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Preliminary communication

Preliminary *in situ* X-ray diffraction measurements of UV-induced photomechanical effects in a mesogenic material

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The aim of this work was to determine by X-ray diffraction the nature of the UV-induced changes in the smectic C* organization of a calamitic liquid crystalline material containing the UV-sensitive azobenzene group in the rigid core moiety. As a result of the reversible *trans–cis*-isomerization, a decrease of all transition temperatures (1.1°C for the SmA–SmC* transition) was observed. In the SmC* phase, this corresponds to an increase in layer spacing (up to 0.5 Å); in the SmA phase, the detected increase in layer spacing was less than a tenth of this. The increase in layer spacing is interpreted in terms of molecules in the *cis*-configuration expelled from the smectic layers.

Ferroelectric liquid crystals have demonstrated exceptionally fast electro-optic switching times and are the basis of the newest generation of LC displays [1]. On illumination with light of suitable wavelength, the bulk properties of a liquid crystal matrix containing a small fraction of photosensitive moieties are seen to undergo isothermal and reversible modifications [2]. The microscopic structural changes which occur on the *trans-cis*-isomerization of the photochromic dopant or constituent group are amplified to create changes in the macroscopic characteristics of the material, such as birefringence, dichroism and spontaneous polarization [3–5].

The aim of this work was to determine the nature of the light-induced changes on the mesophase structure of a calamitic ferroelectric liquid crystal compound containing a UV-sensitive azo-benzene group in the rigid core moiety. The structural changes were studied at a microscopic level using X-ray diffraction (XRD). Our study is focused on the single component system shown below [6] (hereafter denoted as CH3-511):

This compound is stable with temperature and presents a UV absorption peak at $\lambda \approx 340\,\mathrm{nm}$ corresponding to the *trans-cis*-isomerization. We discuss the observed variation of the layer spacing during UV on–off cycles.

Powder XRD patterns were recorded as a function of time and temperature, in the presence or absence of UV irradiation, using the set-up schematically represented in figure 1. Samples were filled into 0.5 mm Lindemann glass capillaries and placed in a home-made oven controlled by an INSTEC unit (residual temperature fluctuation of $\sim \pm 0.02$°C). The X-ray patterns were obtained with an INEL position sensitive gas detector CPS 120 and with a linear $\mathrm{CuK}_{\alpha 1}$ beam produced by an XRG 2500 INEL generator and focused by a bent quartz monochromator.

A special experimental set-up was developed to make it possible to illuminate the sample with X-rays and UV

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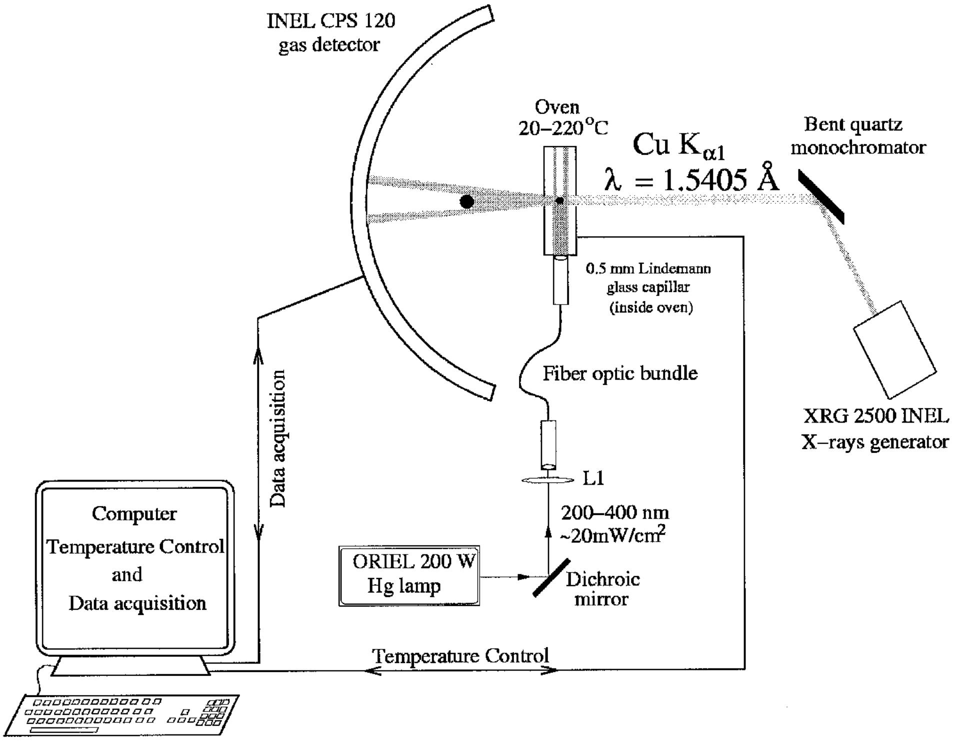

Figure 1. Experimental set-up.

at the same time, as shown schematically in figure 1. In particular, a second window was made in the oven for the UV light. The collimated UV beam was channelled via a fused silica fibre optic bundle from an ORIEL 200 W mercury arc lamp. The spectrum of the source was limited by a dichroic mirror to 200–400 nm and had an intensity maximum of ~20 mW cm^{-2} at 365 nm. This experimental set-up can be easily adapted to use different light wavelengths and can be used to perform similar studies with many different materials containing light sensitive chemical groups.

In the X-ray patterns obtained, only the 1st and 2nd order reflections of the lamellar stacking are visible in the small angle region, while the wide angle region contains the diffuse reflection corresponding to the lateral distances between the molecules. The layer spacing was determined by integration of the 1st order reflection. In figure 2 are presented some time dependent results for the layer spacing for several temperatures over the SmA–SmC* transition. At each temperature, the UV lamp was turned on and off every 10 min while an X-ray pattern was registered every 2 min. In the SmC* phase an increase of the layer spacing followed the UV-irradiation, a plateau being reached within a few minutes. After the UV was switched off, the initial layer spacing value was recovered within a similar period of time. No drifting of the 'on' and 'off' plateaux was observed for further UV cycles. The difference between the two layer spacing states increases with the UV intensity and decreases with temperature.

In figure 3 we present the temperature variation of the layer spacing and the corresponding full width half maximum (FWHM), for both the UV-on and UV-off states. Analysis of these variations shows that the increase in layer spacing and the decrease of FWHM follows the phase transition temperature shift associated with the presence of the *cis*-isomer mixed within the *trans*-isomer matrix, during the UV irradiation. As both isomers have very different geometries and moreover the *cis*-isomer does not favour the liquid crystalline organization, one should expect that the dispersion of a small quantity of the *cis*-species in the *trans*-matrix will decrease the transition temperatures [7]. In fact, in the UV intensity conditions for which figures 2 and 3 were obtained, we determined ~0.50°C and ~0.15°C temperature shifts for the SmA–SmC* and N–SmA transitions, respectively. It is important to note that a decrease was observed in the FWHM of the diffraction lines under illumination. If the sample had been subject to a heating effect, the layer spacing would have increased (since we are in the SmC phase) with the UV illumination time, and the value of the FWHM would have increased too with respect to the non-UV value (since there should be a shift of the corresponding peak). Therefore, these considerations indicate that there is no heating effect in the sample, and that the observed behaviour is due only to

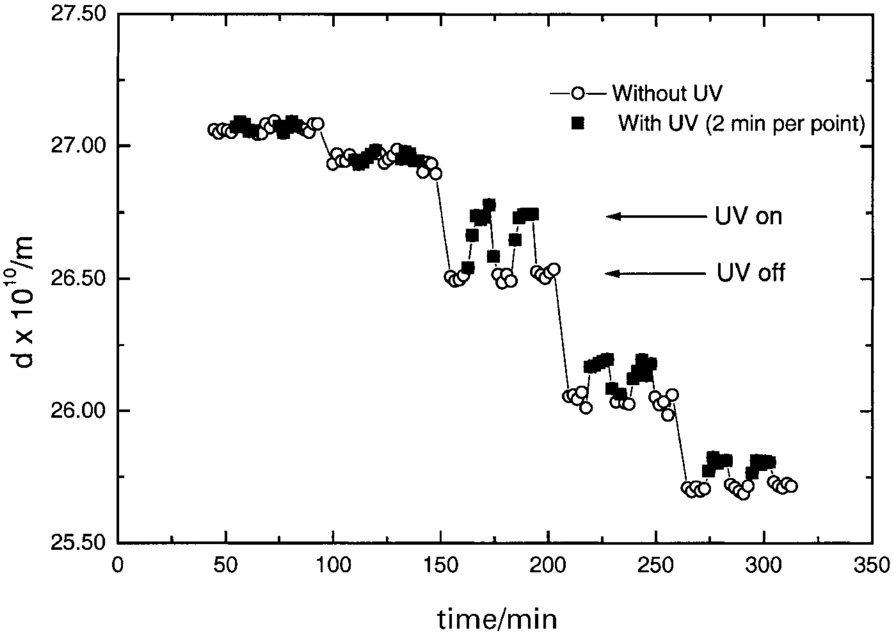

Figure 2. Layer spacing as a function of time, temperature and UV illumination. Each black square corresponds to a 2 min UV illumination. Note that the UV-on values (full squares) correspond to the UV-off values (open circles) shifted by ~0.5°C, due to illumination.

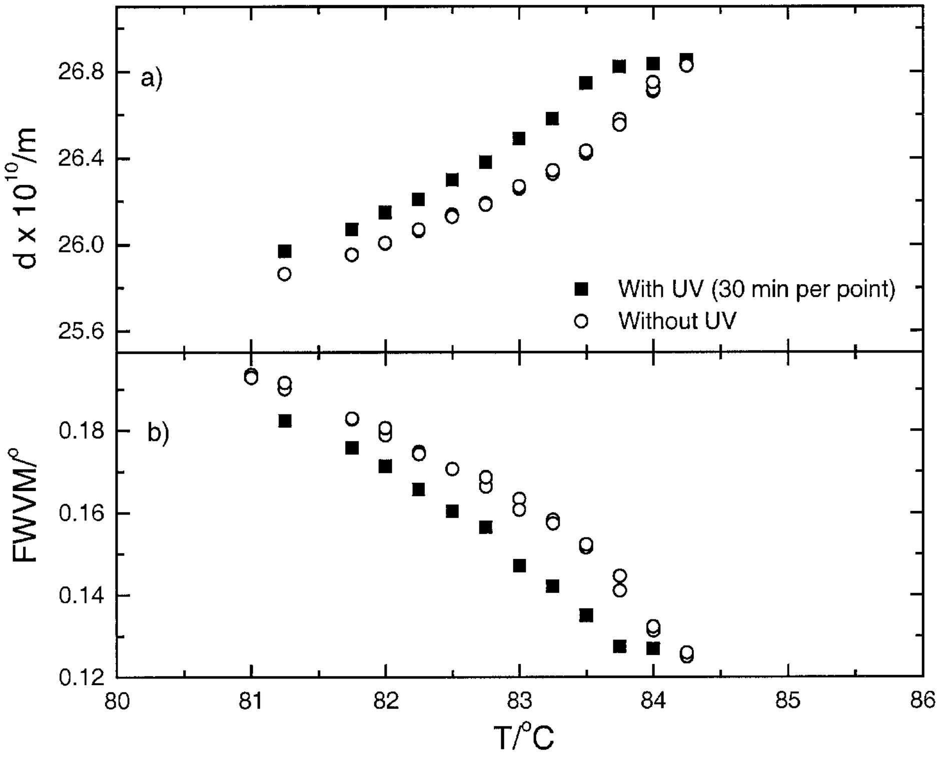

Figure 3. (*a*) Layer spacing as a function of temperature; (*b*) full width at half intensity. Each black square corresponds to a 30 min UV illumination.

UV illumination. Since the layer spacing and FWHM variations versus relative temperature to the SmA–SmC* transition ($T - T_{AC*}$) does not differ significantly in the UV-on and UV-off states, we can conclude that the mixture effect on the molecular packing, at local level, is very small with respect to the effect of loss of long range correlations within the smectic domains.

By using the largest UV intensity possible, besides increasing the temperature shift of the SmA–SmC* phase transition (~1.15°C), we could detect an increase of the layer spacing in the SmA phase less than a tenth of that observed in the SmC* phase (see figure 4). Consistent with molecular simulation studies [8], this small layer spacing increase (certainly masked in the SmC* phase)

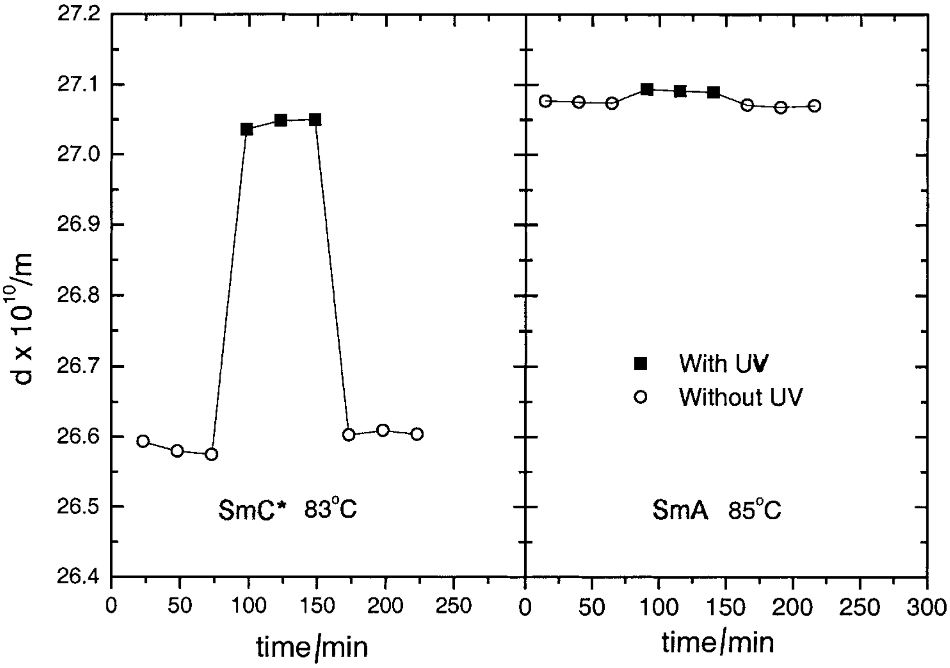

Figure 4. Layer spacing in the SmC* and SmA phases. Each black square corresponds to a 30 min UV illumination.

can be interpreted in terms of the microsegregation effect due to the different geometries of the *cis*- and *trans*-isomer rigid cores, the former isomer being expelled between the layers as proposed previously by Folks *et al.* [9]. In fact, as stated by these authors, it is difficult to imagine strongly bent *cis*-isomer molecules mixed with *trans*-isomers within the same smectic layers, without a change in the nature of the smectic phase. According to this model the expelled amount of *cis*-isomer would be less that 0.1%. However, this value should be considered as a minimum from the *cis*-isomer concentration, since it is not possible to determine now how many molecules having the *cis*-configuration stay within each smectic layer to contribute on the contrary to a decrease of the layer spacing. This very small effect can also be due to the relaxation mechanism mantaining the *cis*-isomer concentration at a very low percentage. Nevertheless, the relatively slow response of the system (a few minutes) may result from the diffusion time of the *cis*-species out from *trans*-rigid core matrix. Finally, because of the presumably small amount of *cis*-isomer expelled, this mechanism is completly reversible and there is no macroscopic phase separation.

In conclusion it should first be pointed out that the experimental set-up described here is able to detect very tiny *in situ* changes of the layer spacing when the liquid crystalline material is illuminated by UV light. Second, although the fact that the *cis–trans*-azo isomerization phenomenon is well known, with the experimental *in situ* XRD measurements reported in this work, it was possible to observe, for the first time to our knowledge, the direct influence of the isomerization effect on the layer spacing in the SmC* and SmA phases of a ferroelectric liquid crystal compound. The increase in the smectic layer spacings can be interpreted in terms of a microsegregation of the *cis*-isomers into the interlayers as a result of the very different geometries of the *trans*- and *cis*-isomers. However, the isomerization effects observed in the SmA phase are very small when compared with those observed in the SmC* for the UV intensity used; further work is needed in particular to validate such an interpretation and to study the influence of the UV intensity on these effects.

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