

Antiferroelectric liquid-crystal mixture without smectic layer shrinkage at the direct Sm-A*–Sm-C_a* transition

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We report results of x-ray, optic, electro-optic, and dielectric investigations on an antiferroelectric liquid-crystal mixture exhibiting a direct second-order phase transition between the Sm-A* and Sm-C_a* phases with virtually no shrinkage in the smectic layer spacing. The birefringence measurements and texture observations suggest that the phase transition follows the diffuse cone model of Adrian de Vries, which explains the constant layer spacing. The antiferroelectric nature of the tilted phase is verified by the presence of twin polarization reversal peaks in the current response and by the absence of strong absorptions in the dielectric spectrum. The threshold for switching this phase to the synclonic, ferroelectric state is sharp and occurs at a very low voltage.

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I. INTRODUCTION

With the understanding of the annoying consequences of the smectic layer shrinkage normally connected to the onset of tilt at the Sm-A*–Sm-C* transition, producing a chevron structure that severely degrades the quality of any electro-optic device based on ferroelectric liquid crystals (FLCs) [1], materials exhibiting little, or no, layer shrinkage at the tilting transition became extremely interesting. So far, efforts have been devoted mainly to finding FLCs with a temperature-independent layer spacing d , and a few such materials have indeed been found [2–5]. But also devices based on antiferroelectric liquid crystals (AFLCs) suffer heavily from the appearance of chevron structures, see, e.g., Refs. [6,7], and absence of layer shrinkage should therefore be an attractive property also in this class of materials.

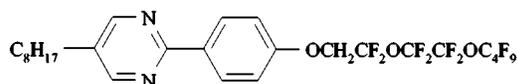
In this work we present a fluoroether-based AFLC mixture exhibiting a direct Sm-A* to Sm-C_a* transition producing virtually no layer shrinkage. The composition of this mixture is shown in Fig. 1. Its chiral component, code named 8422[2F3], has previously been studied by us [5], and we there showed that the compound possesses a tilting transition between paraelectric Sm-A* and ferroelectric Sm-C* at constant d . The mixture keeps many of the peculiar characteristics of the pure compound, including the absence of layer shrinkage, but the polar properties are antiferroelectric as evidenced by optic, electro-optic, and dielectric investigations, presented in the following.

II. EXPERIMENT

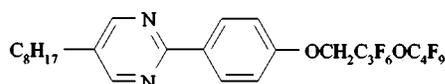
For x-ray studies (CuK_α radiation), the mixture was filled into Mark glass capillary tubes of 0.7 mm diameter. Small-angle scattering data from unaligned samples were obtained

using a Kratky-compact camera (A. Paar) and a one-dimensional electronic detector (M. Braun). For electro-optic and current response studies we used noncommercial cells of 3- μ m cell gap, permitting a light shearing of the substrates relative to one another. By applying an ac electric field above the threshold for switching to the synclonic state during shearing, a relatively homogeneous planar alignment could be achieved. The driving wave form during measurements was produced by a Leader LFG-1300 wave-form generator and an FLC Electronics 20 \times amplifier, and the current response, obtained by measuring the voltage drop over a series resistance, was monitored on a Tektronix TDS 540 oscillo-

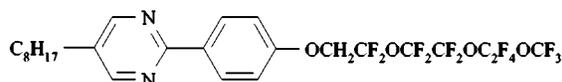
25% 8422:



8.8% 844:



16.2% 81222:



50% 8422[2F3]:

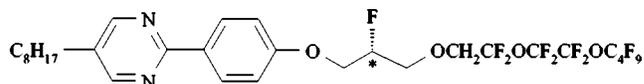


FIG. 1. Chemical composition (in % of weight) of the antiferroelectric liquid-crystal mixture under investigation. The chiral component, code named 8422[2F3], is a ferroelectric liquid crystal [5].

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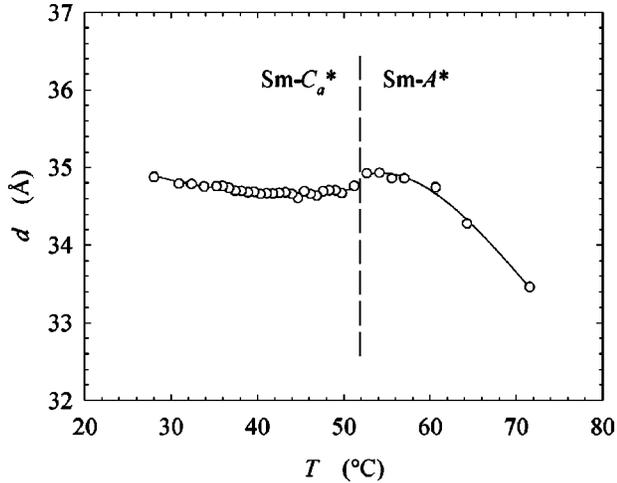


FIG. 2. Smectic layer thickness d of the AFLC mixture as a function of temperature T . Note that the variation within the Sm-C_a^* phase is only $\sim 0.3 \text{ \AA}$.

scope. The optical tilt angle θ_{opt} and the optical path difference Δ_{opt} (related to the birefringence Δn by $\Delta_{\text{opt}} = l\Delta n$, where l is the sample thickness) were measured similar to the method discussed in Ref. [8]: The AFLC sample is placed between crossed polarizers and switched between its polar states by a square ac electric field. The transmissions T_1 and T_2 of the polarization-up and -down states at the He-Ne laser wavelength $\lambda = 633 \text{ nm}$ are recorded (Melles Griot 13 DSI 009 photodetector with amplifier 13 AMP 005) on rotating the polarizer cross by an angle φ . The transmissions $T_1(\varphi)$ and $T_2(\varphi)$ are described by two $\sin^2(2\varphi)$ curves with identical amplitude $\pi\Delta_{\text{opt}}/\lambda$ and a phase shift of twice the optical tilt angle θ_{opt} between each other. Measurements were done either at selected, stabilized, temperatures, or during slow continuous cooling from the Sm-A^* phase, permitting measurements with very high-temperature resolution. For dielectric measurements (HP 4192 impedance bridge) and for texture photos, commercial (EHC) $10\text{-}\mu\text{m}$ planar-aligning cells were used. For temperature control, the sample was inserted into a Mettler FP52 hot stage during electro-optic measurements, and, during dielectric measurements, into a homemade hot stage with temperature control by a thermal liquid circulated in a thermostat (Julabo).

III. RESULTS AND DISCUSSION

Figure 2 shows the variation of smectic layer thickness d with temperature. While d increases steadily on cooling through the Sm-A^* phase, the layer thickness is almost constant below the temperature of the transition to Sm-C_a^* . A small decrease ($\sim 0.3 \text{ \AA}$) occurs directly below the phase transition, but on further cooling, d increases slowly and at room temperature the same value as measured at the low-temperature border of Sm-A^* , 35 \AA , is regained.

Compared with the pure FLC component 8422[2F3], see Ref. [5], the layer spacing is notably smaller in the mixture ($\sim 3.5 \text{ \AA}$ difference). This is first of all a result of the other components being shorter than 8422[2F3], and possibly other factors contribute. Based on the comparison between

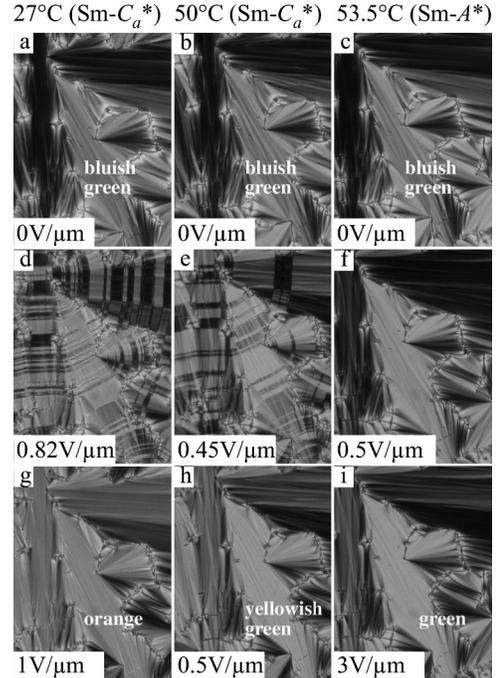


FIG. 3. Textures in the field-free state (a, b, c), during switching (d, e, f) and in the fully switched state (g, h, i), in Sm-A^* (c, f, i) and at two different temperatures in the Sm-C_a^* phase (a, b, d, e, g, h). The applied fields are dc, the cell gap is $10 \mu\text{m}$ and the objective lens $20\times$.

measurements of the orientational order and of the smectic layer spacing in 8422[2F3] we suggested that the molecules of this compound aggregate pairwise in an antiparallel fashion [5]. In the mixture, the packing scheme of different length molecules results in a layer spacing value that corresponds closely to the weighted average of layer spacing values of the individual molecules, each of which show much the same thermal layer response as does 8422[2F3].

In addition, it is noteworthy that (also) another FLC compound exhibiting an essentially tilt-independent layer spacing could exhibit the same type of antiparallel pair aggregation as 8422[2F3]. The compound, code named TSiKN65, is structurally quite different from 8422[2F3] but shows a very similar behavior in many respects. Spector *et al.* measured a layer spacing in TSiKN65 which is actually larger than the length of a single molecule [9]. This is easiest explained by assuming the antiparallel packing scheme and a fairly low degree of orientational order with de Vries behavior. As 8422[2F3], the TSiKN65 molecule has a highly asymmetrical shape, with one end chain much bulkier than the other due to three siloxane units. Packing in an antiparallel manner should thus be favorable also in this compound.

The practical absence of layer shrinkage in our AFLC mixture is also reflected in the textures (Fig. 3) which show no sign of the zig-zag defects typically generated at a phase transition where d changes [10]. In fact, the relaxed state textures of the Sm-A^* and Sm-C_a^* phases [Figs. 3(a), 3(b), 3(c)] are very similar, with more or less the same defects and the same color between crossed polarizers. The latter observation indicates that the birefringence Δn in Sm-A^* is ap-

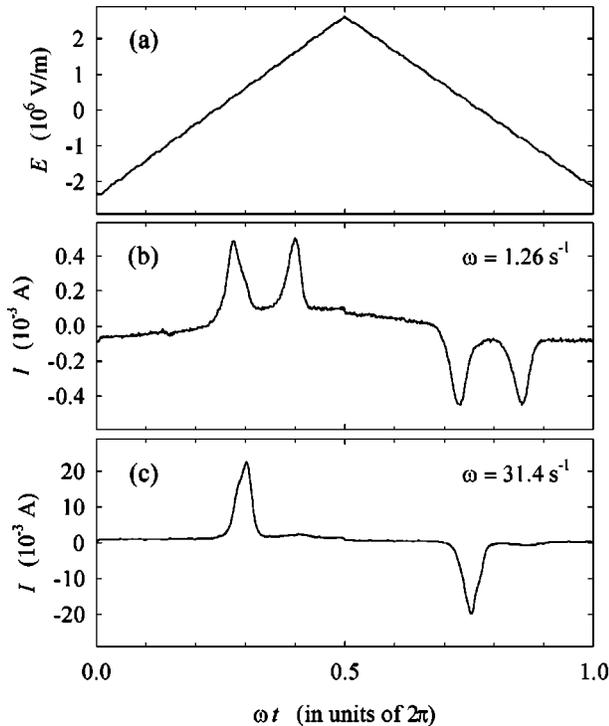


FIG. 4. Electric current response at 0.2 Hz (b) and at 5 Hz (c) to a triangular electric field (a) from the AFLC in a 3- μm cell.

proximately as low as in Sm-C_a^* and thus rules out the common naive picture of Sm-A^* as a phase, where all molecules stand orthogonal to the layers. A much more realistic description is that of de Vries [11], where the molecules on the average are tilted but where the tilt direction is random. Such a state should produce approximately the same Δn as an anticlinic state with well-defined tilt directions but where these alternate between consecutive layers. On the other hand, if the anticlinic state is switched to a synclinic (ferroelectric) state, Δn must be expected to increase since no reduction due to random or anticlinic tilt order is present. Indeed, the textures observed in the Sm-C_a^* phase during the application of an electric field strong enough to switch the sample to the synclinic state [Figs. 3(g), 3(h)] have a color distinctly different from the relaxed Sm-C_a^* or Sm-A^* textures, reflecting the increase in birefringence. As expected from the fact that the orientational order must increase with decreasing temperature, the difference in color continuously increases on cooling.

The typical fingerlike switching between the anticlinic and the synclinic states can easily be seen in the textures taken at intermediate field [Figs. 3(d), 3(e)]. Furthermore, the antipolar response is easily seen in the current response at low switching frequencies [Fig. 4(b)] which exhibits the twin polarization reversal peaks characteristic of AFLCs. However, the peaks rapidly approach one another on increasing the switching frequency and at a switching frequency of 5 Hz angular frequency ($\omega = 31.4 \text{ s}^{-1}$) only one polarization reversal peak can be seen [Fig. 4(c)].

The antiferroelectric nature is also obvious from the dielectric absorption spectrum (Fig. 5), the only strong mode of which is the soft mode, strongly peaking at the

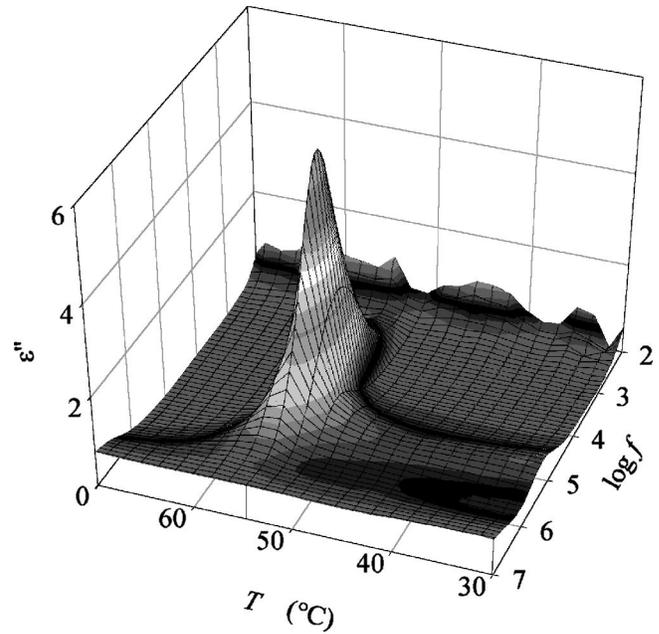


FIG. 5. Dielectric absorption spectrum $\epsilon''(\log_{10}f)$ vs temperature T at 10- μm cell gap on cooling.

$\text{Sm-A}^* - \text{Sm-C}_a^*$ transition. At lower temperatures, in principle only the high-frequency antiferroelectric mode can be seen.

The optic axis of the field-free state is always directed along the layer normal, as expected for AFLCs. Figure 6 shows the field-induced tilt of the optic axis (optical tilt θ_{opt}), for a number of switching amplitudes, as a function of temperature. In no case is there any sign of discontinuity at the $\text{Sm-A}^* - \text{Sm-C}_a^*$ transition, illustrating that this is a second-order phase transition. The continuous, second-order nature is even clearer from the high-resolution birefringence data, taken in the absence of electric fields, shown in Fig. 7. Also in the pure 8422[2F3] FLC component [5] and in TSiKN65 [9] the tilting transition was found to be second order, or possibly very weakly first order.

The switching threshold within the Sm-C_a^* phase is quite

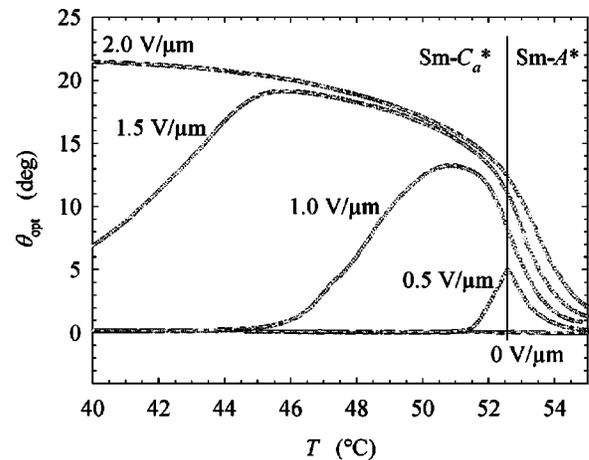


FIG. 6. Optical tilt angle $\theta_{\text{opt}}(633 \text{ nm})$ at different electric field amplitudes, as a function of temperature T .

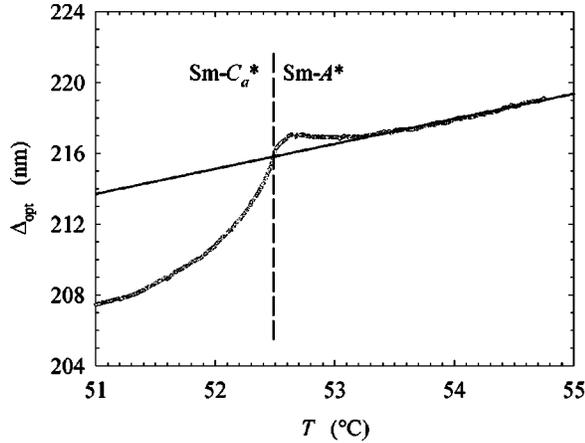


FIG. 7. Optical path difference Δ_{opt} (633 nm) of the field-free 3 μm sample as a function of temperature (on cooling) in the vicinity of the Sm-A*–Sm-C_a* transition, illustrating the second-order nature of the phase transition.

sharp and the saturation amplitude is very low (2 V/ μm is enough for complete switching throughout the phase temperature range). The electroclinic effect in the Sm-A* phase is prominent, despite the absence of a synpolar Sm-C* phase, and just above the transition the induced optical tilt exceeds 12°, i.e., more than half the value of the saturation tilt angle 21.5° observed during complete switching at room temperature. The sharpness in the Sm-C_a* switching threshold is easiest seen in Fig. 8, where θ_{opt} and Δ_{opt} are plotted as a function of amplitude of the applied ac field. The transition from the undisturbed anticlinic state to the fully switched synclinic one takes place over a range of ~ 0.7 V. In the Sm-A* phase, the tilt angle shows a perfectly linear dependence on the field a few Kelvin above the phase transition, while strong nonlinearities appear in the very vicinity of the transition. The corresponding Δ_{opt} data [Fig. 8(b)] are interesting to compare with the texture observations in Fig. 3. The birefringence of the relaxed Sm-C_a* state is only slightly lower than that observed in the Sm-A* phase. Considering that the Sm-C_a* data are taken at a temperature where the optical tilt angle (as observed in the switched, synclinic state) is approximately 20°, the small difference contradicts the “orthogonal molecules” model of the Sm-A* phase, which should exhibit a much larger Δn . Furthermore, the fully switched Sm-C_a* state has a much higher Δn than the Sm-A* phase. However, also the electroclinic effect of the Sm-A* phase should produce an increase in Δn , correlated to the increase in θ_{opt} , in the case of a de Vries type Sm-A* phase [12]. On applying an electric field in the Sm-A* phase, a slight increase in Δn is seen very close to the transition, but a few Kelvin away, where the electroclinic effect is truly linear, the birefringence is in principle unaffected by the field. The correlation between a field-dependent birefrin-

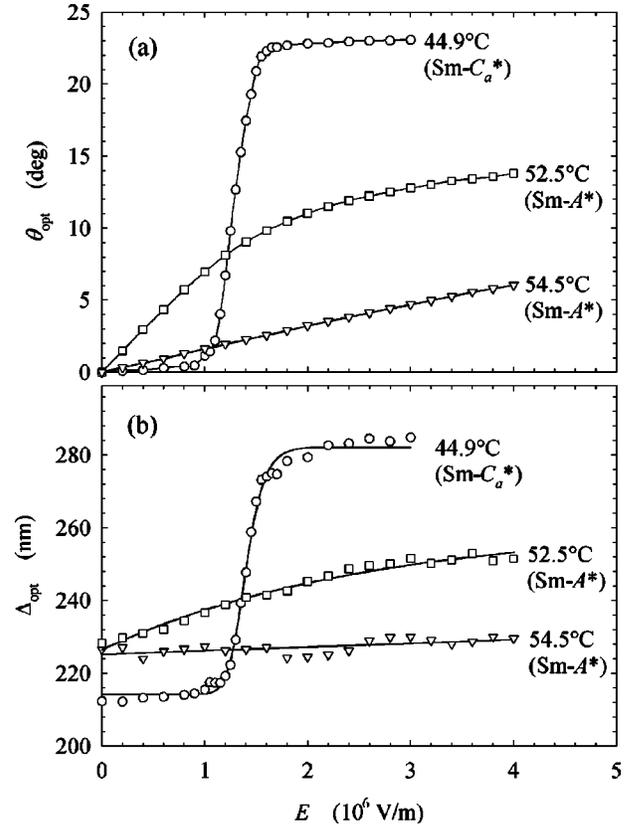


FIG. 8. Optical tilt angle θ_{opt} (a) and optical path difference Δ_{opt} (b) as a function of amplitude of an applied ac field in Sm-C_a* and at two temperatures in the Sm-A* phase.

gence and nonlinearities in the tilt-voltage curve was also seen in the study of TSiKN65 by Selinger *et al.* [12].

In summary, we have demonstrated that the investigated liquid-crystal mixture exhibits an antiferroelectric tilted smectic phase, Sm-C_a* , directly following the paraelectric Sm-A* phase on cooling, via a second-order phase transition. The latter phase is well described by the de Vries model with randomly tilted molecules, and the transition to the Sm-C_a* phase is mainly related to an anticlinic ordering of the tilting directions. In this way the transition can take place with only a minor change in layer thickness, as confirmed by x-ray investigations.

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