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Orientational order of *p*-*n*-alkoxybenzylidene-*p*'-fluoroanilines. X-ray diffraction and electro-optic response of the chiral (*S*)-*p*-2-methylbutyloxy derivative

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This work continues our study of the mesomorphic properties of the *p*-*n*-alkoxybenzylidene-*p*'-fluoroanilines. Previous studies have shown that the straight chain homologues, with the number of carbon atoms in the chain ranging from 4 to 8, form smectic phases. In this paper we describe ²H NMR studies of the homologues with *n* = 4, 5 and 8 and the synthesis and properties of a chiral branched chain derivative, (*S*)-*p*-2-methylbutyloxybenzylidene-*p*'-fluoroaniline. This compound is not mesomorphic, but does show solid state polymorphism. From an optical, electro-optical, DSC and X-ray diffraction study we infer that the higher temperature crystalline form is a CrE phase.

1. Introduction

In previous papers, the mesomorphic behaviour of a few members of the series of *p*-*n*-alkoxybenzylidene-*p*'-fluoroanilines, having the general formula I shown in figure 1, has been investigated by thermal optical microscopy, X-ray diffraction and ²H NMR spectroscopy of partially deuteriated samples [1, 2]. Smectic polymorphism was found by polarizing optical microscopy and X-ray diffraction in all the compounds investigated (*n* ranging from 4 to 8) [1]. The lower temperature mesophase is always a smectic B phase, observed with a monotropic transition in the cases of *n* = 4, 7 and 8. At higher temperatures a smectic A phase is found when *n* ≥ 6; the compound with *n* = 6 also shows a nematic phase. The X-ray structural data exclude an interdigitated molecular arrangement and show that a reduction of 1–3% of the layer thickness occurs on passing from the smectic B to the smectic A phase for the mesogens with *n* = 6, 7 and 8.

The orientational order of the aromatic core of the partially deuteriated homologues with *n* = 6 and *n* = 7

has been investigated by means of ²H and ¹⁹F NMR spectroscopy [2]. The results indicate that in the smectic phases, the core is strongly oriented, the principal order parameter of the deuteriated ring reaching a value of 0.9 in the smectic B phase. Moreover, the orientational order of the aromatic core in the smectic A phase is constant with varying temperature. This behaviour was interpreted in terms of a strong coupling between orientational and chain conformational order in the smectic phases: in the S_B phase, the alkyl chain is locked in a small number of elongated conformations and the temperature increase causes a reduction of the molecular orientational order; in the S_A phase the temperature increase mainly affects the conformational distribution of the alkyl chain. This hypothesis is supported by the observed changing of layer thickness in the smectic phases [1] and was recently confirmed in the case of *p*-*n*-hexyloxy-d₁₃-benzylidene-*p*'-fluoroaniline [3], for which the chain order and dynamics were studied by ²H NMR. Both the local order parameters of the methylene C–D bonds and the respective spectral densities show that the internal motions of the two methylene groups closest to the aromatic core slow down in the smectic A phase and almost freeze in the smectic B phase.

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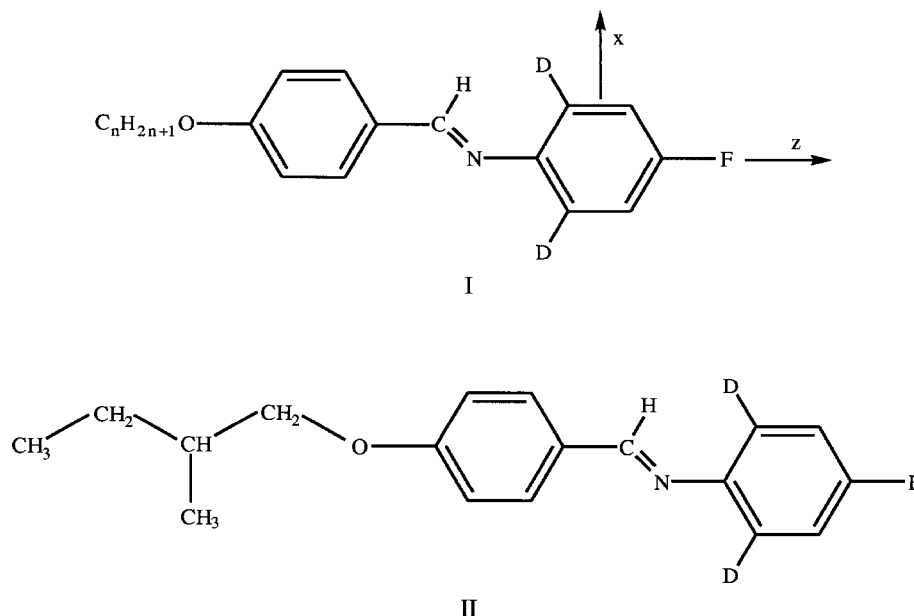


Figure 1. I: structure of deuteriated *p*-*n*-alkoxybenzylidene-*p*'-fluoroanilines and the reference frame used; II: structure of deuteriated (*S*)-*p*-2-methylbutyloxybenzylidene-*p*'-fluoroaniline.

In order to get a better understanding of the influence of the alkoxy chain length on the orientational order of the aromatic core of these mesogens, in the present paper the ^2H NMR study has been extended to the compounds with $n = 4, 5$ and 8 , deuteriated as shown in figure 1. It seemed also interesting to investigate the influence on the mesomorphism of branching the chain, thus introducing a chiral centre in the molecule. So far, compound II of figure 1, (*S*)-*p*-2-methylbutyloxybenzylidene-*p*'-fluoroaniline, has been synthesized and investigated by DSC, polarizing optical microscopy, X-ray diffraction and ^2H NMR spectroscopy.

As will be shown in the following, in the chiral compound, the mesomorphic phase is no longer sustained. However, polymorphism is present in the solid state of this compound. The higher temperature crystalline phase exhibits a layered structure reminiscent of a smectic crystalline modification [4]; a peculiar growth process was also revealed in this phase by means of polarizing microscopy. These results prompted us to study the electro-optic characteristics of the compound, even if this kind of observation is usually limited to chiral compounds forming smectic phases; in effect, an electroclinic response has already been detected, for instance, in the semicrystalline phase of a chiral LC polymer [5]. To support this kind of investigation, we also recall that recently pyroelectric and piezoelectric properties have been found in the solid state of *p*-*n*-hexyloxybenzylidene-*p*'-fluoroaniline [6]. In this case the presence of a non-centrosymmetric space group in

the crystalline phase was definitely a necessary condition for the occurrence of such effects.

2. Experimental

All compounds have been synthesized following the procedure reported in the literature [7] starting from suitably deuteriated materials. The (*S*)-*p*-2-methylbutyloxybenzylidene-*p*'-fluoroaniline was synthesized by heating under reflux (*S*)-*I*-bromo-2-methylbutane for 60 h with *p*-hydroxybenzaldehyde and potassium carbonate. After vacuum distillation, the product was heated in anhydrous benzene with 4-fluoroaniline-2,6- d_2 . The crude product was purified by recrystallization from anhydrous ethanol.

The deuterium spectra were obtained using a Varian VXR300 spectrometer at a frequency of 46.04 MHz. The temperature dependence was recorded by starting from the isotropic phase and cooling the sample slowly. Spectra were taken after equilibrating the temperature for 10 min.

X-ray diffraction measurements were performed on powder samples with an INEL CPS 120 powder diffractometer equipped with a curved position sensitive detector covering 120° in the scattering angle 2θ , with an angular resolution of 0.018° . Ge(111) monochromatized $\text{CuK}\alpha$ radiation was used. The sample, ~ 1 mm thick, was placed between two thin Al sheets and fixed inside the circular hole of an Al sample holder. Heating was provided by a hot stage and the temperature of the

sample was controlled within $\pm 0.1^\circ\text{C}$ by an automatic temperature regulator.

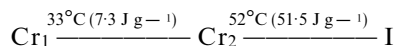
The experimental set-up for measuring the electro-optic response is described in [8]. A sandwich type cell was used. The substrates forming the cell were glass plates covered with indium tin oxide (ITO) electrodes on top of which a SiO protective layer was deposited. In addition, a weak unidirectional mechanical buffing was applied to the SiO layer in order to obtain a planar alignment of the molecules. A cell gap of about $2\ \mu\text{m}$ was assured by evaporated SiO spacers. The compound was introduced into the cell in the isotropic phase, in a vacuum chamber; the cell was then inserted in a Mettler FP 52 hot stage. The material was cooled down from the isotropic phase very slowly ($0.2^\circ\text{C}\ \text{min}^{-1}$). Under these experimental conditions, large mono-crystals with uniform planar alignment of the molecules were grown. After mono-crystals were formed with a size large enough to cover the whole viewing field, the cell was oriented in such a way that maximum modulation of the transmitted light through one chosen mono-crystal could be detected.

3. Results

3.1. DSC and polarizing optical microscopy

The phase diagrams of compounds of type I are reported in [1].

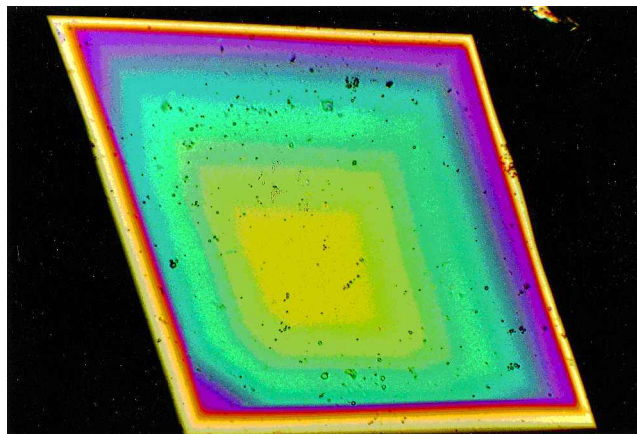
By means of DSC and polarizing optical microscopy, the chiral compound II was found to exhibit, on heating, the phase sequence



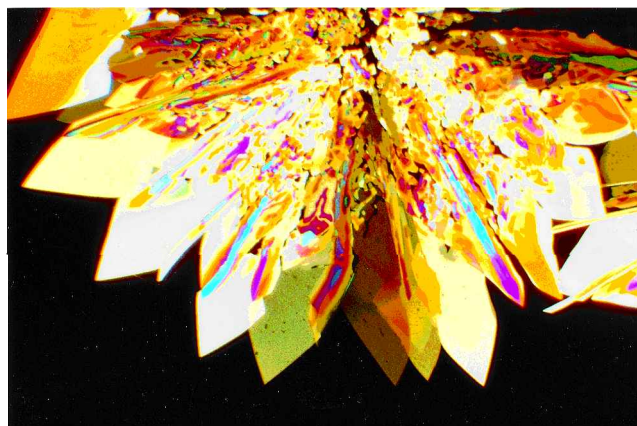
where Cr₁ and Cr₂ are crystalline phases. No liquid crystalline phase has been observed on heating or cooling. However, the growing process of the Cr₂ phase presents an interesting dependence on the cooling rate. Single crystals with rhombic form were found to grow on slow cooling ($0.2^\circ\text{C}\ \text{min}^{-1}$) from the isotropic phase (see figure 2 (a)). The observation of single mono-crystals under the polarizing microscope showed that they possess a perfectly uniform in-plane alignment of the molecules. When the cooling process was speeded up a spherulitic clump of crystals grew (see figure 2 (b)).

3.2. NMR measurements

^2H NMR spectra were recorded on samples of *p*-*n*-alkoxybenzylidene-*p'*-fluoroanilines with $n=4, 5$ and 8 deuteriated as shown in figure 1, as a function of temperature. As previously described for the homologues with $n=6$ and 7 [2], each spectrum consists of a doublet (quadrupolar coupling) of doublets (*ortho-meta* dipolar coupling D–H). The quadrupolar ($\Delta\nu_q$) and dipolar ($\Delta\nu_{\text{DH}}$) splittings can be expressed in terms of the major



(a)



(b)

Figure 2. Growth of Cr₂ crystals from the isotropic phase of compound II in a cell with a $30\ \mu\text{m}$ gap: (a) single crystals obtained on slow cooling; (b) spherulitic clump of crystals obtained on rapid cooling.

order parameter, S_{zz} , relative to the z axis assumed parallel to the D–H internuclear direction, and the biaxiality, $S_{xx} - S_{yy}$, by the well known relations [9]:

$$\Delta\nu_q = (3/4)q\{S_{zz}[3l_{zb}^2 - 1 + \eta(1 - l_{zb}^2)] + (S_{xx} - S_{yy})[1 - l_{zb}^2 + (1/3)\eta(1 + l_{zb}^2)]\}$$

$$\Delta\nu_{\text{DH}} = - \left(\frac{\gamma_{\text{D}}\gamma_{\text{H}}\hbar}{4\pi^2 r^3} \right) 2S_{zz}$$

In the computation, the internuclear distance r is taken equal to $2.46\ \text{\AA}$, and q , the quadrupolar coupling constant, and η , the asymmetry parameter, are taken as $186\ \text{kHz}$ and 0.03 , respectively [10]. A value of 61° is assigned to the angle between the C–D bond and the z axis, from which the direction cosine l_{zb} is calculated. The order parameters S_{zz} and $S_{xx} - S_{yy}$ obtained from the equations are plotted against temperature in figure 3.

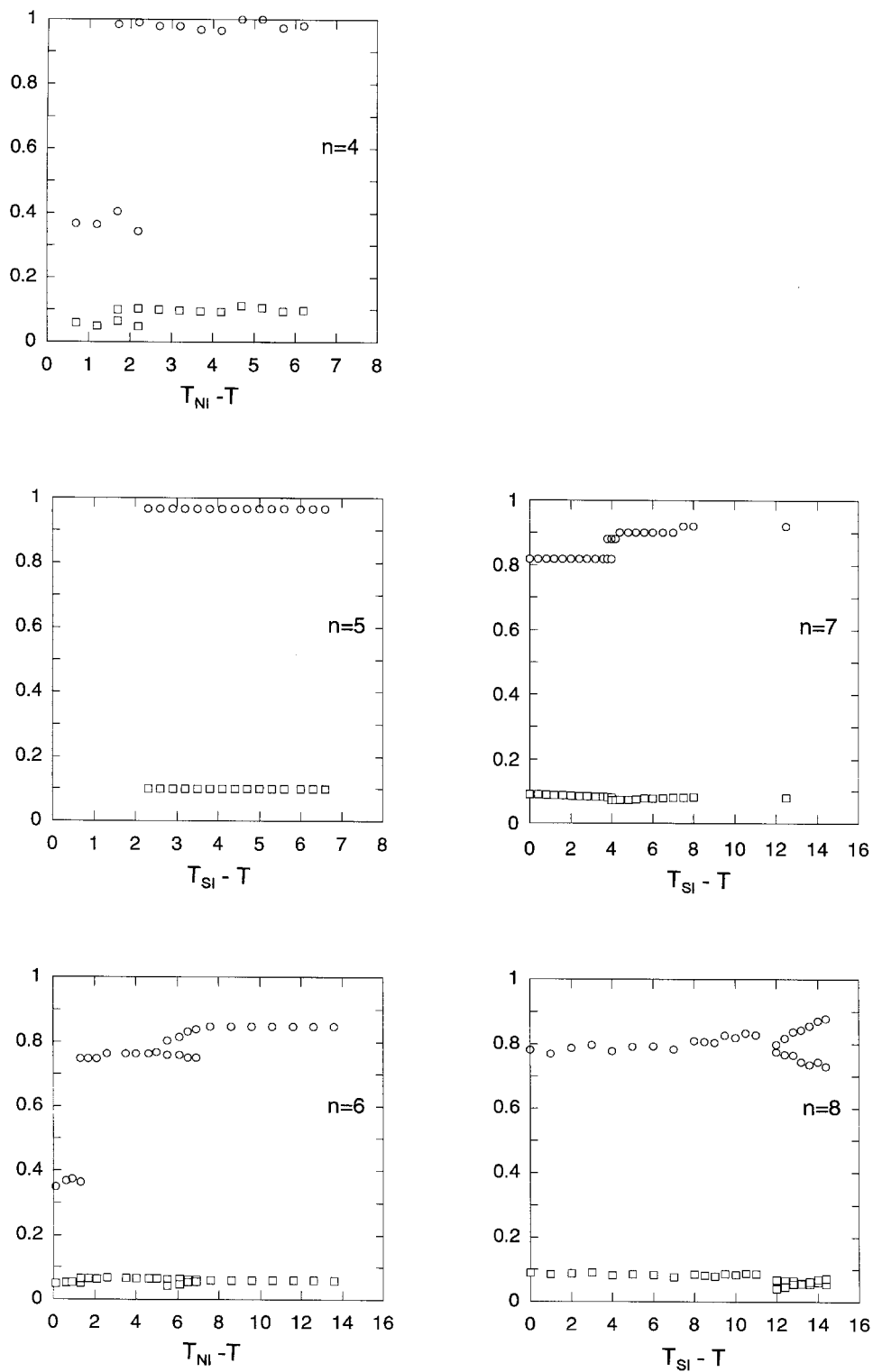


Figure 3. Order parameters, S_{zz} (circles) and $S_{xx} - S_{yy}$ (squares) versus reduced temperatures, $T_{XI} - T$, of the aromatic core of p - n -alkoxybenzylidene- p' -fluoroaniline mesogens with different n values.

Analogous plots relative to compounds with $n=6$ and 7, taken from [2], are also shown. For the homologues with short chains ($n=4, 5$) the order parameter of the

molecular core in the smectic B phases approaches 1, that is its maximum theoretical value.

No high resolution ^2H NMR spectra were observed

for compound II during either cooling or heating cycles. This definitely indicates that the compound exhibits either crystalline polymorphism or a Cr₂ phase that could be a highly ordered crystal smectic phase.

3.3. X-ray diffraction measurements

The X-ray diffraction study of the smectic polymorphism in the straight chain compounds I (*n* ranging from 4 to 8) is already published [1]. Here we will report on the results obtained for the branched chain compound II. The X-ray diffraction measurements performed on a powder sample at different temperatures, between room temperature (RT) and the clearing point, confirmed that the phase sequence of the material is Cr₁–Cr₂–I. In figure 4 A–C the X-ray diffraction patterns obtained at different temperatures in a heating–cooling thermal cycle are depicted. The spectrum in figure 4 A shows the crystalline nature of the RT solid phase (Cr₁). No diffraction peak is present in the small angle region of the spectrum ($2\theta < 10^\circ$), whereas several sharp Bragg reflections are visible in the range of scattering angles between 10° and 30° . The first peak, at $2\theta = 12^\circ$, corresponds to a spacing $d = 7.37 \text{ \AA}$ which represents the maximum periodicity in the solid phase.

On increasing the temperature, a modification of the diffraction pattern is observed above $T \sim 33^\circ\text{C}$, where a phase transition takes place (see figure 4 B). Several sharp peaks are present throughout the whole range of investigated scattering angles, and point to a solid phase with a highly crystalline structure (Cr₂). The indexing of the diffraction lines in the spectrum of the solid phase Cr₂ was performed by using a general trial and error indexing computer program. The unit cell was found to be orthorhombic with lattice parameters $a = 5.691 (2)$, $b = 7.623 (2)$ and $c = 38.25 (1) \text{ \AA}$.

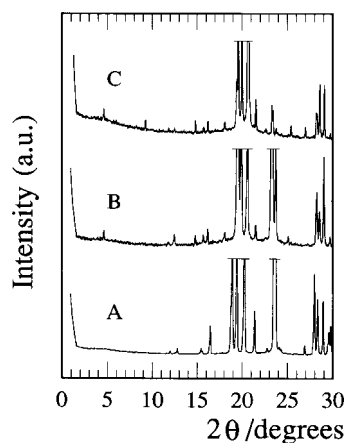


Figure 4. X-ray diffraction patterns obtained for compound II at different temperatures: A, room temperature (RT); B, $T = 33^\circ\text{C}$ on heating; C, $T = 33^\circ\text{C}$ after cooling from the isotropic phase.

The solid phase Cr₂ is also observed on cooling from the isotropic liquid. The diffraction patterns measured at different temperatures between $T = 51.5^\circ\text{C}$ (the clearing point) and $T = 31^\circ\text{C}$ are very similar and the analysis indicates no significant modification of the unit cell with respect to that determined in the heating cycle. The results of the indexing of the spectrum at $T = 33^\circ\text{C}$ (figure 4 C) correspond to an orthorhombic unit cell with the above mentioned lattice parameters. The variations with temperature for A, B and C are very small and in all cases were found to be within experimental error. The noticeable difference in the intensity profile between the spectra of the solid phase Cr₂ measured in the heating (figure 4 B) and in the cooling (figure 4 C) cycle is due to the different orientational distribution of the micro-domains in the powder, possibly promoted by a preferential orientation process occurring in the cooling cycle. This has been verified by performing several measurements, starting with new virgin samples, under the same experimental conditions.

Differently from the low temperature solid phase Cr₁, one sharp and very weak reflection, i.e. the 002 reflection, is observed in the small angle region of the spectra of Cr₂, which corresponds to a spacing $d = 19.1 \text{ \AA}$. The occurrence of this high spacing reflection indicates that some sort of lamellar stacking of the molecules can be identified within the structure of the solid phase Cr₂ (the length of the molecule in its most elongated conformation is about 18 \AA). On cooling, the lamellar stacking of the molecules is even more pronounced than on heating, as indicated by the presence of the first harmonic, i.e. the 004 reflection, of the small angle reflection at $d \sim 19.1 \text{ \AA}$. The above feature of the small angle spectral region makes the diffraction pattern of the solid phase Cr₂ similar to those commonly observed for so-called smectic mesophases of the crystal type [4]. An estimate of the correlation length ζ of the stacking along the *c* axis can be obtained from the experimental data by using the equation

$$\zeta = \frac{2}{\Delta q_{\parallel}}$$

with

$$\Delta q_{\parallel} = \frac{2\pi}{\lambda} \Delta(2\theta)$$

q_{\parallel} being the intensity of the component of the scattering vector perpendicular to the smectic layers and $\Delta(2\theta)$, the FWHM of the small angle peak. The Bragg peaks being resolution limited, an upper limit for the $\Delta(2\theta)$ value of 0.02° has been considered, which gives the lower limit $\zeta > 1500 \text{ \AA}$ (corresponding to about 80 layers) for the correlation length. This result is reasonable for a

crystalline phase and the value obtained is also in agreement with those commonly encountered in the case of highly ordered mesophases (i.e. crystal smectic mesophases) [4]. The very weak intensity of the small angle reflections (which is of the order of 1% of the strongest peak) is to be attributed to the poor electron density contrast along the c axis of the real space, which is a consequence of the molecular structure. On cooling down to room temperature, a transition to the crystalline solid phase Cr_1 , occurring at $T \sim 31^\circ\text{C}$, is finally observed.

3.4. Electro-optic response

An electro-optic response was observed in both the Cr_1 and Cr_2 phases of compound II. As an example, in figure 5 is depicted the response detected on applying a changing field with a triangular saw-tooth waveform to a monocrystal of II in the Cr_1 phase. The linear character of the response did not change on transition from Cr_1 to Cr_2 phase. The field-induced tilt of the optic axis was evaluated by the indirect method described in [8]. It is found to be very small (0.03–0.20 degrees) and increases with temperature in both phases (see figure 6). Moreover the field-induced tilt is larger in the Cr_2 phase than in the Cr_1 phase and shows a jump at the transition. Similarly to the electroclinic effect observed in chiral orthogonal smectic phases [11], the induced tilt of the optic axis is a linear function of the applied electric field (see figure 7). The response time was measured to be very short as 0.5–0.8 μs . The trend in the tilt angle as a function of temperature (figure 6) and the τ values are quite similar to those reported for the semicrystalline phase of a mesogenic polyacrylate [5].

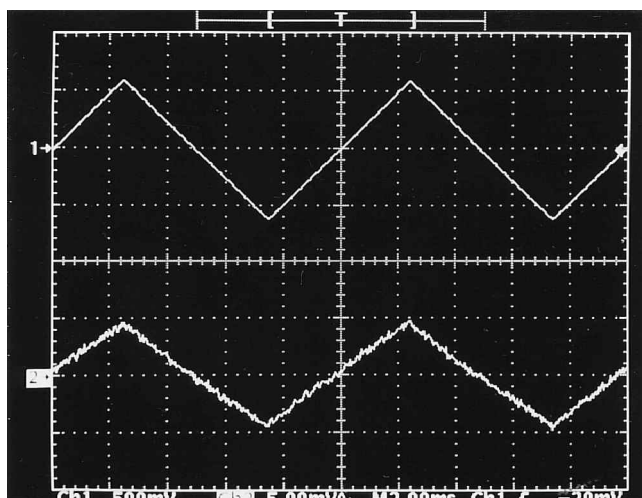


Figure 5. Electro-optic response (lower trace, 2) of compound II in the Cr_1 phase at 25°C recorded on applying a changing field with a triangular saw-tooth waveform (upper trace, 1).

4. Conclusions

Increase in the number of carbon atoms, n , in the chain of p - n -alkoxybenzylidene- p' -fluoroanilines results in a lowering of the orientational order of the molecular core (see figure 3) as also observed in [12]. For the homologues with $n=4$ and 5, the order parameter S_{zz} of the core in the smectic B phase is close to 1, the maximum value allowed, meaning that the motions of the molecules toward the director are severely quenched. Moreover, previous investigations of the dynamic behaviour of polymorphic mesogens, by measurements of ^2H NMR relaxation times, suggest that the rotational diffusion of molecules sensibly slows down on entering the highly ordered S_B phase [3, 13–16]. In particular, while the diffusion coefficient for the rotation of the molecules around their short axes becomes smaller up to a factor of 5, that for the rotation of molecules about their long axes decreases only by a factor of 1.5–2 [14, 15]. Therefore this last motion is confirmed to be the prevailing one, apart from rotations and flips of internal groups.

For the series of compounds I, the increase of the orientational order of the molecular core observed at the S_A to S_B phase transition (see figure 3) may be coupled with a reduction of the conformational freedom of the chains, as already proposed in [2]. This hypothesis has been successfully confirmed in the case of p -hexyloxybenzylidene- p' -fluoroaniline, where the local order parameters and spectral densities, measured by ^2H NMR, showed a freezing of the dynamics for the two methylene groups closest to the phenyl ring [3]. This behaviour has been observed also for the alkyl chain of a compound showing an analogous smectic polymorphism [14] and is generally supported by the increase of the layer thickness measured by X-ray at the S_A to S_B transition [1, 17].

For the branched chain compound II, no high resolution NMR spectrum has been observed since it does not present mesophases that can be aligned by the magnetic field. Polarizing optical microscopy and particularly X-ray diffraction show that the higher temperature phase Cr_2 is crystalline with a layered structure reminiscent of smectic order, so that it could belong to the class of highly ordered crystalline smectic phases [4]. The structural features of compound II, namely the orthorhombic unit cell, the monomolecular thickness of layers and the long range positional order within and between the layers, support the hypothesis that the Cr_2 phase is of the CrE type [4, 18].

Crystal smectic phases have some peculiar properties due to the fact that their constituent molecules are relatively rapidly reorienting, oscillating or rotating about their long axes [18, 19]. This residual mobility

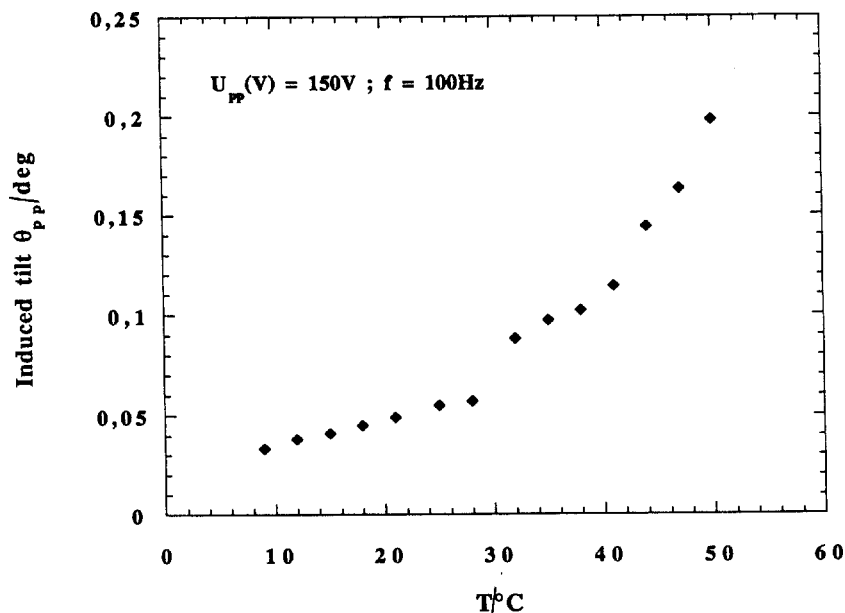


Figure 6. Temperature dependence of the induced tilt angle, θ , of the optic axis in compound II (applied field $U_{pp}=150$ V, frequency = 100 Hz).

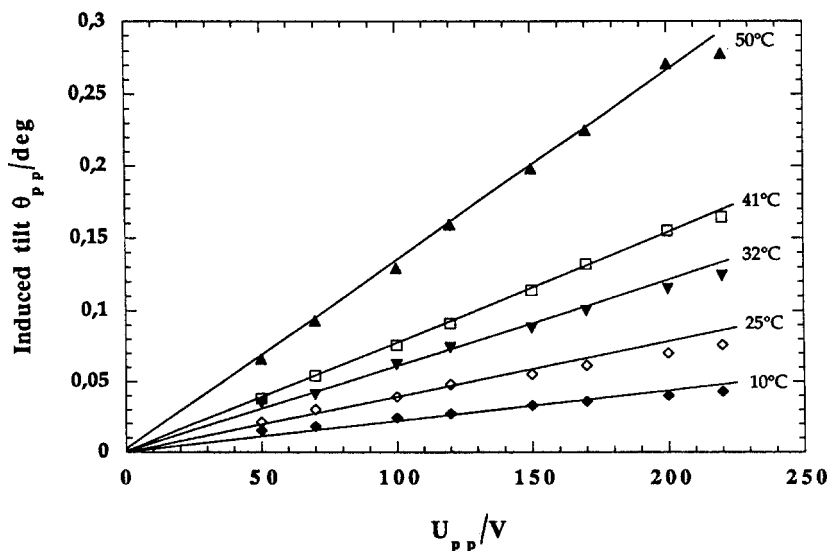


Figure 7. Induced tilt angle, θ , of the optic axis in compound II as a function of the applied field, U_{pp} (frequency = 100 Hz, cell thickness = 2 μ m) at the temperatures indicated.

justifies the possibility of observing an electroclinic effect. A similar behaviour has been described in the past for the semicrystalline phase of a liquid crystalline polymer: in that case a substantial degree of motional freedom of the side chain mesogenic groups supported the existence of the electroclinic effect [5].

In order to investigate the properties and potential applications of chiral compounds forming smectic phases, further studies on homologues of compound II with longer chains are in progress.

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