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# Influence of the smectic A-nematic transitional order on the formation of the smectic phases of 4-*n*-hexyloxybenzylidene-4'-*n*-butylaniline and 4-*n*-butyloxybenzylidene-4'-*n*-octylaniline from an electrically deformed nematic phase

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# Influence of the smectic A–nematic transitional order on the formation of the smectic phases of 4-*n*-hexyloxybenzylidene-4′-*n*-butylaniline and 4-*n*-butyloxybenzylidene-4′-*n*-octylaniline from an electrically deformed nematic phase

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The crucial role of the smectic A–nematic transitional order for the formation of the smectic A, B and G phases from an electrically deformed nematic phase of the liquid crystal 4-*n*-hexyloxy-benzylidene-4′-*n*-butylaniline (6O.4) with a typical smectic A–nematic first order transition and the formation of the smectic A and B phases from an electrically deformed nematic phase of the liquid crystal (4-*n*-butyloxy-benzylidene-4′-*n*-octylaniline (4O.8) with a smectic A–nematic second order transition has been demonstrated. The nematic phase was deformed by an AC voltage of $2U_{th}$, $5U_{th}$ and $10U_{th}$, where $U_{th}$ is the threshold voltage which causes the appearance of the Fréedericksz transition in the homeotropic nematic layer. The smectic textures have been observed on free cooling of the nematic phase or after the use of an oven. The smectic A phase of the liquid crystal 6O.4 was observed with the formation of a clear smectic A–nematic phase boundary while the smectic A phase of the liquid crystal 4O.8 has been formed from intermediate pretransitional stripes, observed by Cladis and Torza [1]. The homeotropic anchoring of the direction was crucial for the formation of the smectic phases of the liquid crystal 4O.8 but not significant for the liquid crystal 6O.4.



## 1. Introduction

In 1975 Cladis and Torza [1] investigated the formation of 4-cyanobenzylidene-4′-*n*-octyloxyaniline (CBOOA), a liquid crystal with a very small smectic A–nematic latent heat, from a bent nematic liquid crystal. They showed that the smectic A phase is formed via an intermediate state, called a striped texture. This state consists of a corrugated layer of a bent nematic which is sandwiched between two smectic A layers whose planes are oriented in two different directions. As the temperature of the sample is further decreased, the striped texture becomes unstable. The corrugated layer undergoes axial buckling leading to the final smectic A with a honeycomb texture. Hinov *et al.* [2–8] elaborated further the results obtained by Cladis and Torza with a systematic study concerning the formation of various smectic phases from an electrically deformed nematic phase. We briefly summarize the main results obtained in these papers.

(*a*) The matching of the oriented smectic A phase, which is in the middle part of the sample, and the strongly deformed smectic A phase in the boundary

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regions are effected with the formation of various kinds of focal conics, edge dislocations or undulations of the smectic A planes.

(*b*) The value of the surface energy of the smectic A director is determined for glass surfaces treated with silicon monoxide to achieve planar orientation of the director and lecithin to achieve homeotropic orientation of the director.

(*c*) The quality of the smectic scattering centres was considerably improved; these scatterings centres might be used in thermally addressed liquid crystal displays.

(*d*) New electrooptic effects were discovered in the smectic phases.

An important problem which still requires solution in clarification of the role of the transitional order on the formation of the smectic phases.

## 2. A brief review on the systems investigated

The method proposed by Cladis and Torza can be applied when the latent heats for the smectic A–nematic, smectic B–nematic and smectic C–nematic, transitions are very small in comparison with thermal energies. The liquid crystals investigated with the elaborated method of Hinov *et al.* [2–8], the latent heat for the smectic A–nematic or smectic C–nematic transitions, the possible order of the phase transitions and the relevant literature are given in the table. The influence of the transitional order on the formation of the smectic A and smectic C phases from the preceding strongly deformed nematic phase is not clear from the data presented in this table. This question might be easily elucidated by studying the formation of the smectic A, B and C, phases of two liquid crystals which should be from one and the same homologous series and should have either a typical smectic A–nematic, smectic B–nematic and smectic C–nematic, first order transition or a typical smectic A–nematic, smectic B–nematic and smectic C–nematic, second order transition.

Survey of results.

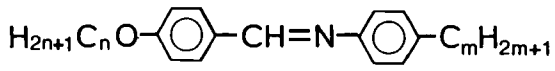
| Liquid crystals and phase transition | Latent heat/kJ mol | Possible order of the phase transition | References |
|---|---|---|---|
| CBOOA | | | |
| Smectic A–nematic | 0·126 | First order | [9] |
| | 0·084 | Weakly first order | [10] |
| | 0·210 | Weakly first order | [11] |
| 8CB | | | |
| Smectic A–nematic | 0·126 | Nearly second order | [12] |
| | 0·200 | Weakly first order | [13] |
| | 0·040 | Very weakly first order | [14] |
| | 0–0·010 | Second order | [15] |
| | 0–0·0004 | Second order | [16] |
| | 0·0000 | Second order | [17] |
| NPOOB/NPOB | | | |
| Smectic A–nematic | 0·092 | Weakly first order | [18] |
| | 0·214 | First order | [19] |
| | 0·200 | Not indicated | [20] |
| NOBA | | | |
| Smectic C–nematic | 1·680 | Not indicated | [21] |

The anomalous latent heat measured at a second order phase transition according to various authors is due to an overestimate because of the smearing of the peaks.

## 3. Formation of the smectic A, B and G phases of 6O.4 and the smectic A and B phases of 4O.8 from the preceding electrically deformed homeotropic nematic phase

### 3.1. *Compounds and sample preparation*

We have used two members of the homologous series 4-*n*-alkoxybenzylidene-4′-*n*-alkylanilines designated usually by *n*O.*m* which are simple Schiff's bases with the structural formula [22]



The liquid crystal 6O.4 has a typical smectic A–nematic first order transition [23–25] while the liquid crystal 4O.8 has a smectic A–nematic transition which is nearly second order [26, 27]. The latent heat for the smectic A–nematic transition has been measured for 6O.4 to be 5·447 kJ mol$^{-1}$ [25] versus 0·0005 kJ mol$^{-1}$ [28] for 4O.8. These two members of the homologous series *n*O.*m* have the following phases and transition temperatures:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6O.4: | $S_G$ | 56°C | $S_B$ | 58°C | $S_A$ | 69·1°C | N | 77·3°C | I |
| 4O.8: | C | 33°C | $S_B$ | 49°C | $S_A$ | 64·5°C | N | 79·0°C | I |

We have used a sample preparation described in detail elsewhere [2]. The tin oxide coated glass plates confining the liquid crystal were previously rubbed with a diamond paste and treated with an ethanolic solution of 1 wt % of lecithin. This combined treatment prevents the formation of reverse tilted walls. The thickness of the liquid crystal layers was determined by teflon spacers with a thickness of 20 $\mu$m. The orientation of the nematic director determined by the lecithin coating was homeotropic. The smectic phases were observed and examined with light polarizing microscope on free cooling of the nematic phase or with the use of an oven.

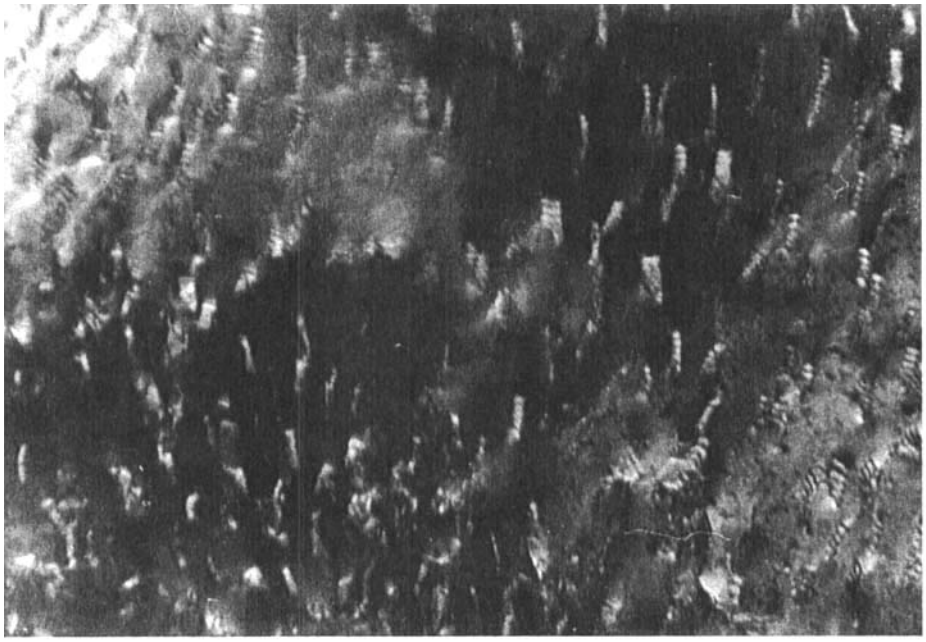
### 3.2. *Experimental results*

The formation of smectic textures from an electrically deformed nematic phase has been described in detail elsewhere [2–8]. We note only that the application of an AC voltage above threshold leads to the orientation of the nematic director in the middle part of the cell and to strong distortion in the boundary regions. The smectic phase was observed on free cooling of the nematic phase or with the use of an oven. After the formation of the smectic A phase the voltage was removed.

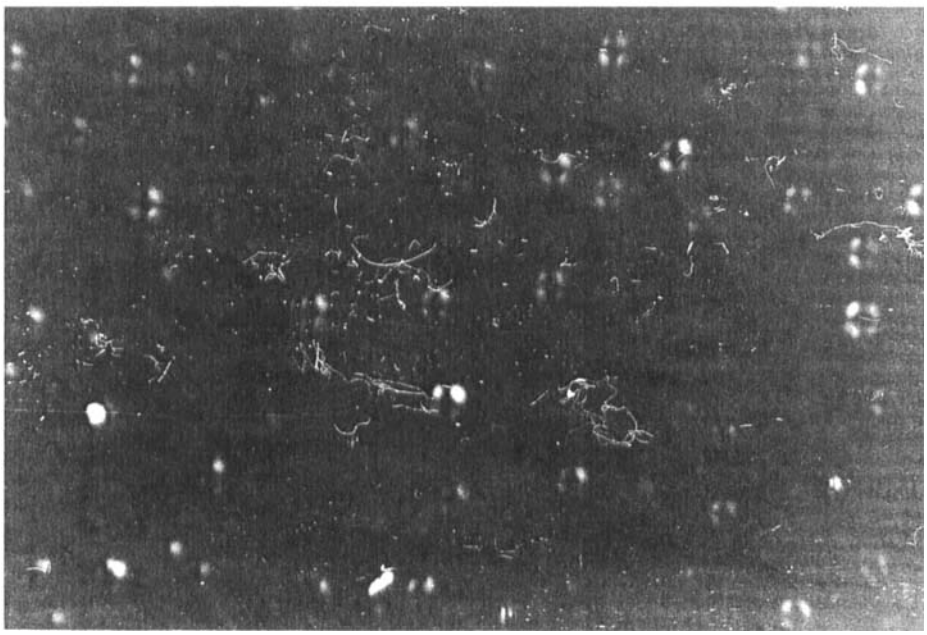
The dielectric properties of 6O.4 and 4O.8 have not been studied. There is no available information for the dielectric anisotropy of either liquid crystal. Applying an electric field with a frequency of 5 kHz up to the appearance of the Fréedericksz transition we have found that the dielectric anisotropy of 6O.4 and 4O.8 is negative. The threshold voltage $U_{th}$ measured with a Textronix oscilloscope was approximately 9–10$V_{rms}$. A voltage of $2U_{th}$, $5U_{th}$ and $10U_{th}$ was applied across the nematic phase. The various smectic phases of both liquid crystals were observed under a polarizing microscope in transmitted white light.

The type of the smectic A–nematic transition is of great importance for the appearance of the smectic phase which is in close relation with the pretransitional behaviour and the influence of the boundary conditions. For example, the appearance of the smectic A phase in both liquid crystals with initial homeotropic orientation of the nematic director is quite different. We have observed the formation of an oriented smectic A phase for 6O.4 with nearly planar orientation of the director and nearly

vertical position of the smectic A planes with respect to the glass plates, accompanied by the creation of isolated focal conics with an elongated form. 4O.8, however, we have observed the formation of an oriented smectic A phase with homeotropic orientation of the director and planar position of the smectic A planes accompanied by the creation of isolated circular line focal conics. These drastic changes were preserved in the smectic B phase with transformation of the smectic A textures into paramorphic smectic B textures while the smectic G phase of 6O.4 has a typical mosaic texture. The drastic changes in the formation of the smectic phases of 6O.4 and 4O.8 were enhanced with the application of an electric field which causes a Fréedericksz transition in the homeotropic nematic phase of both liquid crystals. The application of a voltage of $2U_{th}$ creates isolated striped regions embedded in the oriented smectic A phase with nearly planar orientation of the director of 6O.4 as shown in figure 1 (*a*) while the smectic A texture of 4O.8, as shown in figure 1 (*b*), was unchanged. In the smectic B phase of 4O.8 we observed only a slight change in the circular line focal conics. Increasing the voltage to $5U_{th}$ lead to the formation of quite different textures of the smectic phases. The smectic A–nematic first order transition of 6O.4 was revealed by the creation of complex smectic A dislocations arising directly from the nematic phase as observed by Williams and Kléman [29]. This remarkable transition is shown in figure 2 (*a*). The unstable smectic A dislocations were transformed into many parabolic focal conics studied in detail by Rosenblatt *et al.* [30]. The parabolic focal conics are shown in figure 2 (*b*). They were more visible near the smectic A–nematic transition. They indicate the planar position of the smectic A planes. On further cooling, smectic B–smectic A transitional stripes appeared as shown in figure 2 (*c*). The smectic A–nematic nearly second order transition of 4O.8 was revealed by the creation of the pretransitional stripes observed by Cladis and Torza which were transformed in the final smectic A texture shown in figure 2 (*d*) (the stripes can be seen in the paper by Cladis and Torza [1] or in plate 197 in the book by Demus and Richter [31]). A similar texture has been designated by Cladis and Torza [1] as honeycomb while Demus and Richter [31] have described this structure as diffuse disclination lines exhibiting a zig-zag folding. The smectic A and smectic B textures were clearly related with the rate of cooling. On free cooling of cells with the 4O.8, a number of smectic A and smectic B textures were formed containing various irregularities, dislocations and undulations of the smectic planes arising from typical schlieren textures of the nematic phase. Such typical smectic A and smectic B textures are shown in figures 2 (*e*) and (*f*), respectively. According to Demus and Richter [31] the smectic A undulations disappear in the smectic B phase which is evident on comparison of figures 2 (*e*) and (*f*). Raising the voltage further to $10U_{th}$ lead to the creation of new interesting smectic textures. On free cooling, the smectic A phase became undulated for both liquid crystals; this is illustrated in figures 3 (*a*) and (*b*) while heating of the smectic A phase of 6O.4 in the nematic phase lead again to the creation of parabolic focal conics shown in figure 3 (*c*). Cooling into the smectic B phase of the same liquid crystal lead to the disappearance of the stripes. On slow cooling, using an oven the smectic A phase of 4O.8 appeared as regular dislocations, shown in figure 3 (*d*), which according to Williams and Kléman [32] are created near the boundaries. Similar dislocations being called elongated structures, have been observed by Marignan *et al.* [33] in a smectic A phase under mechanical shear. Novel herringbone dislocations were observed in the smectic G phase of 6O.4; they are shown in figure 4. To our knowledge, such dislocations have not been observed previously.

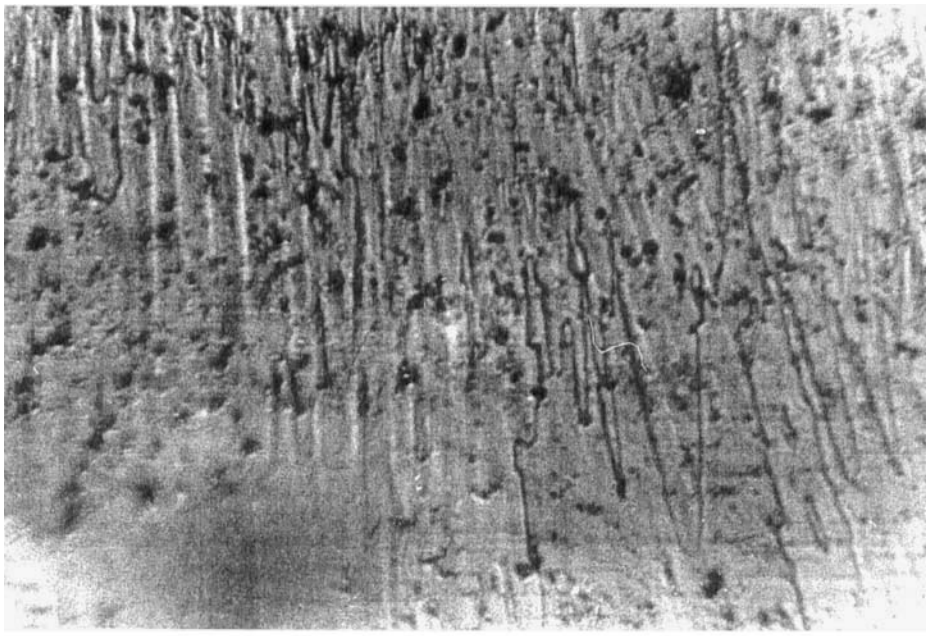


(*a*)



(*b*)

Figure 1. Smectic A textures obtained on free cooling of an electrically deformed homeotropic nematic with a thickness of 20 $\mu$m. A voltage of $2U_{th}$ was applied, where $U_{th} = 10V_{rms}$, $f = 5$ kHz; the long side of the photo corresponds to 475 $\mu$m. (*a*) Smectic A phase of 6O.4: striped regions embedded in a planar smectic A phase, P $\perp$ A. (*b*) Smectic A phase of 4O.8: circular line focal conics embedded in a homeotropic smectic A phase, P $\perp$ A.



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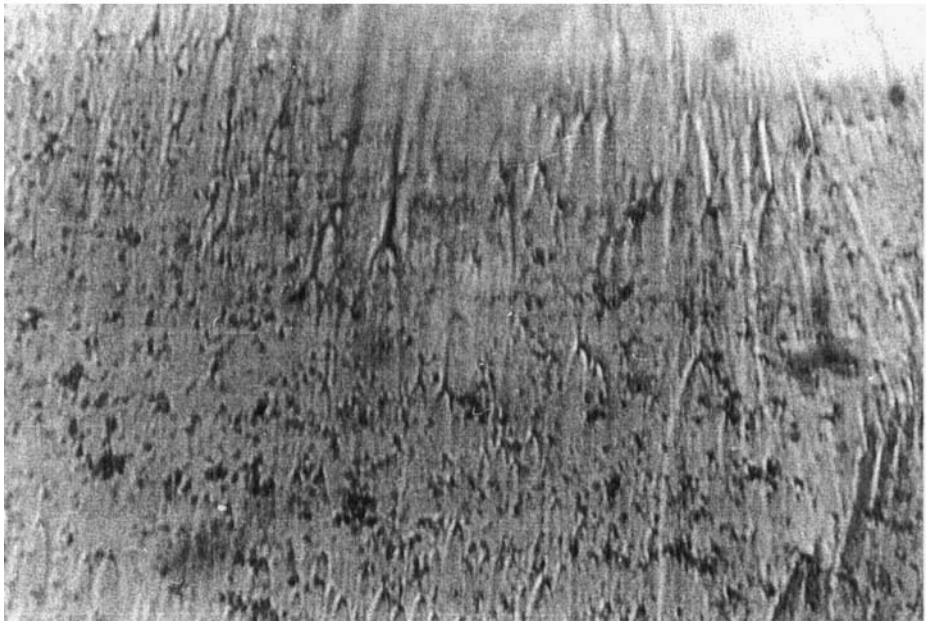
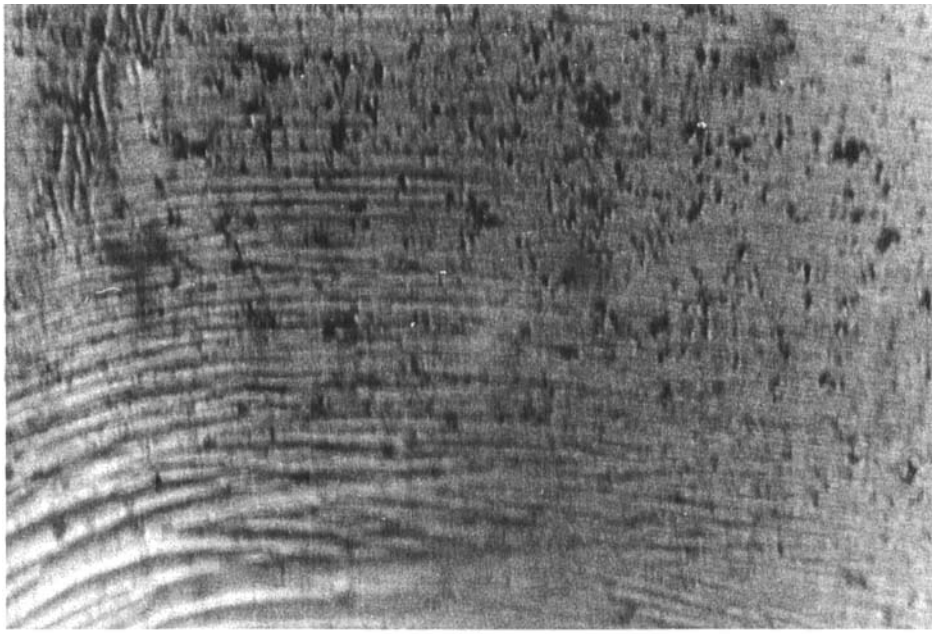


(*b*)

Figure 2.



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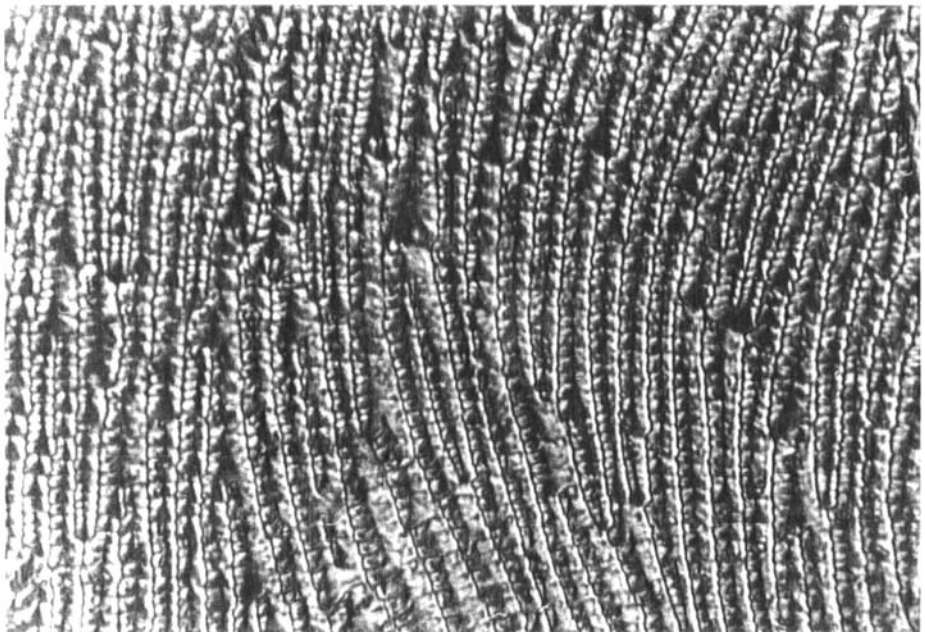
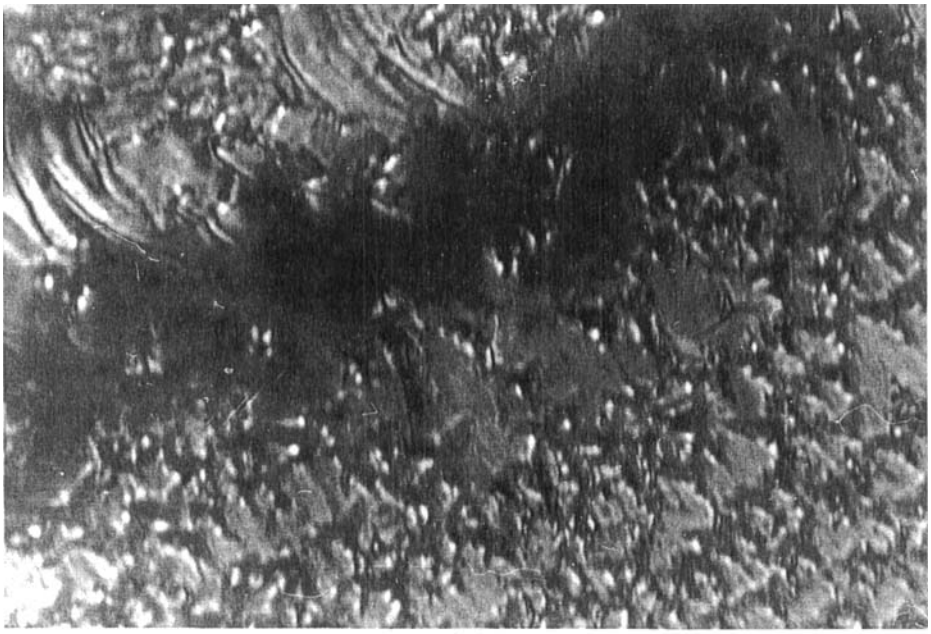
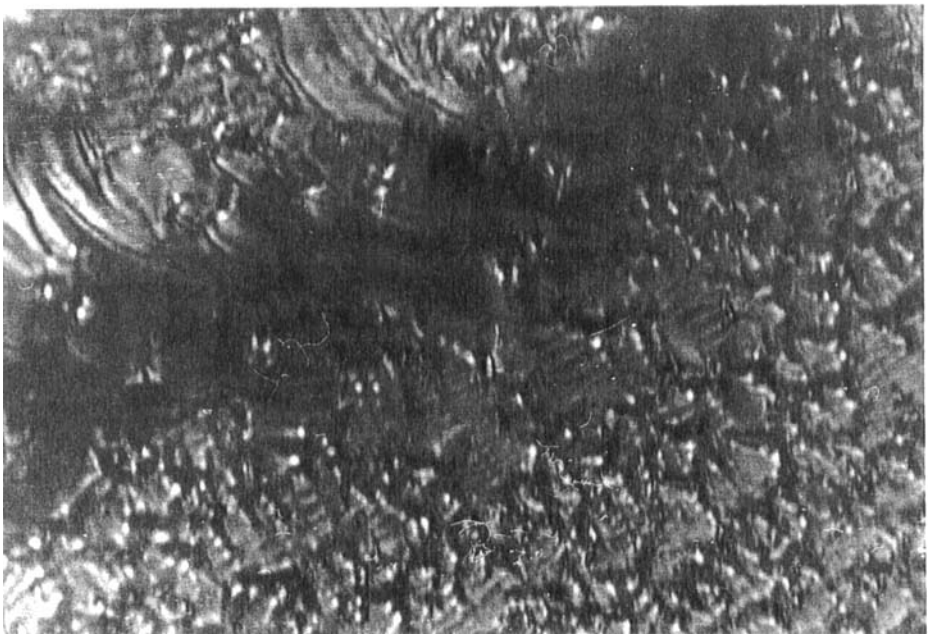


(*d*)

Figure 2.



(*e*)

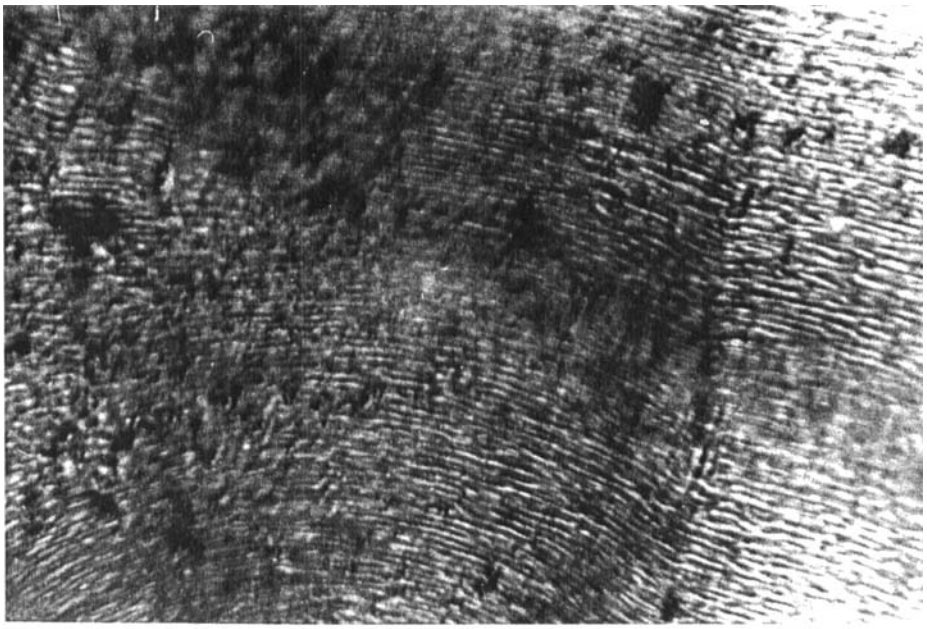


(*f*)

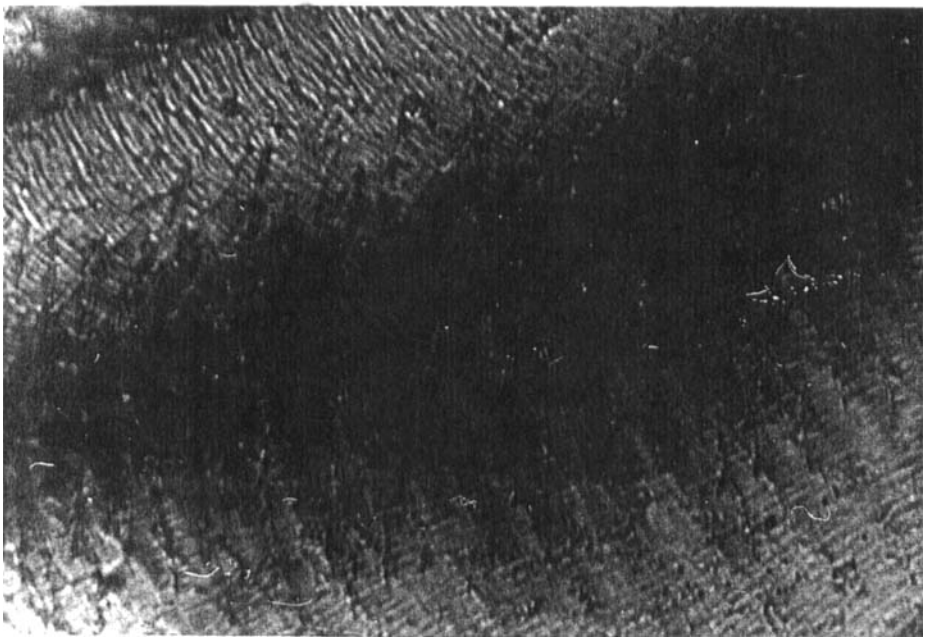
Figure 2. Smectic A and smectic B textures obtained from an electrically deformed homeotropic nematic 20 $\mu$m thick. A voltage of $5U_{th}$ was applied, where $U_{th} = 10V_{rms}, f = 5$ kHz; the long side of the photo corresponds to 475 $\mu$m. (*a*) Smectic A–nematic phase boundary in 6O.4: smectic A dislocations and electrically deformed nematic on free cooling of the sample, P ∥ A. (*b*) Smectic A parabolic focal conics in 6O.4 near the smectic A–nematic transition on heating the sample, P ∥ A. (*c*) Transitional stripes near the smectic B–smectic A transition in 6O.4 obtained on heating the sample, P ∥ A. (*d*) Honeycomb smectic A texture in 4O.8 obtained on slow cooling of the sample with an oven, P ∥ A. (*e*) Smectic A complex texture in 4O.8 with many irregularities, stripes and dislocations obtained on free cooling of the schlieren nematic texture, P ⊥ A. (*f*) Smectic B complex texture obtained from the previous texture on free cooling: disappearance of the stripes, P ⊥ A.

### 3.3. *Discussion of the experimental results*

Many of the physical problems concerning the formation of the smectic A phase from an initially deformed nematic have been already clarified [1–8]. The experimental results are discussed, in this part of the paper, in a more physical fashion. A clear distinction is made between effects particular to the alignment technique and those

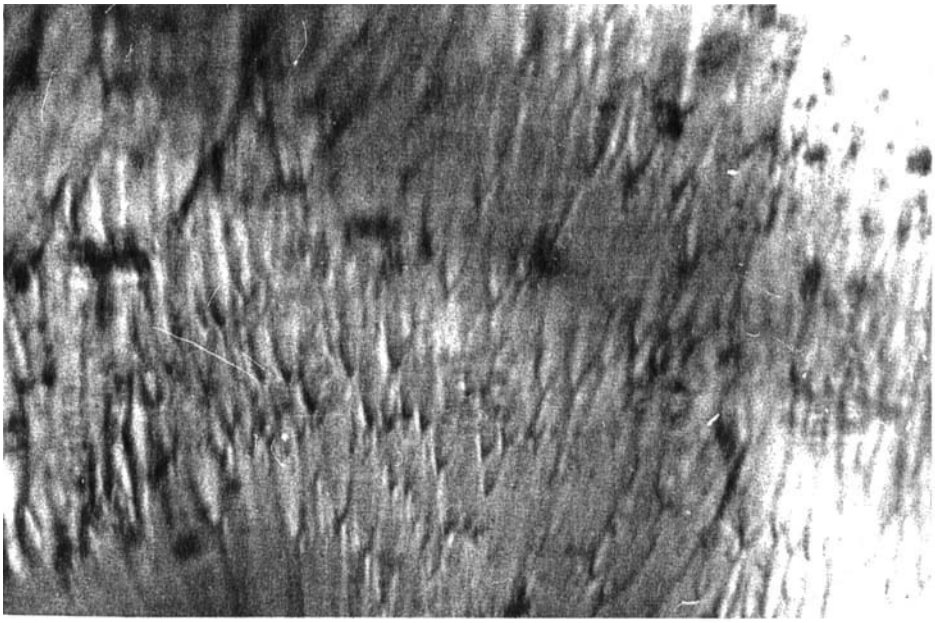


(*a*)

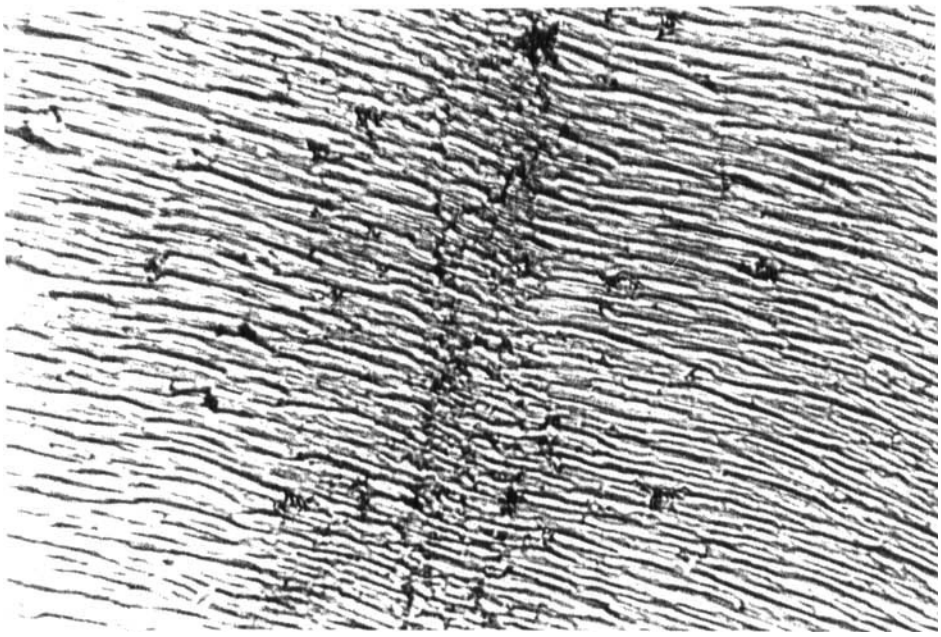


(*b*)

Figure 3.



(*c*)



(*d*)

Figure 3. Smectic A and smectic B textures obtained from an electrically deformed homeotropic nematic. A voltage of $10U_{th}$ was applied, where $U_{th} = 10V_{rms}$, $f = 5$ kHz; the long side of the photo corresponds to 475 $\mu$m: (*a*) Smectic A phase with undulations in 6O.4 obtained on free cooling the sample, P $\perp$ A. (*b*) Smectic A phase with undulations in 4O.8 obtained on free cooling of the nematic schlieren texture, P $\perp$ A. (*c*) Smectic A parabolic focal conics obtained in 6O.4 on heating the sample near the smectic A–nematic transition P $\parallel$ A. (*d*) Regular smectic A dislocations formed near the boundary in 4O.8 on slow cooling with an oven, P $\perp$ A.

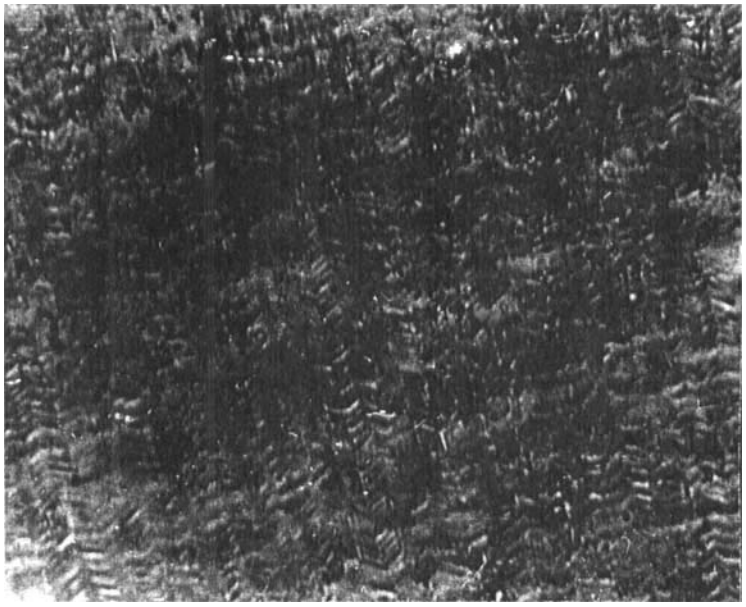


Figure 4. Smectic G herringbone zig-zag dislocations in 6O.4 obtained from an electrically deformed homeotropic nematic phase. A voltage of $10U_{th}$ was applied, where $U_{th} = 10V_{rms}$, $f = 5$ kHz; the long side of the photo corresponds to 423 $\mu$m, P ∥ A.

attributable directly to the size of the discontinuity in the physical parameters near the smectic A–nematic transition.

3.3.1. *Influence of the discontinuity in the physical parameters at a nearly second order smectic A–nematic transition*

The smectic A–nematic transition is widely studied because in many liquid crystals it is weakly first order or nearly second order [34–36]. In the basic theory of the smectic A–nematic transition given by de Gennes [37], the elastic energy, in analogy with the normal metal–superconductor transition, consists of two parts: the Frank elastic energy and the de Gennes elastic energy of the smectic A expressed with a complex order parameter $\psi$. De Gennes has shown that the coupling between the fluctuations of the nematic director and the smectic A complex order parameter leads to an apparent increase in the magnitude of the bend elastic constant $K_{33}$ and the twist elastic constant $K_{22}$ which diverge at the phase transition [37–40]

$$K_{33} = K_{33}^0 + (ckT\zeta_{\parallel}/d^2), \quad K_{22} = K_{22}^0 + (ckT\zeta_{\perp}^2/d^2\zeta_{\parallel}),$$

where $\zeta_{\parallel}$ is the smectic A correlation length parallel to the director, $\zeta_{\perp}$ is the smectic A correlation length perpendicular to the director, $c$ is a constant of order unity and $d$ is the smectic interlayer spacing.

According to a dynamic Landau theory developed by Jänig and Brochard [39] using the helium analogue and by McMillan [41] using the mean field approximation when the liquid moves across the smectic planes, molecules must jump from one smectic plane to the next. This process is dissipative and results in a viscous drag of the smectic A planes on the fluid and a new viscosity coefficient $\gamma_3$. When the director is rotated, the rotational viscosity term $\gamma_1$ diverges near the smectic A–nematic

transition [40]

$$\gamma_1 = \gamma_1^0 + (c'\gamma_3 kT\zeta/c_\parallel),$$

where $c_\parallel$ is the coefficient of the longitudinal kinetic energy of the smectic order parameter. Some of the other viscosity coefficients of the nematic connected with the bend and/or twist reorientations of the director also diverge. According to McMillan [40], the helium analogue should provide the correct critical behaviour when the dimensionless coupling constant $kT\zeta/K_{33}^0 d^2$ is small, i.e. far from the phase transition (according to McMillan this range is $T - T_c > 1$°C in CBOOA; from the literature it is known that this temperature range is much smaller). This is the so-called precritical regime. In the critical regime where the coupling constant is large, the transition may be first order as pointed out by Halperin *et al.* [42]. The physical picture according to McMillan is as follows, the transition is suppressed by thermal fluctuations which also carry an essential entropic contribution. On the other hand, in the smectic A phase bend and twist are forbidden and the apparent transition temperature is higher. According to McMillan it is a delicate question whether or not the stiffening of the elastic constants is strong enough to force a continuous suppression of the director fluctuations. Halperin *et al.* [42], using the Wilson theory, have shown that the stiffening of the elastic constants is not strong enough to suppress continuously the thermal fluctuations of the director, the dimensionless coupling constant is of order unity and the transition should be first order.

Many of the effects predicted theoretically have been observed experimentally. Most of the work is on CBOOA. For example, Hardouin *et al.* [43] have measured the magnetic susceptibilities $\chi_\parallel$ and $\chi_\perp$ and have found a small jump at the first order smectic A–nematic transition. The divergence of the bend elastic constant has been observed by means of a magnetically induced elastic deformation (Fréedericksz transition) [9, 44, 45] while the twist elastic constant has been studied by quasi-elastic light scattering [46–48]. The diverging transport coefficient (the twist viscosity) has been studied by ultrasonic [45] and via a dynamical Fréedericksz transition [49]; the dynamics of the twist director mode and the dynamics of the bend mode [47, 50, 51] have been studied by light scattering. The pretransitional behaviour of the surface tension and the viscosity coefficients have also been investigated by light scattering measurements [52]. Volumetric study of the smectic A–nematic transition has been performed by Torza and Cladin [53]; their observations show a small discontinuity in the density at the transition.

To summarize, the mean field theory of McMillan [54] and the helium-like analogue of de Gennes [37] predicted that the smectic A–nematic phase transition can be second order under certain conditions: the nematic range and the coupling between the nematic and smectic A fluctuations. Measurements of the various physical quantities performed on CBOOA above and below the smectic A–nematic transition undoubtedly show strong pre and post-transitional effects. On the other hand, it is shown in the table that the smectic A–nematic transition for CBOOA, 8CB and NPOOB has been recognized as first order, weakly first order, very weakly first order, nearly second order, second order. In addition, the interpretation of DSC data can often be confusing as claimed by Navard and Haudin [55]. For example, they have pointed out that the smectic A–nematic transition for 4-*n*-octyl-4′-cyanobiphenyl (8CB) is second order using a new method for the interpretation of the DSC data (for comparison see the table). On the other hand, the type of phase transition will certainly change under the influence of external forces such as electric and/or magnetic fields, or in the

presence of many defects. Here we must mention the defect model by Helfrich [56] extended by many authors (see the references in [57]). Special attention should be paid to the theoretical results by Ranganath [58] who claimed that beyond a critical distortion at any given temperature a second order transition should occur. Halperin and Lubensky [59] elaborated additionally the theory by de Gennes making closer the analogy between a smectic A liquid crystal and a superconductor, including a gauge transformation on the smectic system. In this way they have clarified that really the smectic A–nematic transition should be at least weakly first order.

Our experimental results undoubtedly show that the type of phase transition can also be recognized by texture observations. The formation of stripes at the weakly first order (nearly second order) smectic A–nematic transition concerns pretransitional effects in the nematic phase. As noted, 4O.8 has a very small latent heat around the smectic A–nematic transition, measured to be 0·0005 kJ/mol [28]. The measurements of the band elastic constant by Léger [60] and by Känel and Litster [61] indicate also the nearly second order character of the transition. In addition, it has been discovered by a number of groups [28, 62–64] that 4O.8 exhibits a smectic A–nematic transition which is second order to within $\pm 3$ mK.

3.3.2. *Influence of the bend deformation in the boundary regions on the nearly second order smectic A–nematic transition for 4O.8*

de Gennes has shown [37, 65] that the analogue of the Meissner effect at the superconducting transition ($\mathrm{rot}\, A = h$ expelled from a type I superconductor) is the expulsion of the twist and bend deformation at the smectic A–nematic transition. The stripe patterns observed by many authors at a nearly second order smectic A–nematic transition [60, 66, 67] and explained in detail by Cladis and Torza [1] are evidently connected with the enhancement of the bend and twist elastic constants due to the coupling between the smectic order parameter and the director field [37–39, 68, 69]. It is important to note that similar stripe patterns have been observed at weakly first order smectic C–nematic transitions [70–72] due to the enhancement of the splay, twist and bend elastic constants [73]. Chu and McMillan [74] attempted to explain the elastic behaviour of the nematic near the second order smectic A–nematic transition taking into account the coupling between the smectic order parameter and the director field. Their analysis has shown that the bend elastic energy $K_{33}(n \times \mathrm{rot}\, n)^2$ should be replaced by $K_{33}/n \times \mathrm{rot}\, n|^{3/2}$ which leads to a first order Fréedericksz transition. Their model cannot explain, however, the appearance of the strips instability. Furthermore, the magnetic field induced bend-splay deformation experiment by Majoros *et al.* [75] near a continuous smectic A–nematic transition clearly indicated that the linear elastic theory of Frank is still valid just before the appearance of the stripes. The stripe domains have been studied by Gooden *et al.* [76] with the aid of light-scattering measurements. Their experimental results show that the stripes appear at $B_c$ when $T - T_c \lesssim 0{\cdot}06$ K, and not at all for $T - T_c > 0{\cdot}06$ K. They found that for magnetic fields at an angle $\theta$ from the perpendicular the stripe threshold is higher than $B_c$ by an amount which decreases with $T - T_c$ until $B_c$ and the stripe boundary are concurrent for $T - T_c = T(\theta)$. For even slight deviations from $\theta = 0$ the decrease in $T$ is quite dramatic.

All theoretical and experimental results for the pretransitional behaviour at weakly first order (nearly second order) smectic A–nematic transitions including the experimental results in [1–8] and those in our study show that the inclusion of twist or bend in liquid crystals with a very small smectic A–nematic transitional enthalpy

compared to the thermal energy enlarges the temperature interval of the critical behaviour. For the case of a second order smectic A–nematic transition which has been evidenced for 4O.8 the inclusion of bend or twist changes the second order of the phase transition to weakly first order. Consequently we suggest that a second order phase transition in an applied field which leads to bend or twist distortions has a two phase region. This corresponds to the existence of the intermediate state of type I superconductors as noted by de Gennes [37, 65]. The coexistence of the smectic and nematic phase near the smectic A–nematic transition is described in detail by Cladis and Torza [1] and is strongly evidenced also in the experiment with twist [7]. From all of the experimental results concerning the stripe domains it is obvious that the interfacial energy between the smectic A and nematic is negligible for weakly first order transitions. This small interfacial energy permits the easy undulation of the smectic A–nematic interface. For typical first order smectic A–nematic transition as that of 6O.4, the interfacial energy is strong enough and permits the experimental observation of a remarkable smectic A–nematic interface. We clarify that in the latter case the interface is in the plane of observation and shows the temperature gradient.

3.3.3. *Influence of the boundary conditions*

As mentioned previously, the initial orientation of the nematic layer for both liquid crystals was homeotropic. The rubbing technique together with lecithin coating ensured good homeotropic alignment of the nematic. In this way, the Fréedericksz threshold is not accompanied by the creation of reverse-tilted walls. The surface anchoring in both the nematic and smectic A phases is nearly equal: $10^{-2}$–$10^{-3}$ erg/cm$^2$ [3]. Our experimental results show unambiguously that for 4O.8 we obtain a good homeotropic orientation of the smectic A director even with the application of a small electric field, as shown in figure 1 (*b*). In our opinion this experimental result is probably connected with the formation of one or several smectic A layers at the glass plates due to the negligible latent heat whereas the other liquid is in the nematic state. Such a formation of a single smectic A layer at a free boundary has been observed in 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) [77], a liquid crystal with a second order smectic A–nematic transition [78]. For 6O.4 we observed, surprisingly, that the usual formation of the smectic A planes is planar. Our explanation is connected with possible bulk formation of the smectic A phase due to the first order character of the transition and the large latent heat connected with it.

To summarize, the type of smectic A–nematic transition which is either a first order with a large latent heat (6O.4) or nearly second order (4O.8) has a crucial role for the kind of smectic textures formed from an undeformed or a strongly deformed nematic after cooling. We conclude the experimental results as follows.

(*a*) The influence of the boundary conditions determining the homeotropic orientation of the nematic director is significant for the liquid crystal 4O.8 and insignificant for 6O.4.

(*b*) The influence of the bulk electric torques is less important for a low value of the voltage, in the range of $U_{th}$ or $2U_{th}$, and more important for a higher voltage.

(*c*) The rate of cooling is also significant for the smectic textures.

The smectic textures shown on the microphotographs have been formed under the combined action of the transitional order, the influence of the boundary conditions, the influence of the bulk electric torques and the rate of cooling/heating. The drastic changes in the smectic textures of both liquid crystals can be recognized by the

existence or absence of pretransitional effects near the smectic A–nematic transition and from the smectic textures. For instance, the formation of the smectic A phase from an electrically deformed nematic phase of 6O.4 had a clear separation of both phases without any coexistence at a given temperature while the formation of 4O.8 was with the creation of pretransitional stripes and the coexistence of the both phases in the bulk.

## 4. Conclusions

The method for the creation of smectic phases from a deformed nematic phase proposed by Cladis and Torza [1] and elaborated by Hinov *et al.* [2–8] has been applied to two members of the homologous series *n*O.*m*, namely 6O.4 with a typical first order smectic A–nematic transition and 4O.8 with a nearly second order smectic A–nematic transition. The experimental study carried out with polarizing microscope showed unambiguously the crucial role of the transitional order for the formation of the smectic phase from an electrically deformed nematic. The formation of the smectic A phase of 6O.4 was with a clear smectic A–nematic phase boundary accompanied with a weak influence of the initial homeotropic orientation of the director in both phases. In contrast the formation of the smectic A phase of 4O.8 was similar to that observed by Cladis and Torza [1]: coexistence of the nematic and smectic A phases, strong pretransitional behaviour and formation of well defined stripes. It is remarkable that the type of phase transition is crucial for the formation of the smectic A phase also from a undeformed homeotropic phase. The kind of smectic A textures observed clearly showed that the homeotropic orientation of the director is crucial for 4O.8, a liquid crystal with a nearly second order smectic A–nematic transition and insignificant for 6O.4, a liquid crystal with a typical first order smectic A–nematic transition.

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