Conoscopic evidence of the UV light-induced flexoelectric effect in homeotropic layers of nematic liquid crystal doped with azobenzene derivatives

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Abstract. A digitalized version of the standard method of conoscoppy was employed to register the bend deformation of molecular orientation in homeotropic nematic layers caused by an in-plane applied DC electric field, and influenced by UV light illumination. Two guest-host systems prepared by mixing of a nematic liquid crystal and an azobenzene-containing photochromic liquid crystalline material featuring a longitudinal molecular asymmetry, were studied. Upon continuous UV irradiation, a photo-isomerization of the photochromic molecules occurs resulting in an enhanced flexoelectric response of the guest-host mixtures. The dependence of the photoflexoeffect on the field strength and UV light intensity was also examined.

1.  Introduction

Flexoelectricity signifies macroscopic spontaneous polarization developed in orientationally deformed liquid crystals (LCs). It was first hypothesized in 1969 [1] for nematics with non-centrosymmetric wedge-like (or banana-like) dipolar molecules, under splay (or bend) deformation. As later established [2], quadrupole asymmetry of mesogenic molecules also leads to flexopolarization through curvature strains, making the effect universal for all LCs. In the inverse flexoeffect, curvature stresses are induced or modified by an external electric field. The flexoelectric deformations strongly depend on the boundary conditions. Of great importance are the weak anchoring and surface polarization within a few nanometers of the LC-glass interface. An interesting kind of converse flexoeffect is the flexoelectric bending in a homeotropic nematic layer. This effect takes place when a homeotropic layer is subjected to an electric field orthogonal to the nematic director [3].

Photoflexoelectric effects in photosensitive LCs and other soft materials are also known [4-6]. In particular, UV light-induced change of flexoelectric deformations has been reported for bulk thermotropic LC materials [6] and for guest-host dye-nematic mixtures [7,8]. Theory was developed for analysis of flexoelectricity in this case [8].

Conoscopy is a convenient and powerful optical technique to verify homeotropic anchoring and determine the bending of the director field in homeotropic nematic LC structures. Recently this method was successfully utilized in studying mixtures of azo dyes and LCs [9-11]. Moreover,
photoinduced modification by photo-isomerization can be easily distinguished by this method. Here we report experimental results on UV light-induced photoflexoelectric effect in homeotropic nematic layer subjected to an electric field orthogonal to the director. The effect was induced by UV light illumination at 365 nm and studied by conoscopy. The influence of the magnitude of both the in-plane applied DC electric field and the intensity of the irradiated UV light on the photoflexo-response of two guest-host mixtures, was examined.

2. Experimental
Mixtures composed of the nematic LC 4-butyl-cyclohexane carboxylic acid 4-pentyloxy-phenyl ester (CM80 for short) and the photochromic azobenzene derivatives, 4-(4'-ethoxyphenylazo)phenyl hexanoate and 4-hexyloxybenzoloxo-4'-cyanoazobenzene, denoted hereafter as EPH and UI-147, respectively, were the subject of the present study. The chemical structures of these compounds are given in figure 1. The substances were synthesized in the Centre of Liquid Crystal Research in Bangalore, India. They were specially chosen to realize a high degree of photosensitivity as well as photoflexoelectricity caused by photo-isomerization of the azobenzene dye dopants. The LC CM80 was used as a host matrix since the compound is not UV sensitive, and exhibits negative dielectric anisotropy. The two photochromic azobenzene liquid crystalline compounds were selected considering their longitudinal molecular asymmetry. As reported elsewhere [6], this feature is essential for the flexoelectric properties of the guest-host systems studied here.

Both azobenzene dyes (guests) were well soluble in the CM80 matrix (host). The mixtures were prepared at a concentration of the azobenzene guest equal to 1 wt.% in the LC CM80. The sample cell gap was fixed with 100 μm thick stainless steel spacers, also serving as electrodes. The distance between the electrodes was 2 mm. The inside surfaces of the glass plates of the cells were covered with a monolayer of silane to orient the liquid crystalline molecules homeotropically. For this purpose, a 0.032 % solution of ODS-E silane (Aldrich) in distilled water was used. By capillarity, the cells were filled with the mixtures in their isotropic phase. After filling, the samples were cooled slowly to the nematic phase to achieve a good alignment, the quality of which was checked by using a polarizing microscope (Leitz DMRXP).
To induce photoisomerization, the samples were irradiated with non-polarized UV light by using the 365 nm line of a UV spot light source (Hamamatsu LC5 type L8333-01) equipped with a quartz light guide. The distance between the output end of the light guide and the cell was 25 mm. The power of the UV light incident on the cell was measured by Hamamatsu C6080-03 UV power meter positioned at the irradiated spot in the place of the sample. The reduced (70% at $\lambda = 365$ nm) transmission of the glass plates used for making the cells, was taken into account to arrive at the actual value of the UV light intensity (power density) absorbed by the nematic layer. A schematic diagram of the experimental setup is presented in figure 2.

For the conoscopy studies an in-plane (horizontal in the geometry shown in figure 2) electric field was applied through the in-plane electrodes to the nematic layer kept between two crossed polarizers. The electric field was directed at 45° to the polarizers. DC electric field was employed for static flexoelectric measurements. The applied DC voltage from a Keithley Electrometer (Model 6517A) created a static bend deformation that is further influenced by UV illumination.

Our digitalized version of conoscopy operates as follows: The conoscopic images of the LC azo-dye mixtures were acquired by a digital CCD camera (Optronics DEI-750D CE Digital Output Model S60675 PAL) with a resolution of 752 (H) x 582 (V) picture elements. The pictures were taken varying the voltage in the range 20 V – 80 V, and the intensity of UV light from 1.5 mW/cm² to 2.25 mW/cm². By means of a graphical software (Image Tool for Windows, University of Texas Health Science Center), the intensity profiles across images were obtained in a direction normal to the electric field applied. In this case, both initial and final coordinates of the segment through the conoscopic isogyres were kept constant. The separation between the isogyres was determined within an experimental error of ± 1 pixel. The experiments were carried out at room temperature (25 °C).

3. Results and discussion

Conoscopy is essentially an optical method that maps various directions through the LC layer by corresponding points of the conoscopic image. It employs an observation in strongly convergent light of the condenser, by using the microscopic objective lens, and a short focal length Bertrand lens. The conoscopic figure depends on the LC orientation with respect to the microscope stage. A Maltese extinction cross is commonly observed for uniaxial nematics oriented perpendicular to the stage. In such an orientation, a flexoelectric bend deformation [3] developed in the nematic layer under electric field applied in-plane to the layer, can induce a second macroscopic optical axis. As a result, a splitting of the extinction cross into two isogyres takes place. The changes in isogyres’ separation induced by variation in director field bending owing to DC electric field applied can be measured as a function of the magnitude $E$ of this electric field.

![Conoscopic images illustrating the effect of flexoelectric bending in a homeotropic layer: (a) without electric field; (b) the layer is subjected to an electric field $E$ orthogonal to the director; (c) the intensity profile measured along the dashed line in picture (b).](image-url)
Under orthoscopic illumination (parallel beam), in the initial field-off state the light is extinguished between crossed polarizers $P \perp A$ at all angles of rotation of the samples and in the convergent beam optics of conoscopy a uniaxial cross is displayed (figure 3(a)). Applying a small in-plane DC field $E$ and between diagonally crossed polarizers $P(45^\circ)/A(135^\circ)$, a uniform birefringence with maximum transmission is observed. Correspondingly, the conosscopic observation (figure 3(b)) shows a splitting of the isogyres ($\Delta$) that is a measure of the effect of flexoelectric bending. As an example, figure 3(c) presents a graph of the intensity profile measured in this case.

Figure 4 reports conososcopic interference images of homeotropic nematic layers of the two examined mixtures subjected to DC electric field and UV light illumination. The splitting of the extinction crosses due to variation of the flexoelectric bending of the nematic layer with the applied electric field, is clearly seen in the pictures. It should be noted that no hydrodynamic motion is seen up to 100 V (the maximum voltage applied).

![Figure 4](image)

Figure 4. Conoscopic images of the mixtures of CM80 with 1 wt.% EPH (a,b) and CM80 with 1 wt.% UI-147 (c,d) upon increasing electric field: (a,c) no UV light illumination; (b,d) upon UV light ($\lambda = 365$ nm) with intensity 1.9 mW/cm².

Figure 5 displays, for the two mixtures, the separation $\Delta$ between the two isogyres as obtained from the intensity profiles measured from micrographs taken in a sequence varying the applied voltage of the electric field. It is seen that $\Delta$ increases (progressive splitting of the extinction cross) upon voltage increase. This is in accordance with the theory of direct flexoelectric effect [12]. According to [3], for weak anchoring the produced curvature (the first derivative of electric field-dependent angle $\theta$ of the nematic director toward $Z$) is described by:
where $e_{3z}$ is the bend flexoelectric coefficient, $m_p$ is the surface polarization and $K_{33}$ is the bend elastic constant of the nematic. In the case of identical anchoring at both boundaries of the nematic layer, this expression implies that the curvature is uniform bend deformation proportional to $E$. As a result, the obtained bend deformation of the molecular director field produces a macroscopic optical axis in the samples along $E$. Stronger the field, more pronounced will be the optical axis. Thus, our observations are consistent with analogous conoscopy investigation of piled uniaxial crystal [13,14].

In angular units, the splitting $\Delta$ should approximate (be less or equal to) the difference of the two boundary angles, i.e. the quantity given by Eq. (1) multiplied by the layer thickness. This difference is a measure of the field-induced birefringence of the layer. If we imagine the layer as splitted in two horizontal parts which are homogeneously tilted in different directions, the above mentioned difference equals the angle between the optical axes of the two parts. Therefore, the isogyres’ separation $\Delta$ should be linearly related to $E$. Indeed, such a behavior is present for the experimental data in figure 5. Also, both dependencies have to include the zero point (more clearly seen in figure 5(a)).

Figure 5. Separation of the isogyres ($\Delta$) for the mixtures of CM80 with 1 wt.% EPH (a) and CM80 with 1 wt.% UI-147 (b) as a function of the applied DC voltage, upon UV light illumination ($\lambda = 365$ nm) at three values of the light intensity.

By conoscopy, the photoresponse of the guest-host mixtures upon continuous UV irradiation can also be monitored. Data obtained for three values of the UV light intensity (figure 5) shows an increase in $\Delta$ with increasing UV light intensity up to 2.25 mW/cm$^2$. A saturation of the flexoelectric bending effect takes place at this UV light intensity. Even at higher UV light power density, the observed conoscopy figures are still symmetric. This in turn means that the samples are dielectrically stable. It is of importance to note that the mixtures have a negative dielectric anisotropy under considered experimental conditions. Regarding Eq. (1) the enhancement of the curvature of the photoinduced nematic bend deformation is related to a possible modification of the bend flexoeffect $e_{3z}$ or surface polarization $m_p$. Analysis of this effect is planned as a future work.
The conoscopic response of the two mixtures clearly shows an enhancement of flexoelectric deformation by UV illumination, i.e. the presence of a photoflexoeffect, obviously due to photoisomerization of the guest molecules of azobenzene dyes. Under UV illumination, the photochromic subsystem in the examined guest-host mixtures undergo a transformation from \textit{trans} conformers (rod-like forms) to \textit{cis} forms having a pronounced banana shape. Owing to this geometry change, and thereby the orientation of the guest molecules within the host matrix of LC CM80, the bend flexocoefficient $e_{3x}$ of the guest-host mixtures is also modified. This photo-modification is directly reflected in the conoscopic response of the samples. The difference in the magnitude of the splitting observed for the two mixtures could be ascribed to the different efficiency of the guest dye compounds to produce conformers.

4. Conclusion
Homeotropically oriented samples of two guest-host liquid crystalline materials being mixtures of a small content of photochromic azobenzene dye in a photoinactive nematic were examined by digital conoscopery upon application of a DC electric field parallel to the layers in the absence of, and under UV light illumination conditions. The results obtained by this optical technique give evidence for a UV light-induced flexo-electrical effect in the mixtures driven by \textit{trans–cis} photoisomerization of the azobenzene dopant possessing asymmetric molecular structure.

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