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Light-induced anchoring transition in a 4,4′-disubstituted azobenzene nematic liquid crystal

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The behaviour of a liquid crystalline azobenzene material possessing a nematic phase was studied under UV illumination. It was found that a uniformly aligned planar sample of the azobenzene undergoes a reversible orientation transition to homeotropic; this can be interpreted as an anchoring transition caused by the photo-isomerization of the azobenzene moiety in the molecular structure of the nematogen. A simple model taking into account the changes in the molecular shape, as well as the magnitude of the molecular net dipole moment, and the changes in the surface density of the *cis*-isomers with UV exposure time is proposed to explain the light-induced anchoring transition in the azobenzene nematic.

1. Introduction

The phenomena relevant to anchoring transitions in liquid crystals attract the interest of scientists and engineers because such phenomena can be an important source of information about the liquid crystal–solid surface interactions and also due to their large potential for applications. Recently, anchoring transitions caused by various external factors such as temperature [1–3], light [4], electric field [5] and material flow [6] have been reported. Among them, the photo-induced anchoring transition from homeotropic to planar, as well as the photo-induced in-plane reorientation of the preferred direction of liquid crystal alignment [7] are of particular interest since they offer the possibility of light-controlled alignment.

In certain organic materials, which might exhibit liquid crystalline phases, reversible transformations between different isomers can be induced by absorption of light [8]. In some of these materials, *trans*–*cis*-photoisomerization results in a drastic change of the molecular shape and thus also of the distribution of permanent dipole moments in the molecular structure [9]. Such photo-induced alterations of the molecular shape and molecular net dipole moment lead also to substantial changes of almost all parameters characterizing the liquid crystalline material; these include, flexoelectric coefficients [9], cholesteric pitch [10], or spontaneous polarization in ferroelectric liquid crystals [11]. Furthermore, as a consequence of the photo-isomerization, the liquid crystalline phase may completely disappear and be replaced by the isotropic phase when the *cis*-isomer concentration exceeds a certain limit.

In this paper, we describe a phenomenon taking place in a 4,4′-disubstituted azobenzene nematic liquid crystal upon UV illumination, which can be described as a light-induced anchoring transition from planar to homeotropic. This photo-induced anchoring transition is just the opposite to the one already reported in azobenzene derivatives [4].

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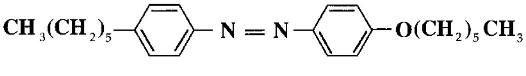
2. Experiment and results

In the experiment, a cell of conventional sandwich type consisting of two parallel glass plates was used. The inner cell surfaces were covered by a SiO_x aligning layer deposited at normal incidence and unidirectionally rubbed. Such an aligning layer, as is well known, results in a uniform planar alignment of most liquid crystals. The cell gap was fixed by evaporated SiO_2 spacers to be about 2 µm. The liquid crystal under study was the photosensitive material 4-hexyloxy-4′-hexylazobenzene with the structural formula depicted in figure 1.

This mesogen exhibits a nematic phase in the temperature range 27–69°C and has a positive dielectric anisotropy ($\Delta\varepsilon > 0$). The liquid crystal was introduced into the cell gap in the isotropic phase by capillary forces. The cell was inserted in a Mettler F-52 hot stage. The optical studies were performed by means of a Nikon OPTIPHOT2-POL polarizing microscope operated with crossed polarizers. The microscope was equipped with a Sony Hyper model HAD SSC-DC38P digital video camera connected to a computer for direct image processing and storage, which made it possible to take pictures of the sample over different time intervals and store them. During the experiments, the cell was protected from the light of the microscope lamp by a yellow light filter. The liquid crystal layer, after cooling from isotropic phase, adopted a uniform planar alignment with the preferred easy direction lying along the rubbing direction of the SiO_x layer. Then, the sample was oriented between the crossed polarizers with its optic axis at 45° with respect to the transmission axis of one of them. In this position of the cell, the intensity of light transmitted through the cell and the crossed polarizers has a maximum value. The cell was subjected to UV light supplied by UV-curing unit (Teklite) with an intensity of $70\,\mathrm{mW\,cm^{-2}}$ at the wavelength $\lambda = 365\,\mathrm{nm}$. During the illumination, one part of the sample was protected from the UV light. The nematic in the illuminated area was found to undergo a transition from planar to homeotropic alignment. The UV illumination dose required for the transition was found to be dependent on the temperature of the sample. The higher the temperature the lower the dose. This transition, which straightforwardly has to be interpreted as an anchoring transition, is illustrated in figure 2. The red part of the picture is the UV light protected part of the sample, where the alignment of the liquid crystal molecules remains the same as before irradiation, i.e. planar. The black area represents the UV illuminated part of the cell where the liquid crystal molecules are aligned homeotropically after the anchoring transition has taken place. It was confirmed by application of mechanical pressure to the cell and by conoscopy that the material in the UV illuminated part of the cell exhibited birefringence, i.e. it was still in the nematic phase, and the alignment of the molecules was homeotropic. After the UV light was turned off, the homeotropic alignment relaxed to the initial planar alignment with a time constant depending on temperature (being about 2 min at a temperature 10°C below the clearing point of the nematic). The UV exposure time necessary to obtain the anchoring transition was found to depend on the sample history, i.e. whether the sample had been illuminated by UV light before and the length of time since the last illumination, because a certain time is necessary for complete recovery of the thermodynamic equilibrium of *trans*- and *cis*-isomers.



Cr 27°C N 69°C

Figure 1. Structure and phase sequence of the 4,4′-disubstituted azobenzene nematic liquid crystal.

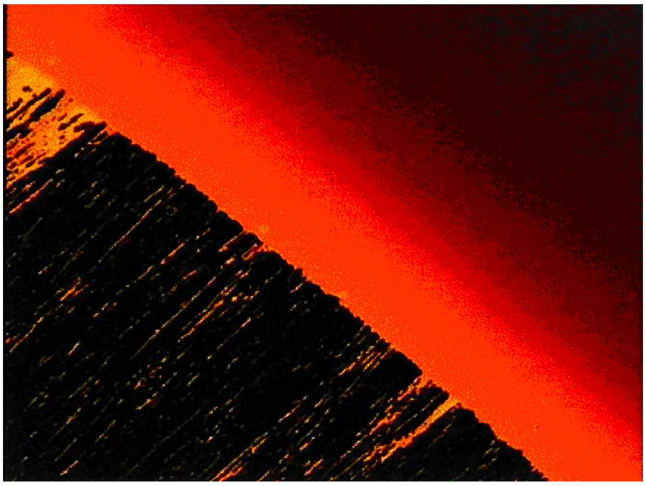


Figure 2. Photograph of cell filled with the 4,4′-disubstituted azobenzene nematic liquid crystal after UV illumination. The cell is inserted between crossed polarizers with the optic axis at 45° with respect to the transmission direction of one of the polarizers. The red part of the photograph represents the light protected area of the cell, whereas the black part is the illuminated area. The alignment of the illuminated area was confirmed by conoscopy to be homeotropic.

3. Discussion

Since the liquid crystal under study contains an azobenzene moiety with the linkage −N=N− as a photosensitive chromophore (see figure 1), the liquid crystal molecules, upon illumination with UV light, undergo a *trans–cis*-isomerization which is schematically illustrated in figure 3. In order to describe the light-induced

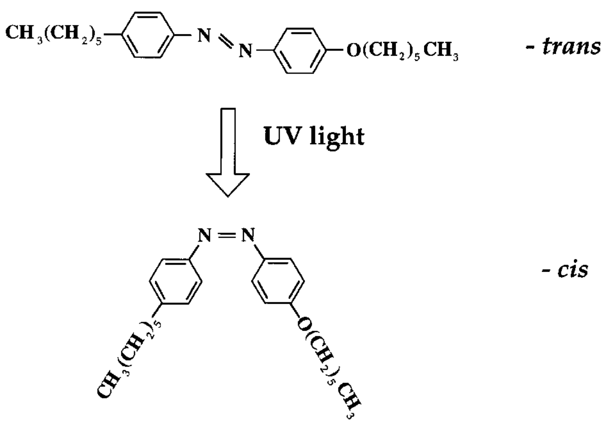


Figure 3. Schematic representation of *trans*- to *cis*-photo-isomerization of the 4,4′-disubstituted azobenzene nematic liquid crystal.

anchoring transition, it is important to know what kinds of process take place in the liquid crystal volume and at the solid–liquid crystal interface, in particular, during illumination with UV light. There are several factors that can be considered very important for this anchoring transition.

With increasing UV exposure time the concentration of the *cis*-isomer increases. As has been reported in [9], the photo-isomerization process results in changes of the molecular shape and also of both the magnitude and the orientation of the molecular net dipole moment: the molecules in their *cis*-form possess a bent shape and a larger transverse net dipole moment. Thus, the *cis*-isomers appear to be of higher polarity than the *trans*-isomers and therefore they will be more strongly attracted by the cell surfaces through dipole–dipole interactions. As a consequence, on increasing the exposure time, the surface density of *cis*-isomer will increase faster at the expense of the *trans*-isomer than it will in the volume or bulk of the sample.

The orientation of *trans*- and *cis*-isomers depends not only on dipole–dipole interactions, but also on the steric interactions among all the molecules. The antiparallel orientation of the net dipole moments imposed by dipole–dipole interactions does not interfere with the uniform planar orientation of the *trans*-isomer imposed by the steric interactions [12, 13]. However, this is certainly not the case with the *cis*-isomer, since the antiparallel orientation of the net dipole moments is hindered by the steric interactions. It is more likely that only the oxygen-containing half of the bent-shaped *cis*-isomer will be kept at a small tilt with respect to the solid surface, whereas the other part (the alkylphenyl group) will point outwards from the substrate and be almost normal to it (see figure 4). Thus, the net dipole moments of the *cis*-isomeric molecules will be oriented almost parallel to each other. Moreover, the solid surfaces, such as the SiO_x aligning layer, possess a certain polarity that may favour such a polar order of the *cis*-isomer.

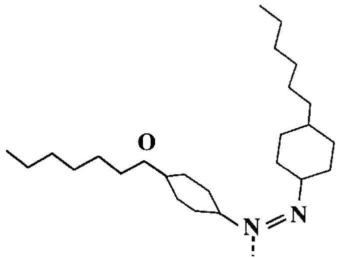


Figure 4. Schematic illustration of the position of a single *cis*-isomeric molecule anchored to the substrate surface.

The surface–liquid crystal interactions also play an important role in the light-induced anchoring transition. As is well known, the anchoring of liquid crystal molecules on a solid surface depends on the magnitude of the azimuthal (W_φ) and polar (W_θ) energies. In most cases $W_\varphi \gg W_\theta$ which means, it is more energetically favourable if the liquid crystal molecules anchored on the solid surface, bend outwards, away from the surface plane when undergoing *trans*- to *cis*-photo-isomerization. Consequently, dipole–dipole, van der Waals and steric interactions, together with hydrogen bonding, are responsible for the actual alignment of *cis*-isomeric molecules in contact with the solid substrate. Up to a certain surface density of the *cis*-isomer, the planar anchoring still remains unchanged even though the anchoring strength does change with the UV illumination [14]. Then, similarly to the alignment effect of surfactants [15], the liquid crystal orientation in the cell changes from planar to homeotropic when the surface density of *cis*-isomers exceeds a certain threshold value. The light-induced anchoring transition is schematically illustrated in figure 5. Due to the incompatibility of the *cis*-isomer with the liquid crystalline order, however, a photo-induced transition from nematic to isotropic phase takes place in the bulk if the sample has been exposed for a long enough time to UV light, i.e. when a certain level of volume concentration of *cis*-isomer is reached. In our case, the critical value of the *cis*-isomer surface density, in order to obtain a light-induced anchoring transition, is reached before the volume concentration becomes critical and causes the nematic–isotropic transition.

The light-induced homeotropic alignment turns out to be metastable with a life time depending on the temperature of the sample. On switching off the UV light, the reverse *cis*- to *trans*-isomerization process takes place. With the decay of the *cis*-surface density, the

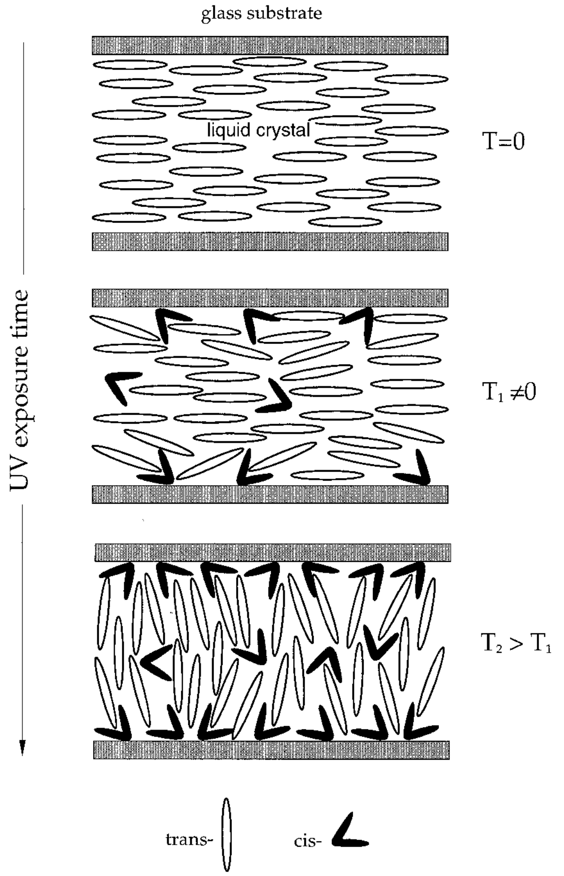


Figure 5. Schematic illustration of the light-induced anchoring transition in the 4,4′-disubstituted azobenzene nematic liquid crystal from planar to homeotropic.

reverse anchoring transition from homeotropic to planar occurs. Finally, the equilibrium of *trans*- and *cis*-isomers is restored.

The question which naturally arises is whether the planar to homeotropic transition in the azobenzene nematic liquid crystal is due to the decrease of the scalar order parameter S during the *trans–cis*-photo-isomerization process. As known, the anchoring strength W depends on S [1]. However, no anchoring transition from planar to homeotropic alignment occurred on heating the azobenzene nematic liquid crystal up to the isotropic phase, i.e. on changing the scalar order parameter of the nematic by temperature. Obviously, changes in S are not alone sufficient for obtaining such an anchoring transition. A certain change in the integrated surface anchoring properties is required as well. During this study, changes in the anchoring strength under UV illumination have been found and the results will be published elsewhere. The changes in the molecular shape prove to be of vital importance for the light-induced anchoring transition from planar to homeotropic alignment [16].

4. Conclusion

A reversible light-induced anchoring transition from planar to homeotropic was found to take place in 4,4′-disubstituted azobenzene nematic liquid crystal upon UV illumination. The combination of the bent shape and stronger net dipole moment of the *cis*-isomer plays a vital role in this phenomenon. The decrease in scalar order parameter due to photo-isomerization could not be considered as the origin of the observed anchoring transition. On the contrary, it seems to compete against it. Instead, the surface density of *cis*-isomeric molecules and their average orientation with respect to the normal to the supporting solid substrates appear to be of major importance. The anchoring transition depends on the UV exposure time, since a critical surface concentration of *cis*-isomer has to be reached in order to trigger the transition. The required exposure time for the anchoring transition to occur depends also on the history of the sample, i.e. whether it has been illuminated previously and the length of time that has passed since the last exposure. The light-induced state is metastable and relaxes to the planar configuration during a certain interval of time when the UV light is switched off. The present study demonstrates a possible way of changing the liquid crystal surface anchoring by illumination with UV light. This method might be useful for a number of implementations.

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