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Electroclinic effect near a smectic A–chiral smectic I transition

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The electroclinic effect in the S_A phase of (S) (4′-decyloxy-2′-hydroxybenzylidene)-4-amino(1-ethoxycarbonylethyl) cinnamate has been studied. The induced tilt angles have been measured as a function of temperature near the S_A–S_I^* transition at 87°C. The response of the material to different voltages and frequencies has been analysed by using two complementary optical techniques. At low A.C. probe fields the amplitude of the induced tilt shows a relaxational behaviour which can be described by a single relaxation time. The relaxation frequencies have been found to be linear in temperature near the transition, in a similar way to the S_A–S_C^* transition.

1. Introduction

Since Meyer et al. [1] established the existence of ferroelectric liquid crystals, a considerable experimental and theoretical effort has been made in order to clarify their interesting basic physical properties. On the other hand, and from the applications point of view, the small switching times and memory effects of thin samples, the so-called surface stabilized ferroelectric liquid crystals, make these compounds particularly promising as fast display devices [2]. Recently, the electroclinic effect in smectic A phases [3–5] and other orthogonal mesophases [6] containing chiral molecules has also attracted some attention as another alternative to the use of these materials in electro-optical modulators. This effect, first described by Garoff and Meyer [7] in homeotropically aligned cells of 4-*n*-decyloxybenzylidene-4′-amino-2-methyl butylcinnamate DOBAMBC, consists in the induction of a molecular tilt when the material is subjected to an external electric field parallel to the smectic planes. Although the magnitude of the induced tilt is not great enough for its practical use with moderate voltages in the compounds investigated so far, it permits, however, faster optical switching than the corresponding surface stabilized ferroelectric liquid crystal mode under the same conditions [3].

This work is concerned primarily with the investigation of the electroclinic effect in (*S*)-(4′-decyloxy-2′-hydroxy benzylidene)-4-amino (1-ethoxycarbonylethyl) cinnamate (DOHBAECEC). The chemical structure of this compound is shown in figure 1. Its synthesis has been described in [8], where a preliminary characterization (observation of textures and D.S.C. measurements) has also been reported. According to this work [8] the compound has the following phase sequence

$$C\ 64{\cdot}1°C\ S_I^*\ 87°C\ S_A\ 117{\cdot}9°C\ I$$

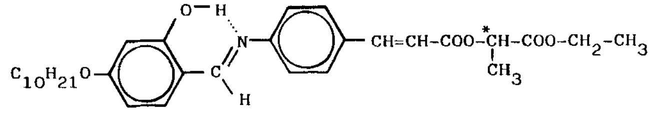

Figure 1. Chemical structure of DOHBAECEC.

with a spontaneous polarization in the S_I^* phase of the order of 100 nC/cm^2 [9]. The S_I^* phase was identified by its bubble texture, similar to that shown in [10]. X-ray measurements of this mesophase are now in progress.

In this paper we report measurements of the dependence of the induced tilt on the voltage and frequency of the exciting electric field. Over the complete S_A range the induced tilt has a relaxational behaviour, which is associated with fluctuations in the molecular tilt amplitude. The corresponding relaxation frequencies have been measured in the vicinity of the S_A–S_I^* transition, and show a temperature dependence similar to that found for other compounds with a S_A–S_C^* transition. Finally, the relaxation in the S_I^* phase is briefly examined.

2. Experimental

The sample was placed into a cell made of tin oxide coated glass plates. The cell thickness, 12 μm, was maintained without spacers simply by the use of glue at three edges. Both inner surfaces of the cell were coated with a thin film of nylon 6/6 as described in [11]. Only one plate was buffed unidirectionally in order to obtain an optimum alignment [12]. The sample was introduced in the isotropic phase by capillary action and cooled slowly (0·2°C/min) into the S_A phase. Alignment of the director was checked optically with a polarizing microscope. Fairly good orientation was achieved over the whole sample area ($\sim$ 1 cm^2). The cell was mounted in a Mettler FP82 hot stage for temperature control; the temperature stability was about 0·1°C. Two methods were used to measure the induced tilt angle θ. The experimental set-ups for both cases are shown in figures 2 (*a*) and (*b*).

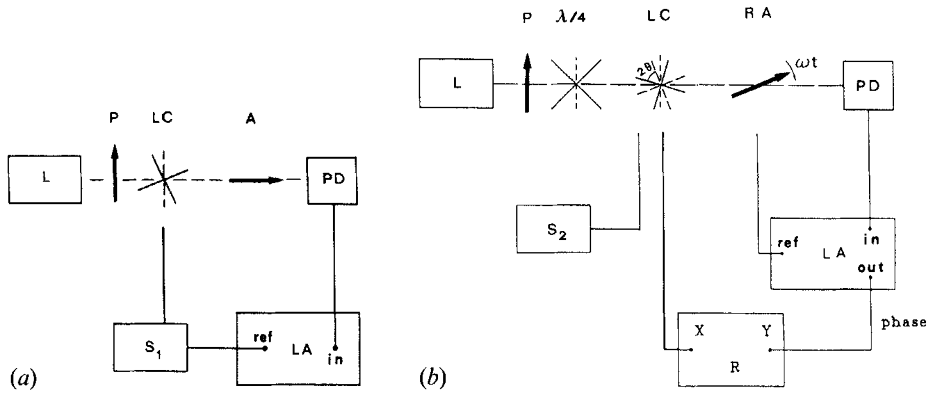

Figure 2. (*a*) Experimental set-up for measuring the frequency dependence of the induced tilt angle. (*b*) Block diagram of the arrangement for the absolute determination of the tilt angles. L, laser; P, polarizer; LC, homogeneously aligned liquid crystal sample; A, analyser; PD, photo-diode; $\lambda/4$, quarter wave plate: RA, rotating analyser; S_1, sine wave source; S_2, square wave source; LA, lock-in amplifier; R, XY recorder.

The frequency dependence of the tilt angle was measured through the light transmission of the sample between crossed polarizers. The sample was driven by a sinusoidal electric field and oriented in such a way that the smectic layer normal made an angle of 22·5° with one of the polarizers (see figure 2 (*a*)). Under these conditions the A.C. signal at the photodiode attains its maximum value and, if the induced tilt is small, the signal amplitude is directly proportional to θ, [3, 4]. In our experiment, the applied voltages were always below 1 V in order to ensure a linear response of the material. The corresponding induced tilt was about 0·1°, so that the linearity between the signal at the photodiode and θ is well justified.

The measurement of the temperature dependence of the electroclinic effect as well as the absolute determination of the tilt angles were achieved with the experimental equipment shown in figure 2 (*b*). This arrangement provides a direct and virtually continuous determination of the tilt angle as a function of temperature. It can only be used for measurements in essentially D.C. regimes (< 1 Hz). Nevertheless, as the material response in the range below 1 kHz is practically constant, the results obtained with this method allowed us to transform all the relative tilt angle data measured with the other technique into absolute units. The principle of operation (throughly described in [13]) is as follows. The polarizer and the quarter-wave plate, set at 45° to the polarizer, produce circularly polarized light which is incident on the sample. A low frequency square voltage (e.g. 0·1 Hz) is applied to the material, which forces its optical indicatrix to rotate back and forth by an angle 2θ. Under these conditions, the elliptically polarized light emerging from the sample has two states of polarization (which depend on the corresponding positive or negative values of the exciting voltage). These two polarization states are described by two ellipses which differ only in their relative azimuthal angles. This difference (which is just 2θ) can then be determined directly at the lock-in amplifier by measuring the relative phase of the light intensity passing through the rotating analyser.

3. Results and discussion

Figure 3 shows the temperature dependence of the half switching angle of DOHBAECEC in the region of stability of the S_I^* and S_A phases. These data were

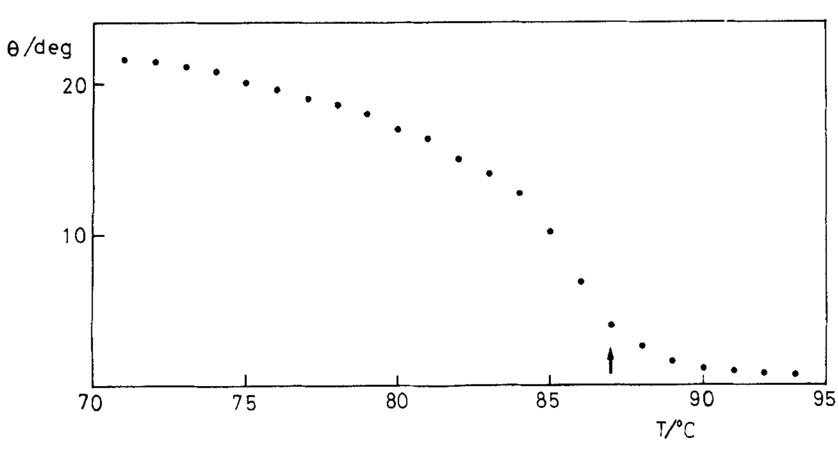

Figure 3. Temperature dependence of the half switching angle of a 12 μm thick sample of DOHBAECEC driven by a square wave voltage of 0·1 Hz and ± 10 V. Only some of the experimental points are shown. The S_A–S_I^* transition temperature is indicated by an arrow.

obtained with the arrangement shown in figure 2 (*b*) by using a square-wave of 0·1 Hz and ± 10 V. It was found that below this voltage the measured tilt angle in the S_I^* phase depended on the magnitude of the electric field, but that it practically saturated above ± 10 V. As can be seen, the electroclinic effect in the S_A phase is moderately strong even for relatively low applied electric fields. This is due to the proportional relationship between the tilt angle in the S_A phase and the spontaneous polarization in the lower temperature ferroelectric phase [5].

Figure 4 shows the electric field dependence of the effect at several temperatures. The measurements were performed with the experimental arrangement shown in figure 2 (*a*), using a sinusoidal voltage of 140 Hz and a lock-in amplifier detection system. These results correspond to an essentially static regime, since, as we shall show, the relaxations of the system take place well above 140 Hz in the complete temperature range. As is clearly visible, the electroclinic effect is linearly dependent on the applied field, which is in agreement with theoretical predictions [7]. Nevertheless, close to the transition temperature a slight deviation can be noticed. This non-linear effect has also been reported by other authors [5], who have found in the induced tilt angle a much stronger tendency to saturation near the corresponding para-ferroelectric phase transition. The phenomenon may originate in a slight shift of the transition temperature with the electric field [14, 15], which may be noticeable when moderate voltages are used.

The frequency dependence of the optical modulation amplitude was measured by applying a small sinusoidal voltage (± 1 V) to the sample in order to ensure a linear

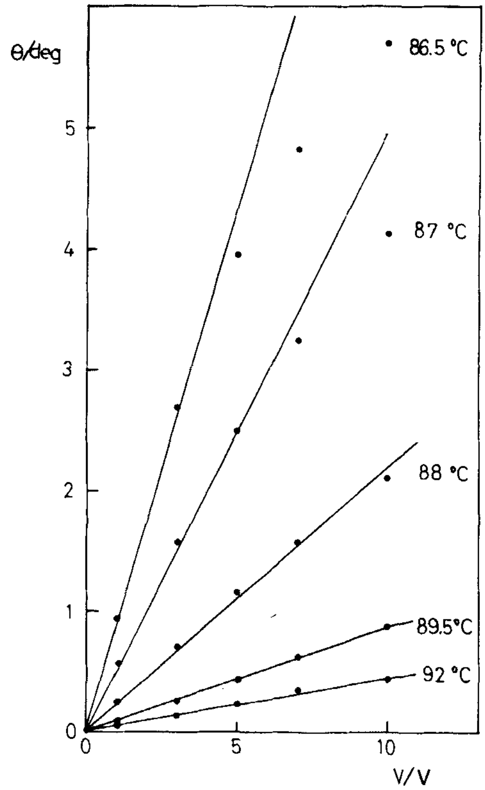

Figure 4. Voltage dependence of the induced tilt angle at several temperatures.

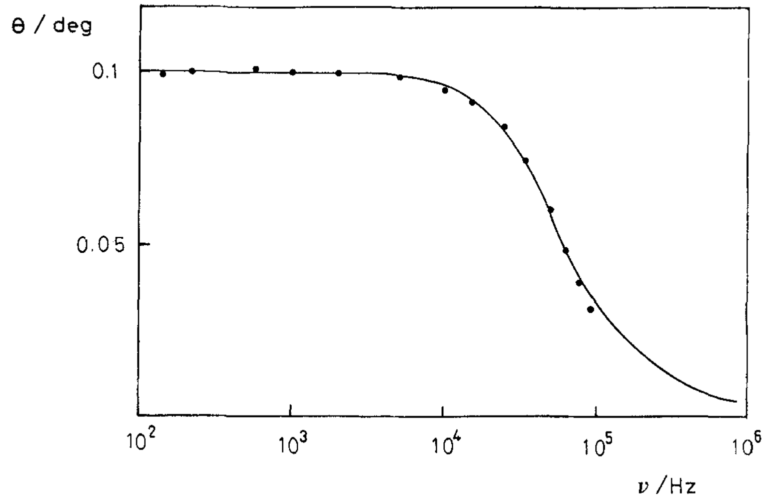

Figure 5. Frequency dependence of the tilt amplitude induced by a sinusoidal voltage of ± 1 V at 91°C. The continuous line represents the best fit of the data to a Debye law.

response regime; a typical result is shown in figure 5. As is clearly seen the induced tilt angle exhibits a relaxational behaviour which can be fitted satisfactorily to a simple Debye law over the complete S_A range. This relaxation is associated with amplitude fluctuations of the tilt angle (soft mode) as has been already reported by Andersson *et al.* [3] and Bahr and Heppke [4]. The temperature dependence of the relaxation frequencies is given in figure 6. Close to the S_A–S_I^* transition the experimental points vary linearly with temperature, decreasing their values when the transition is approached. This dependence is identical to that found for a S_A–S_C^* transition and can be accounted for within a mean field theoretical scheme [16]. In fact, the group theoretical argument which predicts this behaviour is not affected by the fact that the low temperature phase is S_I^* instead of S_C^*. The frequencies obtained are rather small compared with those reported for other compounds [3, 4, 7], which does not allow switching times below 10 μs for DOHBAECEC. This may be due to a presumably high value of the viscosity of the material.

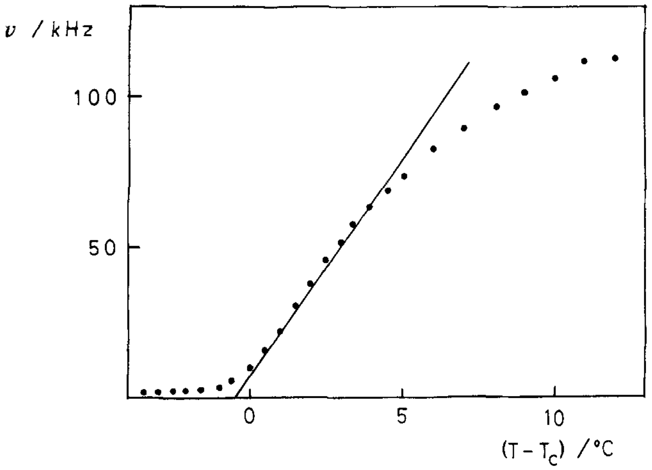

Figure 6. Temperature dependence of the relaxation frequency around the S_A–S_I^* transition.

At temperatures within the S_I^* region the optical response of the sample still shows the same features found in the S_A phase if small voltages are used. However, in this case, the interpretation of the results is different because of the presence of the helicoidal structure. The relaxation in this temperature range is more likely to be connected with fluctuations in the director azimuthal angle. The same fact has been pointed out in [17], where a similar experimental arrangement was used. This hypothesis is supported by the fact that the relaxation frequencies are practically independent of temperature (see figure 6) and their values are almost coincident with those obtained from dielectric measurements [9].

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