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To cite this version:
M. Petrov, A. Braslau, A. Levelut, G. Durand. Surface induced transitions in the nematic phase of 4-n octyloxybenzoic acid. Journal de Physique II, EDP Sciences, 1992, 2 (5), pp.1159-1193. <10.1051/jp2:1992194>. <jpa-00247700>

HAL Id: jpa-00247700
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Submitted on 1 Jan 1992

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Surface induced transitions in the nematic phase of 4-n octyloxybenzoic acid

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(Received 28 May 1991, revised 15 October 1991, accepted 9 January 1992)

Résumé. — L’acide octyloxybenzoïque (ainsi que l’heptyl et le nonyl) présente des phases cristal liquide nématic et smectique C. En utilisant la microscopie optique en lumière polarisée et la diffraction des rayons X, on mesure l’orientation et l’ordre près de la surface d’un monocristal nématic orienté par des lames de verre évaporées SiO. En température décroissante, on observe une rotation spontanée et la bifurcation de l’orientation de surface, une instabilité texturale induite par la surface, et la croissance de couches et de bâtonnets smectiques A près de la surface. Ces transitions pourraient être expliquées par une augmentation de la concentration des monomères à la surface. La baisse corrélée de l’ordre nématic permettrait la croissance de surface du smectique A plutôt que C. La rotation de l’orientation de surface et l’instabilité de texture pourraient être les premiers exemples des instabilités flexoelectriques de surface récemment prédites.

Abstract. — The heptyl-, octyl- and nonyl-benzoic acids present dimerized nematic and smectic C liquid-crystal phases. Using polarized optical microscopy and X-ray scattering, we have measured the orientational and positional order close to the surface of the nematic single-crystal, oriented between SiO evaporation-coated glass plates. Decreasing the temperature, we observe a spontaneous twist and bifurcation of the surface orientation, a surface induced texture instability and the growth of a surface layer with "batonnets" of smectic A. These transitions are tentatively explained by an increase of the surface monomer concentration. The correlated decrease of surface nematic order would allow for the growth of surface smectic A rather than C. The surface twist and textural instability could be the first examples of recently predicted surface flexoelectric instabilities.

1. Introduction.

The physical properties of the nematic phase preceding a smectic A or C phase are significantly different from those of a normal (classical) nematic. This pre-smectic phase is

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characterized by local (short-range) smectic order fluctuations. The correlation length of these smectic fluctuations increases in the low temperature nematic region, as demonstrated by X-ray investigations [1].

Such a nematic phase (preceding a smectic C phase) is found for the homologous series 4-n-heptyl-, octyl- and nonyl-oxybenzoic acids (HOBA, OOBA and NOBA). These substances, however, possess a peculiarity different from other nematics having short-range smectic order in that the molecules are cyclic dimers [2]; open dimers and monomers (in small percentages) can also exist in addition to the cyclic dimers in the nematic phases of HOBA, OOBA and NOBA [2, 3]. The short-range smectic order and the thermodynamical equilibrium between cyclic and open dimers and monomers obviously have a strong influence on the microstructure as well as on the macroscopical properties of the nematic phases in these substances. As a result, some anomalies in the temperature dependence of $\sigma_{\parallel}/\sigma_{\perp}$ for thick OOBA samples, aligned by a magnetic field, have been reported [4] ($\sigma_{\parallel}$ and $\sigma_{\perp}$ are the electrical conductivities parallel and perpendicular to the nematic director n, respectively). In addition, for very thin samples cells (< 50 μm) of HOBA, OOBA and NOBA in the nematic phase aligned by the walls, it has been demonstrated using textural analysis and depolarized light scattering that a definite temperature exists at which the texture and the depolarized, scattered light intensity change sharply [5, 6]. This temperature depends on the boundary conditions and divides the nematic phase into high and low temperature regions with different macroscopic properties. Recently, the existence of this transition in the nematic phase for the 4-n-alkyloxybenzoic acids has been independently confirmed [7]. For certain boundary conditions, the described phenomenon is enhanced, and a strong textural transition is observed. Up until now, however, the evolution of the textures has only been studied qualitatively, due to the difficulty in controlling the boundary conditions for the texture orientation. The purpose of the present investigation, with good control on the boundary conditions using SiO oblique evaporation at different angles of incidence to the substrate’s normal, is to characterize this phenomenon quantitatively.

2. Optical properties of textures.

In this section we first describe the methods used to determine the orientation of various textures of OOBA in samples held between glass plates that were, in most cases, treated by SiO evaporation [8]. We report the observed surface orientation, its temperature dependence and some other related phenomena such as surface instabilities and the surface-induced growth of smectic-like fingers or whiskers («batonnets»). A tentative analysis of these observations is finally presented.

2.1 EXPERIMENTAL METHODS.

2.1.1 Sample preparation. — The sample consists of a drop of OOBA (4-n-octyloxybenzoic acid) sandwiched between two SiO-evaporated glass plates. The phase transition temperatures of this compound are reported to be [4, 9]:

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$\leftrightarrow$</th>
<th>$\approx$</th>
<th>$\approx$</th>
<th>$\approx$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>$101.1^\circ$ C</td>
<td>N</td>
<td>$108^\circ$ C</td>
<td>I</td>
</tr>
</tbody>
</table>

In fact, the observed temperatures can vary widely from these values; for instance, we found that the N-I transition may be observed at any temperature ranging from 142 $^\circ$C to 146 $^\circ$C, the SC-N transition anywhere from 102 $^\circ$C to 106 $^\circ$C and the Crystal-SC transition from 90 $^\circ$C to 100 $^\circ$C. The reasons for these discrepancies are multiple: firstly, the absolute calibration of the Mettler FP-5 oven used in this study is no more accurate than 1 $^\circ$C, although a temperature resolution of better than 0.1 $^\circ$C can be obtained. Secondly, the sample may not
be completely pure; we do observe some effect of aging. The main reason is probably that all the transitions are strongly first-order and, thus, hysteretic. At the N-I transition, for instance, we observe the coexistence of the nematic and isotropic phases over an unusually wide temperature range of ~ 10 °C. This coexistence is not stable: after one day at constant temperature, a sample initially with N-I coexistence displays only the N phase. One explanation for this observation might be that impurities present in the material segregate in the I phase. After cooling, these impurities should reach a uniform concentration by diffusion; taking a typical diffusion coefficient of $D \sim 10^{-6} \text{cm}^2/\text{s}$, it would take $10^6 \text{s} (~1 \text{ day})$ to re-equalize the concentration between domains located 1 mm apart. Note that these impurities cannot be monomers or dimers of OOBA, since chemical equilibrium could be reached within molecular times. Effects related to the change in surface concentration of monomers shall be described below. In all that follows, unless otherwise specified, we shall describe the behavior of uniform phases.

The boundary glass plates which hold our sample were treated by oblique evaporation of SiO, a treatment which yields an oblique director orientation [8]. The evaporation angles (see Fig. 1) were $\alpha = 66^\circ, 70^\circ, 75^\circ, 80^\circ$ and $86^\circ$ with SiO nominal thicknesses of $\delta = 18.3 \text{ nm}, 19.3 \text{ nm}, 19.4 \text{ nm}, 19.1 \text{ nm}$ and $13.4 \text{ nm}$, respectively. The evaporation direction was noted on each plate. Samples either with parallel expected surface orientations $e$ and $e'$ (the «homogeneous» samples), as shown in figure 2a, or with antiparallel surface orientations $e$ and $e'$ (the «inhomogeneous» samples), as shown in figure 2b, were prepared. Since we were interested in the thickness (plate separation $d$) dependence of the texture orientation, we prepared not only uniform thickness samples in the range $10 \mu\text{m} \leq d \leq 100 \mu\text{m}$ using Mylar spacers, but also wedge samples (see Figs. 3a and 3b), where $d$ varies continuously from zero to the spacer (stainless steel cylindrical wire) thickness of $h = 50, 100$ or $200 \mu\text{m}$. The thickness $d$ is then calculated using $d = h \cdot x/L$ and by

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**Fig. 1.** — Oblique evaporation of SiO on the glass plates. P and $\alpha$ are the plane and angle of evaporation, respectively; $e$ is the evaporation direction and $\delta$ is the thickness of the obliquely evaporated layer.

**Fig. 2.** — Uniform thickness sample. $e$ and $e'$ are the evaporation directions and $d$ is the cell thickness. (a) Homogeneous orientation and (b) non-homogeneous orientation.
measuring the relative distance \( x/L \) of the point of observation \( x \) to the wedge corner (\( L \) is the total distance to the wire spacer). A steel spring, placed as shown in figure 3, was used to mechanically squeeze the sample so that \( d \) be reasonably well defined over the total lateral size (~1 cm). To fill the sample, the empty cell of treated glass plates was placed in the Mettler FP-5 hot stage and the temperature set in the range of the isotropic phase. The sample crystallites were melted along the open sides of the sandwich and drawn in between the glass plates by capillary action. We systematically verified that the entire sandwich was filled with the isotropic liquid crystal sample.

2.1.2 Orientation analysis methods. — To analyse the orientation textures (defined by the usual director \( n \) with \( n^2 = 1 \)), one must determine the orientations of \( n \) on the two boundary surfaces, with the geometry defined in figure 4. The sample is illuminated with linearly polarized light, propagating normal to the glass plates (see Fig. 5) in a Leitz polarizing microscope. Because \( d \) and the birefringence \( \Delta n = n_e - n_o \) (\( n_e \) and \( n_o \) are the extraordinary and ordinary indices, respectively) are large, we can assume that we are always in the Mauguin wave-guide regime, i.e. the horizontal projections \( \phi \) and \( \phi' \) of \( n \) are the surface optical eigen-axes (see Figs. 4 and 6a) at the input and the output surfaces. \( \phi \) and \( \phi' \) can be determined by the measurement of the azimuthal rotations of the polarizer and analyzer of the microscope that result in optical extinction. Since, in practice, only the sample rotation stage and the analyzer allow accurate azimuthal angular measurements, it was found

![Fig. 3](image)

Fig. 3. — (a) Homogeneous wedge sample and (b) non-homogeneous wedge sample. \( d \) is the sample thickness at an arbitrary position, \( x \) and \( L \) are the distances of the observation point and the wire spacer to the wedge corner and \( h \) is the maximal thickness of the sample corresponding to the wire diameter.

![Fig. 4](image)

Fig. 4. — The geometry of the nematic director \( n \) at the boundary surfaces. \( \theta \) is the mean angle of the director \( n \) with respect to the vertical axis \( Z \) and \( \phi \) is the azimuth of \( n \).

![Fig. 5](image)

Fig. 5. — The propagation of linearly polarized light in the sample. \( P \) is the polarizer and \( A \) is the analyzer.
more convenient to fix the polarizer and to rotate the sample by $\phi$ and then to turn the analyzer by $\phi + \phi'$ (see Fig. 6b). In the extinct (crossed) position, the absolute angle between the polarizer and analyzer is thus $90^\circ + \phi + \phi'$.

The mean angle $\theta$ of the director $n$ with respect to the vertical $z$-axis can, in principle, be obtained by measuring the birefringence. Assuming that the director $n$ has a uniform orientation $\theta$ in the cell, the ordinary ray «sees» the optical index $n_o$; the extraordinary ray «sees» an optical index $n'$ given by:

$$ n'^{-2} = n_e^{-2} \sin^2 \theta + n_o^{-2} \cos^2 \theta. $$

The measured birefringence $\Delta n(\theta) = n' - n_o$ gives $\theta$ if $n_e$ and $n_o$ are known, which is not the case for OOBA. However, since most nematic liquid crystals have an ordinary index $n_o \sim 1.5$, we measured $\Delta n(90^\circ) = n_e - n_o$ and used $n_o = 1.5$ to calculate $n_e$, and, hence, to determine $\theta$ from $\Delta n$. This is equivalent to assuming the small birefringence law: $\Delta n(\theta) \sim \Delta n(90^\circ) \sin^2 \theta$. To measure $\Delta n$, we rotated the polarizer and analyzer by 45° away from the extinction directions previously determined (see Fig. 7a) and illuminated the sample with a Hg green ($\lambda = 0.546$ μm) filtered light. Fringes parallel to the wedge corner were observed (see Fig. 7b). The local texture birefringence is deduced from the local distance $\ell$ between two adjacent fringes as $\Delta n(\theta) = (\lambda / h) (L/\ell)$. A rotating compensator is then used.

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Fig. 6. — (a) Horizontal projections $\phi$ and $\phi'$ of the optical eigenaxis at the input and the output surfaces. (b) Absolute angle $(90^\circ + \phi + \phi')$ between the analyzer and the polarizer in the extinction position.

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Fig. 7. — (a) The birefringence $\Delta n$ measurement method. The polarizer $P$ and analyzer $A$ are each rotated by 45° with respect to the extinction positions. $\ell$ is the interfringe distance. (b) Fringes parallel to the wedge corner for a homogeneous sample with $\alpha = 86^\circ$. The magnification is $\times 125$. 
to determine, from the shift direction of the fringes, the absolute orientation of the long molecular axis, defined as the $n_e$ optical field direction.

In some cases, to check the relative orientation of $n$ compared to the evaporation direction, we tilted the sample by a few 10 or 15° about the X-axis (see Fig. 4). From the increase of the decrease in the absolute birefringence, one can distinguish between the two possible director orientations $n$ and $n'$ of same $n_z$ component, with the two azimuths $\phi$ and $\phi + \pi$ (see Fig. 8) which give the same birefringence as for normal incidence.

![Figure 8](image)

**Fig. 8.** — Method to determine the relative orientation of $n$ compared to the evaporation direction, as described in the text.

2.2 **Texture description in OOBA.** — OOBA presents a wide variety of unusual textures in its nematic phase. We first describe these textures and their hysteretic behavior. More quantitative measurements are presented after.

2.2.1 **Texture observations.** — We first prepared a sample in between two glass plates, coated by SiO evaporated at $\alpha = 86^\circ$ and $\delta = 13.4$ nm, with parallel evaporation directions, as in
figure 3b. The sample was a wedge cell with a $h = 50 \, \mu m$ spacer. The nematic phase was homogeneous with its director $n$ tilted along the evaporation direction, i.e. $\phi = \phi' = 0$ (see below for the determination of $\theta$). We call this the normal tilted texture (NTT) which appears uniformly black when observed between the crossed polarizers along X and Y. Upon cooling, at a temperature $T^* = 125 \, ^\circ C$ (for an observation point with a sample thickness of $d \sim 30 \, \mu m$), we observe the rapid onset of a nematic scattering texture (NST), shown in figure 9. This new texture is completely different and quite unusual: the nematic phase is highly distorted with a characteristic length in the range of $\mu m$ or below, beyond the limit of resolution of the microscope. Keeping $T$ below $125 \, ^\circ C$, but without entering the lower-temperature $S_c$ phase, the NST is stable. To erase this NST, one has to heat the sample to a temperature $T^+ = 133.5 \, ^\circ C$, well above $T^*$. Above $T^+$, one restores the original uniform NTT with $n$ oblique, tilted along the evaporation direction. Cooling, one again finds the onset of the NST at $T^*$. This cycling between the NTT and the NST can be repeated many times. The hysteretic behavior indicates that the NST results from the NTT as a first-order transition, and $T^*$ depends on the thickness $d$. We shall discuss this thickness effect later.

Upon further cooling of the NST, one observes the normal $N \rightarrow S_c$ transition at $T = 105 \, ^\circ C$ as a small, yet unambiguous rearrangement of the NST, becoming a smectic scattering texture (SST). Heating again, one observes the melting of the SST to the NST at $T = 106 \, ^\circ C$, i.e., a very small change in textural aspect. Absolutely nothing happens at $T = T^*$, and one must again heat up to $T^+$ to re-observe the vanishing of the NST and then onset of the transmitting, non-scattering NTT.

However, the passage into the bulk smectic C phase has changed the nature of the surface layer. The novelty is that, now, upon cooling below a temperature $T_\phi = 128 \, ^\circ C$, this nematic texture is constituted of twisted domains (see Fig. 10), with twists $\phi$ and $\phi'$, the magnitudes of which are temperature dependent. These domains can present very well-defined edges separating regions of constant $\phi$ and $\phi'$, or may show a more-or-less continuous variation of $\phi$. The smallest size of these domains is in the range of $\mu m$, and the largest size is a few tens of

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Fig. 9. — Two domains (+ + and − − ) of the nematic scattering texture (NST). In this homogeneous sample, $d = 30 \, \mu m$, $T = 122 \, ^\circ C$ and $\alpha = 86^\circ$. The magnification is $\times 125$. 

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μm. Sometimes, a granular aspect is observed, uniformly or in isolated patches, as if the domains were constituted of smaller units. For all of these domains, θ is the same; n remains oblique and only φ changes.

Upon cooling this novel twisted nematic texture (TNT), one observes an increase in the twist angle φ. Then, at T* = 125 °C, we re-observe the onset of the NST, which can be once again cleared by heating up to T+, yielding the TNT, as before; nothing special changes by cycling back through the S_C phase. In all cases, remaining above T*, θ decreases with increasing temperature, and one eventually finds the normal tilted texture NTT. The measurement of φ, φ' and θ versus T in the NTT and the TNT will be described later.

The texture transition sequence can be schematized as follows:

\[
\begin{align*}
\text{SST} \quad & \leftrightarrow \quad \text{NST} \\
& \overset{T_C}{\leftrightarrow} \quad \text{TNT} \overset{T*, T^+}{\leftrightarrow} \quad \text{NTT}
\end{align*}
\]

where the arrows indicate reversible and irreversible paths and with no implication of unique transition temperatures upon cooling or heating.

2.2.2 Textures and boundary plate nature. — To try to elucidate the origin of these textural changes, we studied samples sandwiched between glass plates with various coatings. Using the same glass plates without an SiO coating, we obtained the same change of texture, with the difference that the nematic alignment was not well defined. We again observed the onset of the NST close to T*, however appearing to be more progressive in temperature.

Alternately, we used indium tin oxide (ITO) coated Baltracon glass plates (Balzers, surface resistance ~ 100 Ω) and reproduced the same SiO evaporation (α = 86°, δ = 13.4 nm) as previously. As one cools the sample down from the isotropic phase, a homogeneous, uniform NTT is built. Cooling further, we do not observe anything like the NST and the texture remains perfectly black between crossed polarizers. The smectic C phase appears as relatively large single-crystals, with the director titled at random to each side of the evaporation plane.
(with $\phi \sim \pm 10^\circ$). Heating back into the nematic phase, one again observes the standard NTT in the thick region of the sample ($d > 10 \mu m$); in the thin region ($d < 10 \mu m$), on the other hand, a memory of the $S_C$ crystallites can be seen (Fig. 11). The director remains twisted by a few degrees, as found in the $S_C$ phase. The twist is only a small perturbation of the TNT. Why this memory effect is only visible in the thin region is not clear. We believe that it corresponds to the regions of the sample where the $S_C$ single crystals have exerted a large enough constraint on the surfaces to destroy the surface (nematic) alignment. One might compare this phenomenon with a different memory effect reported previously by Clark [10].

The important point is that, whatever may be the cycling procedure, one never observes any twisted texture, nor any scattering texture with ITO-coated glass plates; the presence of the conducting ITO layer seems to inhibit both the TNT and the NST. This inhibition does not depend on an applied voltage across the sample. In fact, we can excite electrohydrodynamical instabilities in the nematic phase by applying a DC or a low-frequency AC field.

We then prepared an homogeneous wedge sample (as in Fig. 3a) having the same maximum thickness $h = 50 \mu m$, but with differing plates: one was the standard, $86^\circ$ SiO-evaporated directly on glass, the second was a $86^\circ$ SiO-evaporated over an ITO conducting layer on glass. With this sample we re-observed the NST at $T^* = 114.5^\circ$ for a sample of thickness $d = 6 \mu m$. Using the highest available magnification (a $\times 32$ lens), it is possible to localize the scattering texture close to the ordinary glass plate, the one without the ITO layer. Cooling down to the $S_C$ phase, we again found the memory effect of the $S_C$ crystallites on the ITO-coated plate. We can infer from these observations that the mechanism responsible for the scattering texture onset (the NST) is a surface effect, inhibited by a finite, surface electric conductivity. Later, we shall show that the temperature varying twist of the TNT is also a surface-induced mechanism.

2.2.3 Scattering texture and sample thickness. — The thickness dependence of $T^*$ for the first sample (two standard $86^\circ$ SiO-evaporated glass plates in the homogeneous geometry of

Fig. 11. — The stored surface « picture » in the nematic phase of smectic C single crystals. This homogeneous sample was prepared with ITO-coated and SiO oblique evaporated glass plates with $d \approx 20 \mu m$, $T = 120 \degree C$ and $\alpha = 86^\circ$. The magnification is $\times 125$. 
Fig. 3a) will now be presented. Using a thick spacer for the wedge \((h = 300 \mu m)\), we observed a strong decrease of \(T^*\) with increasing sample thickness, from \(129 \degree C\) for the smallest possible observable thickness of \(d \sim 2 \mu m\) down to \(108.5 \degree C\) for \(d = 200 \mu m\) (plotted in Fig. 12). The curve extrapolates from \(130 \degree C\) for zero thickness and, for large thicknesses, asymptotically close to, or slightly above, the \(108 \degree C\) \(N \rightarrow S_C\) transition temperature. For any fixed temperature in the nematic phase below \(130 \degree C\), this wedge sample shows a critical thickness \(d_c\) corresponding to \(T^*\): in the thin region of the sample \((d < d_c)\), one observes the NST; in the thick region \((d > d_c)\), the texture remains transmitting (and non-scattering) — either the TNT or the NTT, depending on the temperature. Cooling further, one observes transitions from the NST to the \(S_C\) and even crystal phases for \(d \sim 200 \mu m\), and a direct transition from the NTT or TNT to \(S_C\) and crystal phases at the very thick end of the sample.

We reproduced this thickness dependence of \(T^*\) for a sample with differing glass plates: one with ITO, the other without, both SiO-evaporated at \(86^\circ\). The results, presented in figure 13, show a much more abrupt variation of \(T^*(d)\). As in figure 12, the curve approaches

![Diagram of transition temperatures](image)

Fig. 12. — Dependences of the transition temperatures \(T^+\) (circles), \(T\phi\) (squares) and \(T^*\) (triangles) on the thickness \(d\) for a homogeneous sample prepared with two, standard \(86^\circ\) SiO-evaporated glass plates. The different observable textures are labeled and the transition sequences are indicated with arrows.

![Diagram of thickness dependence](image)

Fig. 13. — The thickness of \(T^*\) for a homogeneous sample prepared with differing glass plates: one with ITO, the other without, both SiO-evaporated at \(\alpha = 86^\circ\).
108 °C asymptotically, just above the N \rightarrow S_C transition temperature, and the curve might extrapolate for \( d = 0 \) to the same intercept of 130 °C as previously. However, the transition temperature rapidly diminishes in the range \( 0 < d < \sim 10 \) \( \mu m \). For thicknesses larger than 40 \( \mu m \), one does not observe a transition to the scattering texture at all, but just the previously quoted memory effect on the ITO plate (when cooling down to the \( S_C \) phase and up again into the nematic phase).

Secondly, the temperature at which the scattering texture clears upon heating, \( T^+(d) \), is constant except for the thinnest regions, where it then increases slightly (see Fig. 12). This texture transition temperature seems to depend more on the surface properties then on the bulk.

Finally, the thickness dependence of \( T^{\phi}(d) \), the temperature at which the azimuthal splitting begins, follows \( T^+(d) \), remaining about 5-6 °C above.

### 2.2.4 Scattering texture and « batonnets » growth

On very slow cooling (0.2 °C/mn) of a NTT or a TNT, arriving at a temperature \( \sim 2 °C \) above \( T^* \), one observes (between crossed polarizers, eventually rotated for the TNT to obtain a uniform, black field-of-view) the onset of thin, broken white straight lines (see Fig. 14), more or less aligned parallel to the evaporation direction. With their interconnections, these lines resemble a « railway switching yard ». Their lateral spacing of \( \sim 25 \mu m \) is comparable to the local sample thickness of 20 \( \mu m \). By focusing, one notices that this pattern of thin, bright straight lines is doubled, one on each surface, and has inter-surface connections. In the thinnest regions \( (d < 15 \mu m) \), the lines appear more rounded and less sharp, and one also observes many black dots (see Fig. 15).

The lateral mean distance between the lines is 7 \( \mu m \) for a sample thickness of \( d = 8 \mu m \). More black dots appear on the rounded, birefringent lines upon cooling closer to \( T^* \); these black dots propagate along the lines towards the thinnest region near the corner of the wedge, just as one observes for bubbles of the isotropic phase at the higher-temperature nematic-isotropic transition upon heating.

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**Fig. 14.** — Lines and dots in a standard, homogeneous sample with \( d \approx 20 \mu m \), \( T = 126.5 °C \) and \( \alpha = 86° \). The magnification is × 125.
Fig. 15. — Lines and dots in the thinnest regions ($d = 8 \mu m$). In this homogeneous sample, $T = 126.5^\circ C$ and $\alpha = 86^\circ$. The magnification is $\times 125$.

In thicker regions, one sees that the thin, straight lines actually appear in the shape of birefringent rods or « batonnets ». The lengths of these « batonnets » are also comparable to the sample thickness. The « batonnets » grow slowly from a point on the surface in pairs or in triplets. By gently touching the upper glass plate (in the absence of a spring), one can induce a lateral flow of the nematic phase. Some of the « batonnets » clearly rotate like solid objects around their point of junction with the glass boundary. In the thickest regions of the sample, the « batonnets » seem to be oriented at random; in the thinner regions, the « batonnets » orient more or less parallel to the horizontal evaporation direction $\mathbf{Y}$ to form a broken array of straight lines (see Fig. 14). More precisely, a double « batonnet » orients generally with its two axes symmetrically about the evaporation direction at $\phi = \pm 30^\circ$ to $45^\circ$. A triple « batonnet » orients as a double one, with its center element along the evaporation direction. The combination of these double and triple « batonnets » on each surface and extending from one surface to the other explains the « railway yard » appearance of the broken lines seen in figure 14. Upon heating, one observes that the « batonnets » unbind themselves from one surface, rearrange by rotating like solid needles and eventually melt continuously. On cooling, one sees that the NST generally originates from the point of junction of pairs or triplets of « batonnets » (see Fig. 16). In the thinnest regions, the scattering texture grows from the dark points attached to the more rounded, birefringent lines.

We also investigated the cooling of this sample under the influence of an applied magnetic field $\mathbf{H}$, initially oriented along the horizontal projection of the evaporation direction. A field strength of $H = 4.5 \, kG$ is sufficient to align the nematic phase for $T > T^*$. Cooling down close to $T^*$, we re-observe the growth of « batonnets » aligned with $H$ (parallel to the evaporation direction). After rotating $\mathbf{H}$ perpendicular to the evaporation direction, the « batonnets » still grow aligned with $\mathbf{H}$, overriding the evaporation alignment. On the other hand, the application of $\mathbf{H}$ has no influence on « batonnets » grown with $H = 0$ (aligned along or about the evaporation direction), nor on the scattering texture obtained at $T^*$.

The nature of the defects previously described has not been completely understood. If only for continuity, we would like to believe that the soft, rounded lines for thin samples, the
Fig. 16. — «Batonnet» arrangements in a 30 μm thick homogeneous sample with α = 86° at T = 123.5 °C. The NST is visible around the «batonnets». The magnification is × 125.

sharp, broken straight lines for thicker regions and the «batonnets» for the thickest samples are of the same nature and correspond to a more rigid, lower-temperature phase growing from the surface: a smectic or even a crystalline phase. Another possibility would be to describe the lines in thin samples as a textural breaking of a surface smectic phase.

The black dots, on the other hand, which propagate along the bright lines toward the wedge corner upon cooling, are thought to be droplets of the isotropic phase. As mentioned above, we know that the isotropic phase fills the wedge corner and the nematic phase gathers in the thicker parts of the cell, under conditions where these two phase are in equilibrium. This is probably due to the minimization of angular constraints on the nematic. Here, it is likely that the growth of a new smectic or crystalline phase at the glass surface induces a local increase in the concentration of «impurities» or to a surface induced change in the relative concentration of monomers-dimers, resulting in isotropic drops. These drops should be attracted to the thinner part of the wedge, explaining their flow toward the corner.

Finally, the scattering nematic texture which starts from the «batonnet» junctions or from the isotropic drops might be simply a highly distorted nematic phase; on a very small scale, the director n could rotate to follow the rapidly varying surface optimal directions, resulting in intense light scattering.

2.3 QUANTITATIVE ANALYSIS OF THE TWISTED NEMATIC TEXTURES. — To understand the nature of the TNT domains, we measured the absolute orientation of the director n as a function of the temperature T at the surface of SiO-evaporated glass plates. To determine θ, one needs to know the birefringence Δn. We first describe our calibration method, then explain the domain formation and finally give the measured surface orientation of n versus T.

2.3.1 Birefringence measurement. — To measure Δn = n₁ - n₀, we need to find a situation where n is uniform and in a well-defined and known orientation. To fulfill the first condition, an homogeneous sample would be best. However, its absolute orientation must also be know,
otherwise the calibration cannot be done. In fact, we chose to work with a non-homogeneous wedge sample. We shall see that the thickness variation of the orientation allows for a measurement of the birefringence.

We first prepared a 50 μm wedge cell using glass plates with SiO evaporated at α = 66° and δ = 18.3 nm. These conditions of evaporation normally result, for typical nematics, in a simple planar orientation with the surface director normal to the evaporation direction (θ = 90° and φ = 90°). Seen from above, the evaporation directions of the two glass plates are parallel, i.e. they should induce an homogeneous texture for this orientation (θ = 90° and φ = 90°) and a non-homogeneous texture otherwise (θ < 90° and φ ≠ 90°). We fixed T = 134 °C and measured the optical eigen-axis and the sample birefringence as a function of the variable cell thickness d, using green Hg light. The textures of this sample are very complicated and depend on the temperature in an unusual way. For instance, 2 or 3 °C below T_NI, the nematic-isotropic transition temperature, one observes a 90° rotation of the texture which goes from a splayed planar distortion in the vertical evaporation plane to a twisted distortion. Apparently, the planar and the oblique orientations seem to represent similar energy states for these 66° SiO-evaporated plates. These observations and their thickness dependence allow, in principle, the determination of the surface anchoring energy. They will be detailed in another paper [11]. Let us just state that we observe an increase in the birefringence from 0.14 for large d to 0.28 for d = 2 μm. Close to the thin corner of the wedge, φ is observed to be 90°, i.e. the sample seems to be in a planar orientation. We assume that Δn = 0.28 is a maximum and represents the full birefringence, although we have not directly checked the value for θ = 90°. With a thickness of d = 2 μm, we did vary the temperature and kept observing the same φ orientation, but we did not check that Δn was maximum at each temperature. These large values of birefringence compare well with the largest known Δn. The birefringence thus obtained is plotted as a function of the temperature in figure 17. We use these Δn values to determine the θ tilt of the uniform textures, to be presented below.

![Graph](image)

**Fig. 17.** — The temperature dependence of the maximum birefringence for a non-homogeneous wedge sample with d ≈ 2 μm and α = 66°.

### 2.3.2. Nature of the twisted domains.

We now focus on the homogeneous samples obtained with 86° SiO evaporation. We have seen that when the sample is cycled, first down to the S_C phase, then up to the high-temperature nematic phase and then cooled, one first observes the uniform nematic tilted texture (NTT). Then, below T_φ = 132 °C, one finds the (twisted) domains of figures 18a-d, i.e. the twisted nematic texture (TNT). This domain formation poses several questions: some domains are separated by thick surface lines and some are not,
for instance. Rather than discussing such questions in this preliminary work, we shall focus on understanding the systematic properties of domain formation.

We measured $\phi$ and $\phi'$, the relative optical axis orientations at the light input and output surfaces, as previously explained. For a 20 $\mu$m thick sample and for a fixed temperature of 130 °C, for instance, $\phi$ and $\phi'$ are uniform inside each domain. We find that optical fibres...
extinction can be obtained by choosing $\phi = 25^\circ$, $\phi = 0$ and $\phi = -25^\circ$, $\phi' = 0$ and $\phi' = -25^\circ$. These values of $\phi$ and $\phi'$ are determined with an accuracy of $\pm 1^\circ$. Apparently $\theta$ is the same in all cases but is difficult to measure since the fringe spacing can only be measured accurately for the largest domains. There exists, therefore, 9 possibilities, combining upper and lower surface twists of 0, $+\phi$ and $-\phi$, with $\phi = 25^\circ \pm 1^\circ$, and we do find all 9 domains. This combination law remains valid for all temperatures between $T_\phi$, where the twist $\phi$ begins, down to $T^*$ where the scattering texture (NST) appears. A
single (+, −) domain, for instance, remains a (+, −) domain while cooling, and only the value of \( \phi \) changes with temperature. A particular domain pattern can be reproduced when cycling through \( T_\phi \). The (0, 0) domain is simply the initial NTT and does not require any special attention. More generally, the domain formation appears as resulting from independent upper and lower surface twists \( \pm \phi \) and equal \( \pm \phi' = \phi \). This is visible from the overlap of two domains: (+, −) and (−, +), for instance, where one can see the same −\( \phi \) lower twist combined with two different \( \pm \phi \) upper twists. The same is true for any combination of the three 0, + and − signs. The conclusion is that, due to some unknown mechanism, each surface can induce, below \( T_\phi \), a texture twist \( \pm \phi \) of same absolute value \( \phi \). We find that the (+, +), (−, −) and (0, 0) domains are formed more often than the crossed one (+, −), a.s.o. This is easy to explain: the first three combinations do not imply any twist or bend curvature distortion, as opposed to the others. These more frequent combinations are shown in figures 18a-d, where the black regions are extinct for the various \( \pm \phi \) adjustments of the polarizers and analyzers, as indicated in the figure captions.

2.3.3 Tilt and twist measurement versus temperature. — We now choose a (+, +) domain, in the \( d = 20 \mu m \) range, and vary the temperature. The twist \( \phi(T) \) is found to be zero for \( T > T_\phi = 132 ^\circ C \) and \( \theta \) is \( \sim 55^\circ \), i.e. just above the «magic» angle \( \theta_M = \cos^{-1}(3^{-1/2}) = 54.7^\circ \). \( n \) aligns obliquely in the vertical evaporation plane \( P \) and along the evaporation direction, as is usually the case for the NTT. At \( T_\phi \), \( \phi \) starts to grow rapidly from zero (see Fig. 19) and tends to saturate toward \( \phi = 43^\circ \) for \( T \) just above \( T^* \). Above \( T_\phi \), \( \theta \) remains essentially constant at 55° and below rapidly drops decreasing to 43° at \( T^* \) (see Fig. 20). This temperature-induced surface transition can be repeated at will, as long as one does not go below \( T^* \) where the NST appears.

We reproduced the surface tilt transition using glass plates evaporated at other angles: \( \alpha = 80^\circ \) with \( \delta = 19.1 \) nm, \( \alpha = 75^\circ \) with \( \delta = 19.4 \) nm and \( \alpha = 70^\circ \) with \( \delta = 19.3 \) nm. We find the same behavior as described previously (see the comparisons in Figs. 21 and 22): the same types of domains exist. Note the general tendency that \( T_\phi \) increases with decreasing \( \alpha \), as does \( T^* \) (see Fig. 23). Figure 24 presents a plot of the temperature independent value of

![Fig. 19. — Temperature dependence of \( \phi \) which becomes non-zero below \( T_\phi \) and saturates with a maximum value at \( T^* \). In this homogeneous sample, \( d = 20 \mu m \) and \( \alpha = 86^\circ \).](image-url)
Fig. 20. — Temperature dependence of \( \theta \) which remains constant at higher temperatures, then dropping for temperatures below \( T_d \). In this homogeneous sample, \( d = 20 \mu m \) and \( \alpha = 86^\circ \).

Fig. 21. — Comparison of the temperature dependences of \( \phi \) for different angles of surface SiO-evaporation: \( \alpha = 86^\circ \) (circles), \( 80^\circ \) (squares), \( 75^\circ \) (up-triangles) and \( 70^\circ \) (down-triangles). These homogeneous samples were all of thickness \( d = 20 \mu m \).

The tilt \( \theta_0(\alpha) \) at higher temperatures \( (T > T_\phi) \) with \( \phi = 0 \) and its value: \( \theta^* \) for \( T = T^* \), as a function of the evaporation angle \( \alpha \). We note that, in the limit \( \alpha \to 90^\circ \), \( \theta_0 \) approaches the magic angle \( \theta_M \) and increases, perhaps towards \( 90^\circ \), for \( \alpha < 66^\circ \). Note that we did observe a \( 90^\circ \) \( \phi \) rotation for the « non-homogeneous » sample at \( \alpha = 66^\circ \). At \( T^* \), \( \theta^* \) varies between \( 52^\circ \) and \( 43^\circ \) and generally follows the behavior of \( \theta_0 \) remaining about \( 5^\circ \) or \( 10^\circ \) below.

These results are summarized in figures 25a-d plotting the bifurcation of the orientation of
Fig. 22 — Comparison of the temperature dependences of \( \theta \) for different angles of surface SiO-evaporation: \( \alpha = 86^\circ \) (circles), 80\(^\circ\) (squares), 75\(^\circ\) (up-triangles) and 70\(^\circ\) (down-triangles). These homogeneous samples were all of thickness \( d = 20 \mu m \).

Fig. 23. — \( T_\phi \) (circles) and \( T^* \) (squares) dependence on the evaporation angle \( \alpha \) in homogeneous samples with \( d = 20 \mu m \).

The nematic director \( \mathbf{n} \) on the unit sphere \( n^2 = 1 \), where SiO-evaporation direction is along the \( x \)-axis. The points represent the temperature dependence of observed pairs of \( \phi \) and \( \theta \), the lines radiating from the origin symbolize the nematic director at the surface. For each value of \( \alpha \), we obtain a bifurcated curve, splitting about the \( y = 0 \) evaporation direction at the temperature \( T_\phi \). Each curve ends at \( T^* \).

The four curves for the different angles of evaporation are compared on the surface of the unit sphere in figure 25e and in the projections on the \( n_x - n_y (\sin \theta \cos \phi, \sin \theta \sin \phi) \) and
Fig. 24. — Maximum $\theta_0$ (circles) and minimum $\theta^*$ (squares) tilt angle dependence on the evaporation angle $\alpha$ in homogeneous samples with $d = 20 \, \mu m$.

Fig. 25. — Temperature variation and bifurcation of the director $n$. (a) $\alpha = 86^\circ$, (b) $\alpha = 80^\circ$, (c) $\alpha = 75^\circ$ and (d) $\alpha = 70^\circ$. (e) Comparison of the four different angles of evaporation. Projections on the (f) $n_z - n_s$ and (g) $n_y - n_s$, planes.
Fig. 25. — Continued.
Fig. 25. — Continued.
Fig. 25. — Continued.

$n_y - n_z (\sin \theta \sin \phi, \cos \theta)$ planes (Figs. 25f and 25g). All curves open-up, approaching a limit with $\theta \to 45^\circ$ or $n_z = 0.7$, particularly evident in figure 25g.

A discussion shall follow after the presentation of X-ray measurements performed on these samples.
3. X-ray structural analysis.

The existence of smectic phases can be proven by small-angle X-ray scattering. However, these experiments are difficult to perform, due mostly to the thin sample geometry sandwiched between treated glass plates. This is made even more exasperating by the fact that the alkylxybenzoic acids are highly volatile and sublime significantly. Nevertheless, we did succeed in observing evidence in OOOA both of the expected tilted smectic C as well as of the homeotropic smectic A phase.

3.1 SMALL-ANGLE X-RAY SCATTERING. — The small-angle X-ray scattering geometry is illustrated in figure 26. For most of the experimentation, a rotating anode X-ray generator was used with a $0.1 \times 0.1 \text{ mm}^2$ point source operated at 1.2 kW (60 kV, 20 mA) and a copper target anode. The $\lambda = 0.154 \text{ nm Cu-K}_\alpha$-characteristic radiation was selected using a bent graphite focusing monochromator. A collimator formed by a pair of slits of variable height $\sim 0.1 \text{ mm}$ and width of 1 mm separated by $\sim 60 \text{ mm}$ defined the incident beam dimensions and divergence. A specially constructed oven contained the treated glass wedge and sample, to be detailed below. The passage between the glass plates was aligned with the fine X-ray beam by a rotation stage combined with a vertical translation. Different sample thicknesses in a wedge sample were explored by a transverse translation of the oven. The transmitted and scattered X-ray beams traveled through a helium filled flight path with thin Mylar windows to the detector located at a variable distance from the sample (between 100 and 400 mm). The unscattered direct beam was absorbed by a small brass beamstop. The detector was normally a $12.5 \times 12.5 \text{ cm}^2$ X-ray film, but a bidimensional gas detector [12] was occasionally employed for a more rapid characterization.

Experiments were also performed at the synchrotron laboratory Lure at Orsay on beamline D16. The storage ring DC1 was operating at 1.85 GeV with an electron beam current of $\sim 300 \text{ mA}$ (lifetime $\sim 45 \text{ hours}$). A focusing Ge(111) monochromator was tuned to select $\lambda = 0.12 \text{ nm}$ radiation, slightly more penetrating than the Cu characteristic radiation of the rotating anode source. A cylindrical 0.2 mm collimator defined the X-ray beam incident on the sandwich sample. The sample to film distance was $248 \pm 1 \text{ mm}$.

![Fig. 26. — Small angle X-ray scattering geometry. (a) Thin, SiO coated glass strips ($2 \times 12 \times 1 \text{ mm}^3$) with a 0.2 mm thick glass or Kapton spacer formed a wedge holding the liquid crystal sample by capillarity. A fine, collimated monochromatic X-ray beam passed through the gap, illuminating the sample. (b) Wedge sample of variable thickness (200 $\mu\text{m}$ $\rightarrow$ 36 $\mu\text{m}$) along the path of the X-ray beam.](image-url)
A constant difficulty was the volatility of this particular liquid crystal molecule; a sample used for X-ray investigation necessarily has a small dimension along the beam path, as the absorption length in liquid crystalline materials is typically ~1 mm for Cu radiation, somewhat more using the harder synchrotron radiation. The entire sample of volume \( \sim 2 \times 10^{-3} \text{ cm}^3 \) (~2 mg) would sublimate at high temperatures in a matter of hours or less. We were, unfortunately, not able to fabricate samples using more complicated glass shapes that would incorporate a liquid-crystal material reservoir. In addition, although the X-ray oven was also designed to allow optical measurements, \textit{in situ} microscope observations at the X-ray setup were impractical and we had to settle for comparisons between the two techniques while under the same conditions.

3.2 Smectic C Fluctuations. — The bulk smectic C phase in this sandwich sample is a powder, yielding a fine, uniform ring of scattering at \( 2 \theta = 3.70 \pm 0.02^\circ \) as measured on a high-resolution Guinier camera, corresponding to a layer spacing of \( 2.38 \pm 0.02 \text{ nm} \). In the bulk nematic phase, fluctuations of this tilted smectic phase with short range order are seen as diffuse scattering which condenses as the transition to the smectic phase is approached.

Conducting ITO coated glass plates with SiO evaporated at grazing incidence (87.5°) can be used to construct aligned, uniform orientation nematic samples. An X-ray scattering image in the nematic phase with the nematic director obliquely oriented and an azimuthal splitting about the direction perpendicular to the X-ray beam shows the intersection of four superimposed diffuse rings (tilted left and tilted right as well as \( \pm q \)) corresponding to a doubly-degenerate director tilt along the direction of evaporation (Fig. 27). The measured tilt angle of \( \theta = (\pm ) \ 47.5 \pm 1^\circ \) corresponds exactly to the smectic C value, with the diffuse lobes on-axis. The meridional spots are weak due to the azimuthal director orientational splitting.

Upon cooling this sample into the smectic C phase, the molecular orientation is lost and one measures a powder ring with a layer spacing of \( 2.38 \pm 0.02 \text{ nm} \) (Fig. 28), as was found with a bulk sample in a capillary tube (1.5 mm \( \mathcal{D} \)).

Fig. 27. — Smectic C fluctuations. The nematic director in well-oriented sample held between ITO coated plates is oblique with an azimuthal splitting about the direction perpendicular to the X-ray beam.
Fig. 28. — Smectic C bulk phase powder pattern. $T = 100.2^\circ$C, $d = 100$ µm. The smectic layer spacing is $2.38 \pm 0.02$ µm.

3.3 SMECTIC A STRUCTURE. — Without the conducting ITO coating, a nematic scattering texture is observed at lower temperatures ($T < T^*$ upon cooling, or $T > T^*$ upon reheating); the surface appears «shattered» with a very fine scale texture. X-ray diffraction reveals the existence of smectic A layering with a spacing of $3.52 \pm 0.05$ nm, exactly $2.38/\cos(47.5^\circ)$. In figure 29, one can clearly distinguish the disoriented condensed smectic A ring interior to the diffuse spots of smectic C fluctuations. The nematic director has some misalignment, as the diffuse scattering is also spread over a ring, which was revealed in this image thanks to the high intensity of the synchrotron source.

The previous image was recorded with X-rays traversing a relatively thick region of the sample ($d = 100$ µm). Optical observations show a large difference in textures as a function of sample thickness, which we hoped to understand by the X-ray experiments. Being unable to cleanly probe very thin regions of the wedge samples with the X-ray beam, we attempted a different geometry, one that allowed the scattering along a continually reducing sample thickness. This wedge geometry is drawn in figure 26b: the combination of Kapton and glass spacers gave a sample of variable thickness from $\sim 200$ µm down to 36 µm over a length of $\sim 3.5$ mm. The dimensions were chosen such that the glass surfaces were separated by an angle that was approximately $2 \theta_B$ of the smectic A layers, favoring Bragg diffraction by layers parallel to the liquid-crystal/rough SiO interface. The results are presented in figure 30b: in addition to the previous smectic A ring of the thick sample, a pair of well oriented surface smectic A reflections can be seen. The smectic A diffraction spots ($\pm$) are offset and differ slightly due to the sample and scattering geometry, yielding respectively $3.4 \pm 0.1$ nm and $3.5 \pm 0.1$ nm, which, within the experimental uncertainties, is the untilted smectic A layer spacing. In this photograph, the scattering in the ring is enhanced along the direction for layers parallel to the glass plates. The implications of this result and the correspondence with the optical observations will be discussed below.

This well-aligned, macroscopic smectic A surface state can also be observed for a thin,
Fig. 29. — Smectic A scattering. Disoriented ring of smectic A scattering interior to the diffuse smectic C fluctuations spots. Image measured at Lure at a temperature of \( \sim 110 \, ^\circ \text{C} \).

Fig. 30. — Variable sample thickness X-ray image. Oriented smectic A layering for thin samples, less-oriented layering for the thicker regions is revealed using the geometry of figure 26b. The horizontal streaks are due to scattering from the illuminated glass surfaces. \( T = 110 \, ^\circ \text{C} \).
uniform-thickness sample. In this case, a two-dimensional wire gas detector was used to combat the weak signal and rapid sublimation of the liquid crystal sample. The smectic A layering persists upon cooling into the bulk smectic C phase, and figure 31 shows the coexistence of the two aligned smectic A spots with the (unoriented) smecting C ring at $T \approx 100 ^\circ$C.

3.4 SECOND-ORDER MONOMER SCATTERING. — Under certain conditions that were difficult to control (poorly evaporated SiO, probably due to an improper pre-evaporation cleaning of the glass surfaces), diffraction from the monomer spacing (second-order peaks) was observed (Fig. 32). Two particularities are to be noticed: a pair of strong, second-order peaks ($\pm$) corresponding to half the smectic A period or $1.79 \pm 0.05$ nm ($3.57/2$) is well defined,
Fig. 32. — Monomer and intermediate smectic period, presented in two photographs of differing printing exposure. (a) Two pairs ($\pm$) of oriented second-order spots are seen at the exterior of the zone of nematic diffuse scattering in this image taken at $T = 115^\circ$C. (b) First-order half rings are revealed hidden in the nematic diffuse scattering of this same X-ray image.
with the layers parallel to the glass plates. A second pair of weaker peaks is also observable with a layer spacing of $1.48 \pm 0.05$ nm (2.97/2). Figure 32b reveals the half angle (primary) scattering hidden in the (overexposed) nematic diffuse scattering. Disoriented half-rings of period $3.6 \pm 0.1$ nm and $3.1 \pm 0.1$ nm are found. The bottom half of the rings are missing, suggesting, perhaps, that this structure only exists on the bottom glass plate in this case (the glass absorbing the scattering in the direction towards the lower part of the film). In fact, in addition to the poor optical orientation observed with these samples, sublimation was also a real problem, the entire sample evaporating over the time of the long X-ray exposure. It cannot be excluded that these fleetingly observed, second-order peaks correspond to the condensation of a crystalline phase.

3.5 POWDER SAMPLES. — In order to understand the previous small-angle X-ray diagrams produced in our very particular geometry, we present standard powder patterns measured with this mesogen (OOBA). A high-resolution Guinier camera was used with the sample placed in a sealed, 0.7 mm $\varnothing$ glass capillary tube and rotated about the cylinder axis. A high-temperature diffraction pattern shows the diffuse scattering of the smectic C fluctuations in the nematic phase. At a temperature of $\sim 136^\circ$C, a single fine line appears with a layer spacing of $2.98 \pm 0.05$ nm (Fig. 33a): a macroscopic zone ($\sim 100 \mu$m) of smectic of intermediate tilt ($\sim 34^\circ$). This line is still found at 102 °C in the smectic C phase, in addition to the fully tilted smectic C diffraction at $2.26 \pm 0.05$ nm (Fig. 33b). For comparison, in the high-temperature crystalline phase the first small angle reflections are measured with periods of 1.28, 0.71 and 0.61 nm (1.87, 0.93 and 0.73 nm in the room-temperature crystalline phase).

In this experiment, one is not limited by a sublimation of the liquid-crystal material in the sealed capillary tube, nor by effects of the sandwich and oven geometry. The curiosity is the 3.0 nm period structure that is always observed in fine capillary tubes, beginning at relatively high temperature in the nematic phase (sometimes also observed in sandwiched samples in the presence of monomer scattering, as described above). No evidence for the smectic A phase is found for these relatively thick and untreated samples.

![Fig. 33. — Guinier camera powder diffraction. (a) Smectic scattering with an intermediate period of 3.0 nm in the bulk nematic phase at $T = 136^\circ$C. (b) Coexistence with the 2.3 nm bulk smectic C period at $T = 102^\circ$C.](image-url)
3.6 SUMMARY. — The smectic A phase forms at the surface of treated glass plates. The smectic layers are well oriented parallel to the surface for thin samples (~ 36 μm) and less-well oriented for thick samples. The thickness of the smectic must be macroscopic (many layers) in order to be observable by small-angle scattering as fine, resolution-limited lines or rings, yet remains undetectable directly by optical microscopy. This smectic A surface structure remains even down into the bulk smectic C phase. No such smectic surface layering forms with glass plates having a conducting layer.

Bulk samples in thin capillary tubes always present an intermediate smectic layering with a spacing of 3.0 nm that appears in the nematic phase and remains even into the high-temperature crystalline phase upon cooling. This intermediate tilted phase might be due to an intimate mixture (of dimers with monomers, for example) as it corresponds to a single, well-defined smectic period. Because this phase is observable in the absence of a particular surface treatment or, in the sandwich samples, with a poor quality of surface evaporation, it may not be related to the other phenomena reported in this article and remains an unanswered question. We note that one does not observe this ray when using large capillary tubes (1.5 mm Φ) for several reasons: surface effects are less important, the ratio of bulk to surface scattering is greater and the fine X-ray beam is aligned to pass through the center of the capillary, avoiding the side walls and thus decreasing even further any surface induced signal.

4. Discussion.

The behavior of OOBA and HOBA close to the glass boundary surfaces is quite unusual among nematic liquid crystals. We shall attempt to explain most of the observed phenomenon without involving extrinsic causes such as impurities. After all, usual nematics with impurities or nematic-isotropic mixtures are often much « better » behaved than our present materials. One important difference to be noted between the alkylolxybenzoic acids and simple rod-like nematic is in their dimer molecular structure. At equilibrium, the nematic phase is richer in dimers than the isotropic phase. This equilibrium must be perturbed by the boundaries, which can change the local monomer/dimer concentration. In what follows, we shall speculate on how these boundary effects could explain the observed surface phase [13] and texture transitions.

4.1 THE NEMATIC-ISOTROPIC SURFACE COEXISTENCE. — The first effect of a glass surface is probably to force a larger surface·monomer concentration than in the bulk nematic. The reason for that change can be as simple as an effect of the glass polarity. The H-bonds which link two dimers can also link monomers to the glass. The monomer surface concentration could be large enough to decrease or to suppress the surface nematic ordering. This could explain the anomalously large temperature coexistence between nematic and isotropic phases for these particular compounds. If the surface were to be always wet by the monomer rich phase, one would expect a permanent isotropic layer of thickness ~ 20-100 nm to persist close to the glass plates, where ξ is the coherence length associated with the nematic-isotropic transition.

4.2 NEMATIC SCATTERING TEXTURE AND SURFACE FLEXOELECTRIC INSTABILITY. — We can now remark that two of the observed surface-induced effects (the nematic scattering texture or NST and the twisted nematic texture or TNT) disappear when the glass-nematic interface is conducting (ITO coated). As the NST can appear in the absence of the appearance of the TNT, we can assume that these two surface instabilities are more-or-less independent. It is reasonable to believe that their existence can be related to an electric
polarization or to an electric field parallel to the glass since this field would be zero along the conducting ITO coating.

The NST seems to correspond to a spontaneously distorted nematic phase close to the glass. To this distortion can be associated a flexoelectric polarization, which can be viewed as due to the angular change in orientation of the nematic electric quadrupole density. The dimers, indeed, possess a strong molecular quadrupole, essentially due to the two, central H-bonds with opposite electric dipoles. Such a flexoelectric surface instability has been recently predicted [14]. The instability is provoked by the unstable coupling between the flexoelectric surface polarization and the depolarizing electric field parallel to the surface. This instability does not exist when the surface is conducting. We suggest that the NST in OOBAs could be a good candidate for this surface flexoelectric instability. At lower temperatures, the dimer concentration increases, as does the flexoelectric quadrupolar coefficient. The temperature $T^*$ of the instability would correspond to the threshold value of the flexoelectric coefficient.

An interesting consequence of the surface flexoelectric model is that the threshold for a nematic sandwiched between two surfaces should be lower than that for a single, isolated interface for distortion wavelengths which compare with the nematic cell thickness $d$. This could explain the large observed thickness dependence of $T^*$ for macroscopic thicknesses $d \gg \xi$.

4.3 The twisted nematic texture. — Another way to create a surface electric polarization without a distortion of the nematic director is to change the nematic order-parameter modulus $S$. This would occur at the glass surface if the surface-induced monomer/dimer concentration change were to be believed. $S$ is assumed to go from zero at the surface to its bulk equilibrium value $S(T)$ at a distance $\xi$ from the surface. The corresponding gradient $|V S|/\xi$ breaks inversion symmetry, and an « order-electric » polarization [15] $P_0$ appears, proportional to $V S/\xi$. For molecules having their director $n$ tilted at the magic angle $\theta_M = \cos^{-1}(3^{-1/2})$ from the surface normal, the order polarization $P_0$ is exactly parallel to the interface. It is tempting to relate the twist instability of the nematic to the coupling between $P_0$ and its associated, horizontal depolarizing field $E$, since we know that the effect disappears in the presence of a conducting layer parallel to the interface. Assuming an $E$ produced by surface irregularities, by symmetry normal to the evaporation direction, i.e. along $X$, the dielectric energy stored in such a depolarizing field would vary as:

$$W_E = (1/2) \left( \varepsilon/4 \pi \right) E^2,$$

where $\varepsilon$ is the (isotropic) dielectric constant. Because of the absence of free charges, $D_y = \varepsilon E + 4 \pi P_y = 0$, i.e. $W_E$ becomes $(1/2) (4 \pi/\varepsilon) P_0^2 \cos^2 \phi \sim - (1/2) (4 \pi/\varepsilon) P_0^2 \phi^2$. This is a destabilizing effect. The stabilization comes from the elastic curvature energy $(1/2) K \phi^2 / \varepsilon^2$ where $K = L S^2$ is the usual curvature constant.

Calling $e_0 S$ the isotropic flexoelectric coefficient, $P_0$ is of the order $\sim e_0 S/\varepsilon$. The twist threshold is not obtained for $(4 \pi/\varepsilon) e_0^2 S^2 \varepsilon^2 \sim L S^2 \varepsilon^2$, i.e., for $e_0^2 \gg L S^2 \varepsilon$. This condition is quite analogous to defining the threshold of the flexoelectric instability, stating that the flexo-coefficient $e_0$ must be larger than some critical value. Note that, in a normal nematic, $e_0$ and $L$ are independent of the temperature. Also, $\varepsilon$ being the temperature-invariant mean dielectric constant, the twist surface instability (and the flexoelectric instability) may or may not occur at any temperature. Probably $e_0$ depends indirectly on the temperature, through the dimer concentration. As stated above, the OOBAs dimers possess, in their center, a strong, localized electric quadrupole from the two, opposite dipoles of the H-OH hydrogen bonds. The dimer concentration increases on cooling, explaining why the mesomorphic phases are more stable at lower temperature [2]. The onset of the surface twist instability upon cooling is, thus, probably due to an increase in the flexoelectric coefficient $e_0$. 
This suggested flexoelectric origin for both the twist and the scattering instabilities would explain the constant temperature difference between $T^*$ and $T_\phi$ for all cell thicknesses. As we have experimentally demonstrated, the instability threshold of two, neighboring surfaces is observed at a higher temperature than the instability of a single, independent surface. Previously, this was explained by the mechanical coupling of the two surfaces through the nematic layer, raising both $T^*$ and $T_\phi$; for a given coupling (i.e. a given thickness $d$), $T^*$ and $T_\phi$ would correspond to the two neighboring values of the threshold flexoe-coefficient $\varepsilon_0$ increasing with decreasing $T$. To explain why $T^*$ tends toward $T_{NC}$, the $N \rightarrow S_C$ transition temperature for large $d$, we recall that a surface transition is induced at a fixed temperature with decreasing $d$. The growth of a surface $S_C$ phase, which effectively decreases the thickness of the nematic, must play the same role; when the $S_C$ phase grows, a decreasing $d$ prevents $T^*$ from going below $T_{NC}$.

4.4 THE SMECTIC A SURFACE GROWTH. — Using X-rays, we have observed the growth of both an ordered (parallel to the plates) as well as a disordered smectic A phase close to the glass boundaries and not in the bulk. Let us first discuss the optically observed « batonnets » which could correspond to the observed X-ray scattering from unoriented $S_A$ layers. We suggest that these « batonnets » are smectic A single crystals which grow from the surface into the bulk. This identification is supported by their observed growth along an applied magnetic field $H$: the molecular long axis must be oriented parallel to the nematic director, the diamagnetic anisotropy direction. In this respect, it is striking to relate the growth of the double or triple « batonnets » to the two or three possible orientations of the surface director $(\pm \phi$ and 0). Indeed, it is known since the early observations of Friedel [16] that « batonnets » grow with their director along their long axis. As there exist three possible orientations of $n_s$, the correlation is obvious.

For thin samples, the observed X-ray scattering indicates the presence of a $S_A$ phase, here oriented with the layers parallel to and localized to the glass plates. At first sight, it seems mysterious to observe the onset of a $S_A$ phase which does not exist in the bulk. Here, also, the explanation could be found in the low surface concentration of OOBA dimers. We have already suggested that the flexoe-coefficient in nematic OOBA was large, due to the presence of the large H-bond quadrupole localized in the center of the nematogen dimer. This large, localized quadrupole moment could explain the onset of the surface $S_A$ phase: it has been suggested [17] that one of the mechanisms responsible for inducing the $S_A - S_C$ transition is the amplitude of the electric quadrupole modulation across the layer in the smectic phase. In this model, the $S_C$ tilt is understood as a way for the material to keep a smectic ordering without building-up too much orderelectric depolarization energy from the layer quadrupole modulation. When the effect is small, the untilted $S_A$ is stable. The tilt to the $S_C$ phase would increase progressively upon cooling, with a second-order (continuous) $S_A \rightarrow S_C$ transition. On the contrary, when the quadrupole modulation is large enough, the $S_A$ phase is no longer stable, and a first-order $N \rightarrow S_C$ transition is predicted (with a $S_C$ tilt nearly equal to the magic angle $\theta_M \approx 54^\circ$). OOBA and all members of the homologuous series of diacids possess a strong quadrupole modulation since most of the electric quadrupole moment (produced by the two acid H-bonds) is localized at the dimer center. In the bulk, OOBA indeed shows a strong, first-order $N - S_C$ transition and a $S_C$ tilt angle of $\sim 50^\circ$. We have suggested that, close to the glass boundaries, the nematic order is lower due to a large induced monomer concentration on the glass. A smectic A phase can become stable in this region, as in the phase diagram of reference [17], whereas it is not stable in the bulk where the nematic ordering is larger. This might explain the observed growth of $S_A$ close to the boundaries, over a thickness of $\sim \xi$, but does not explain, however, the growth
of large « batonnet ». The observed striation of very thin samples could correspond to a textural instability of this surface $S_A$ phase.

5. Conclusion.

The optical and X-ray observations presented in this work demonstrate the highly unusual behavior of the alkylxybenzoic acids in their mesomorphic phases. We have observed new and strange surface phenomena: first, an apparent coexistence of the nematic and isotropic phases over an anomalously large temperature span. Then, at lower temperatures in the nematic phase, two surface textural instabilities in the form of a spontaneous surface curvature distortion at all visible length-scales (the scattering texture), and a spontaneous twist and bifurcation of the surface tilted director orientation, which breaks the symmetry of the SiO-evaporation aligning plates used. These two instabilities do not appear on conducting electrodes. In parallel, a surface growth of $S_A$ in the shape of thin oriented layers parallel to the plates or disordered (powder) « batonnet » is detected using X-rays. These observations are valid for all members of the homologous series of these diacids, which exist as dimers in their mesomorphic states.

All of these apparently unrelated phenomena could be understood if one were to assume that the glass boundary fixes a monomer concentration above that of the bulk equilibrium value. The induced surface nematic order melting would explain the observed wetting of the isotropic phase at the glass boundary as well as the surface growth of the $S_A$ phase. The increase of dimer concentration upon cooling, increasing the flexoelectric coefficient, could explain the observed surface scattering and twist instabilities as being the first examples of a recently predicted flexoelectric instability. This interpretation is only tentative, since no surface concentration measurement of monomers/dimers has been made for these materials. Further experiments are required to ascertain this proposed interpretation and to investigate the additional, observed surface $S_C$ phase of intermediate tilt revealed by X-ray diffraction which remains unexplained.

6. Acknowledgments.

The authors wish to thank M. Boix for the stillful preparation of the SiO evaporated glass plates.

A. Braslau was supported for this research performed at the University Paris-Sud, Laboratoire de Physique des Solides by a grant of the French government (Bourse Chateaubriand) underwritten by Elf-Aquitaine under the scientific responsibility of Mme Christiane Taupin. M. Petrov was supported by an exchange program between the Bulgarian Academy of Sciences and the French C.N.R.S.

References

[13] The authors are aware that referring to the observed changes in texture as surface phase transitions might be an overstatement.