of the 4,4′-azo dye is attached to the substrate surface and the hexyloxyl chains are highly tilted with respect to this surface. As mentioned, such an orientation of the *cis*-isomer of 4,4′-azo has been proved experimentally for monolayers of this isomer. As a consequence, above a certain surface concentration and similarly to the effect of surfaces treated with surfactants, the *cis*-isomer of 4,4′-azo dye triggers an alignment transition from planar to homeotropic.

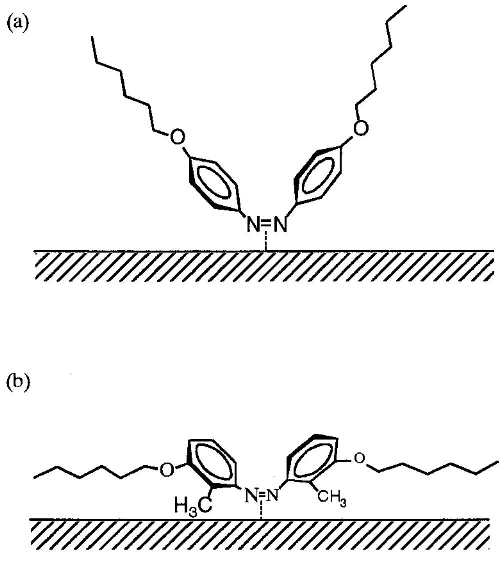

Figure 7. Schematic representation of the anchoring of the *cis*-isomers of (*a*) the 4,4′-azo and (*b*) the 3,3′-azo dyes to the solid surface.

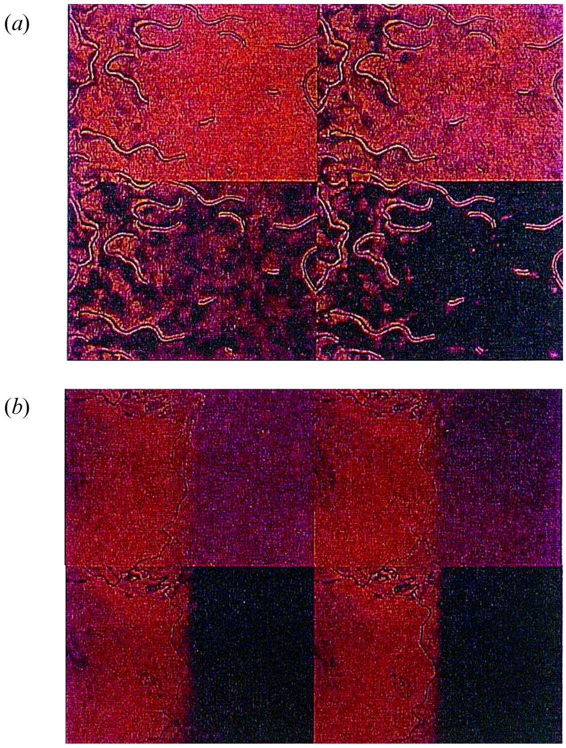

Figure 8. Photomicrographs of the light-induced transition from random planar to uniform planar alignment (in-plane anchoring transition) in the (*a*) 3,3′-azo and (*b*) 4,4′-azo dye mixtures after illumination with linearly polarized UV light of intensity of 0.5 mW cm^{-2} for 15 min and 1 min, respectively. The four sections in each picture correspond to 0, 15, 30 and 45 degree rotations of the cell optic axis with respect to one of the polarizers, respectively, reading from left top to right bottom of the picture.

Finally, in-plane reorientation of the liquid crystal molecules, i.e. an anchoring transition from random planar to uniform planar, took place in both mixtures on illumination with linearly polarized UV light (figure 8). A more detailed report on the in-plane reorientation of such nematic mixtures doped with 3,3′- and 4,4′-azo dyes will be published elsewhere [12]. Here, it should simply be mentioned that the required energy of illumination for completing this kind of anchoring transition differs in the two cases.

In the absence of external electric or magnetic fields, the solid surface plays a vital role in the alignment of liquid crystal molecules, and therefore the anchoring conditions at the surface are very important. In our case, these conditions undergo changes under light illumination, due to the adsorption of the *cis*-isomer of the dye molecules. On illuminating the samples with linearly polarized UV light, the axial selective light adsorption of the dye molecules gives the preferred direction of the their alignment on the surface, thus triggering the anchoring transition from random planar to uniform planar.

4. Conclusions

This study of the anchoring behaviour of guest–host liquid crystal mixtures, containing 3,3′- and 4,4′-azo dyes was carried out with the aim of evaluating the validity of a model previously proposed by us for a light-induced anchoring transition of an azobenzene nematic. The comparison between the dyes demonstrated unambiguously the key importance of the bent *cis*-isomeric form for the occurrence of the planar to homeotropic anchoring transition induced by light, so supporting the main argument of the model. Moreover, the higher polarity of the *cis*-isomer compared with the *trans*-isomer explains how the modification of the surface anchoring conditions, resulting in the transition from planar to homeotropic alignment (out-of-plane anchoring transition), takes place in the case of the 4,4′-azo dye under light illumination, thus confirming the second important argument of the model. To conclude, the comparison between the 3,3′- and 4,4′-azo dyes reveals the relations between photoisomerization behaviour and anchoring transitions and confirms the model for light-induced anchoring transitions proposed in [5].

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