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IN-SITU X-RAY MEASUREMENTS OF LIGHT-CONTROLLED LAYER SPACING IN A SMECTIC-A LIQUID CRYSTAL

TATIANA A. KRENTSEL (LOBKO), OLEG D. LAVRENTOVICH, and SATYENDRA KUMAR

Department of Physics and Liquid Crystal Institute, Kent State University,
Kent, Ohio 44242, USA

Abstract The smectic-A phase of octylcyanobiphenyl (8CB) doped with a photosensitive azo-compound has been reported to exhibit structural changes and formation of periodic layers distortions upon exposure to low-level radiation. It is caused by changes in the smectic layer spacing triggered by light-induced molecular photoisomerization of the dopant azocompound. Our *in-situ* high-resolution x-ray scattering study reveals that the light irradiation controls the smectic spacing. The exposure to UV light increases the layer spacing by as much as 0.5% (0.155Å for the studied mixture of 8CB and diheptylazobenzene 7AB at $T = 24.00^oC$). Irradiation by He-Ne laser at 633 nm causes the contraction of the layers.

INTRODUCTION

The dilation of homeotropically aligned smectic-A (SmA) liquid crystal (LC) in the direction perpendicular to the layers causes undulations of the layers as a compromise between the requirement of constant layer thickness and the tendency of the system to fill the extra space (so called Helfrich-Hurault effect) produced by the dilation. At higher stresses the undulations transform into strongly scattering texture of periodic parabolic focal conic domains (PFCD'c). In practice, this effect can be introduced in several ways[1]: by applying mechanical tension perpendicular to the cell with homeotropically aligned SmA (mechano-optic effect), by heating the cell with a high-power light beam which causes thermal expansion of LC followed by contraction after abrupt reduction in the light intensity (thermo-optic or Kahn effect[2]). Displays devices based on the thermo-optic effect have the premise of high resolution and good response time but the consumption of power is high.

Recently, a new method to generate the layers instabilities requiring low power was found[3]. It was shown that irradiation with a low-power ($< 10mW$) He-Ne laser

(633 nm) produces a periodic array of PFCD's in homeotropically aligned SmA doped with a photosensitive compound capable of photoisomerization. This texture could be erased by another beam with shorter wavelength (e.g. UV). It is believed that light-induced transformations of the photosensitive molecules determine the smectic layers spacing and thus is responsible for the layers instabilities.

In this paper, we report the results of our *in-situ* high-resolution x-ray scattering study of layer spacing and dynamics of layers contractions and dilations in a photosensitive SmA mixture. The results confirm that previously observed optical effects[3,5,6] were indeed caused by light-induced layers contraction and dilation: the formation of PFCD's under the red-light irradiation is caused by layers contraction, while the disappearance of the PFCD patterns under shorter wave-length UV light is caused by the expansion of layers.

EXPERIMENTAL TECHNIQUE AND MATERIALS

X-ray measurements were carried out using the CuK_α line on a Rigaku 18kW rotating anode source[4] with a pair of Ge(111) single crystals as monochromator and analyzer. The instrumental resolution was $\sim 4\times10^{-4}\mathring{A}^{-1}$ (half width at half maximum (HWHM)) in the longitudinal direction. Sample was placed between two 10 μm thick Mylar sheets, separated by 1.4 mm teflon o-ring, in a special holder and mounted on a Huber two-circle goniometer in an oven that had a temperature stability of $\pm 1\ mK$. Two permanent magnets placed inside the oven provided a field of 6.5 kG at the sample and aligned the LC during cooling from the N to SmA phase.

We investigated a binary mixture of 4 - octyl - 4'- cyanobiphenyl [8CB] $(Cr - 21.5^\circ C - SmA_d - 33.5^\circ C - N - 40.5^\circ C - I)$ and p, p' - diheptylazobenzene [7AB] $(Cr - 41.0^\circ C - N - 48.6^\circ C - I)$. Since previous optical experiments[3,5,6] were done on a mixture of 9.6 mol% 7AB in 8CB [M9.6] $(< 24^\circ C - SmA - 37.8^\circ C - N - 43^\circ C - I)$, we used the same concentration. 8CB is a typical LC material, molecules of wich possess a strongly polar cyano group at one end (dipole moment[7] $\mu = 4.05D$), Fig.1a. It forms a partially bilayer smectic A_d phase with the layer thickness $d = 31.432\mathring{A}$ at room temperature $(T = 24.00^\circ C)$. d increases with increase in temperature. The compound 7AB is a derivative of azobenzene, Fig.1b. The presence of double nitrogen bonds makes it susceptible to trans-cis photoisomerization[8]. The dipole moment of trans isomer is zero. The cis isomer has a high dipole moment[7] $\mu = 3.0D$ directed along the symmetry axis of the bent molecule as shown. The lengths of the trans and cis isomers of 7AB with extended carbon tails are $\sim 29\AA$ and $\sim 17\AA$ respectively[5].

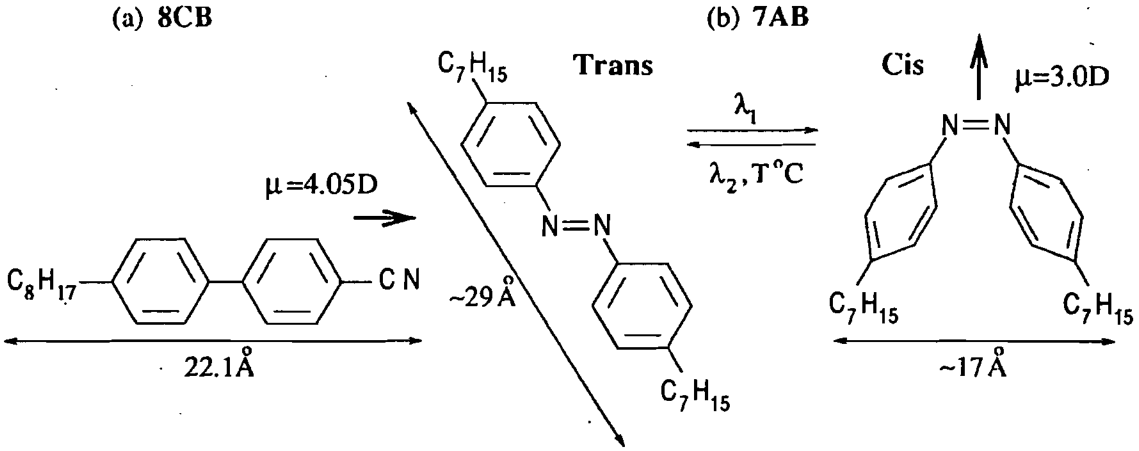

FIGURE 1 Molecular structure of the (a) 8CB and (b) 7AB.

The ground state of 7AB is the trans form as it is generally more stable (by about $50kJmol^{-1}$ in case of azobenzene) than the cis form without any external illumination. The photoisomerization occurs when 7AB molecules are electronically excited by UV irradiation. As shown for azobenzene by Zimmerman et al.[9], the concentration of cis isomers at photostationary state depends on the wavelength of light; it is relatively high, $\sim 40\%$ in the UV region and decreases drastically when the light wavelength increases, becoming 15% at 436 nm and 5% at 578 nm. When UV irradiation is turned off, cis isomers relax back to trans. This transformation can be accelerated by an increase in temperature or by exposure to light with longer wave length.

To investigate the dynamics of light-induced instabilities in the smectic phase, we measured the evolution with time of smectic layer spacing while irradiating the sample to non-polarized UV light ($\lambda = 366nm$) followed by relaxation with (a) no illumination or (b) exposure to unpolarized red light ($\lambda = 632.8nm$). All measurements were carried out in dark environment. The intensities of light sources were stable during the measurements.

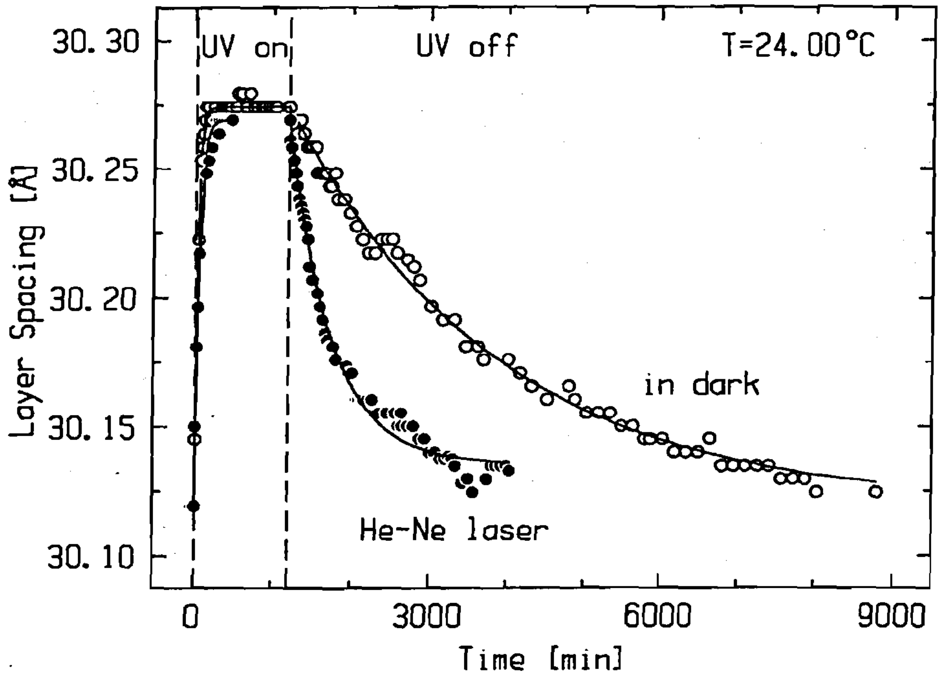

FIGURE 2 Evolution of the smectic layer thickness under UV illumination and consequent relaxation with UV off. Open circles: UV - no illumination; solid circles: UV - He-Ne laser.

RESULTS AND DISCUSSION

The time evolution of smectic layer spacing in sample M9.6 after UV radiation was turned on and following relaxation with UV off is shown at Fig.2. Experiments were carried out near room temperature, at $T = 24.00^{o}C$, stable to $\pm 1\ mK$. The layer spacing in the initial state was $d_0 = 30.119\mathring{A}$. It increased by $\Delta d = 0.155\mathring{A}$ after reaching equilibrium in $\sim 500\ min$. The characteristic rise time was calculated to be $\tau_{r1} = 33 \pm 3$ min. It was very sensitive to the intensity of UV beam, initial state of the sample, and varied slightly from experiment to experiment. After UV light was turned off, d immediately started to decrease. The relaxation was observed under two different conditions: in the dark with a characteristic decay time $\tau_{d1} = 2790 \pm 40$ min and under He-Ne illumination with $\tau_{d2} = 580 \pm 20$ min. The value τ_{d1} was consistent with the time reported by Sekkat at al[10] for relaxation in dark in a monolayer of azosilane molecules.

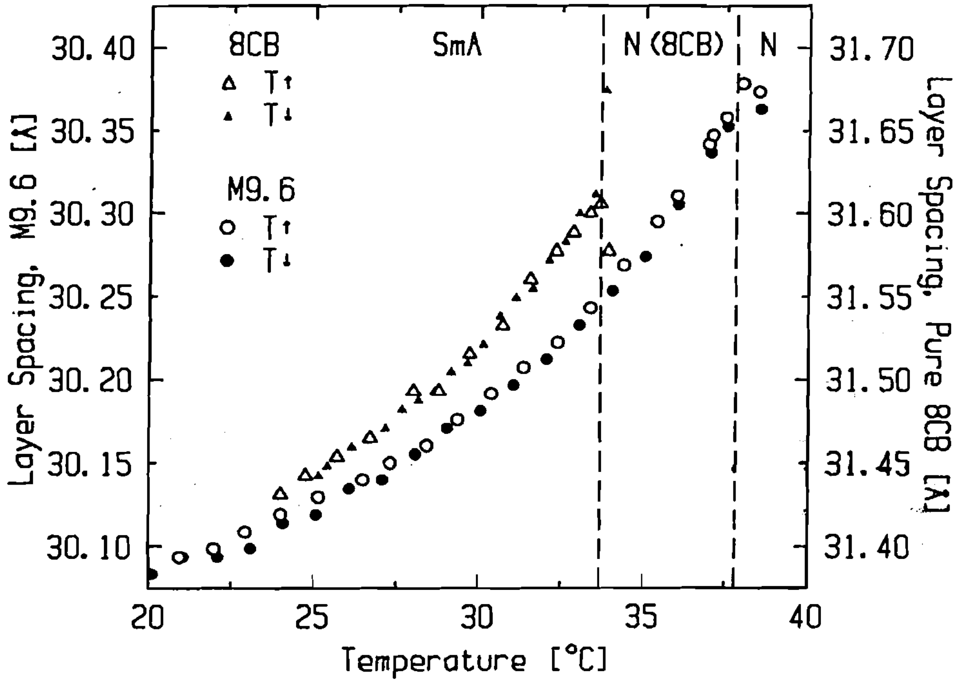

FIGURE 3 Temperature dependence of layer spacing in the M9.6 (left side) and pure 8CB (right side) for heating and cooling cycles.

As previously mentioned, the light illumination appears to have two possible effects on the sample: heating and molecular phototransformation. The temperature dependence of layer spacing d for the M9.6 and pure 8CB samples is shown at Fig.3. d-spacing for both substances increased slightly with temperature. From the similarity of two curves we conclude that layer spacing in the mixture was determined mainly by the temperature behavior of 8CB matrix. If the increase in layer spacing $\Delta d = 0.155 Å$ were caused by heating under a light beam, then the increase of the sample's temperature should be about $10^{\circ}C$, which is unlikely under the condition of good thermal stabilization.

The same experiment was conducted at $T = 35.30^{\circ}C$ (close to SmA-N phase transition, $T_{SmA-N} = 37.80^{\circ}C$) and similar behavior observed. Before UV illumination, the layer spacing was $d_0 = 30.295\AA$, and under UV exposure Δd was measured to be $0.235\AA$. The saturation value $d_s = 30.530\AA$ was in excess by as much as $0.178\AA$ of the maximum value $d_{max} = 30.352\AA$ of the SmA layer spacing for the mixture. The sample remained in the smectic phase at the all stages of the experiment. This again confirms that thermal effects, if any, were inconsequential and that the layer spacing was determined by molecular photo-transformations. The characteristic rise time was $\tau_{r3} = 73 \pm 2$ min. After UV irradiation was turned off, the system relaxed back with characteristic decay time $\tau_{rel3} = 660 \pm 20$ min. The experimentally observed fact that the contraction of layers was accelerated at higher temperature ($T = 35.30^{\circ}C$) and upon expouse to He-Ne irradiation (Fig.2) also pointed out that the mechanism of molecular phototransformations was primarily responsible for the phenomenon.

To check the direct heating effect at the pure 8CB matrix we irradiated it under similar conditions by UV light for 24 hours. No change in d was detected.

Now let us consider the possible mechanisms of dilation-contraction of the layers. UV exposure enhances the amount of short cis component in the system, increases the layer spacing. Red light, enriching the system with long component - trans isomers, decreases the d as discussed below. It is conceivable that, from sterical point of view, the bent cis-molecules could play the role of impurity in well organized smectic matrix and have a higher probability of being thermally distributed at the smectic layer interspace. It will result in an effective increase in the thickness of smectic layers. Simple calculations show that 10% of 7AB molecules is enough to convert to cis form and put them between layers to increase layer spacing by $0.1 - 0.2\AA$. Second possible mechanism based on the fact that the cis isomer has a dipole moment which could favor formation of dimers with 8CB molecules. The presence of such sterically asymmetric dimers may generate free volume inside the smectic layer. To fill this free space molecules of 8CB could distribute around the dimers in such a way that the thickness of the layer increases. Under the influence of He-Ne laser cis isomers are converted to trans, which are easily incorporated back into the smectic matrix causing a layer spacing decreas.

In summary, *in-situ* x-ray study of light-induced transformations in the mixture M9.6 shows that UV light increases smectic layer spacing by $0.155\mathring{A}$ at $T = 24.00^\circ C$. Illumination by He-Ne laser decreases d and accelerates the relaxation of the system when UV light is off. Evidently, the cause of changes in d is the photoisomerization of dopant molecules. Possible mechanisms for the increase in d are either the migration of cis-isomers into the interlayer regions or the formation of cis7AB-8CB dimers inside the smectic layers with subsequent displacement of neighboring 8CB molecules.

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