Anchoring Orientation of Nematic and Smectic A Liquid Crystals on PTFE Treated Plates

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Classification
Physics Abstracts
61.30-v — 68.10-m

Anchoring Orientation of Nematic and Smectic A Liquid Crystals on PTFE Treated Plates

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(Received 16 March 1995, received in final form 17 May 1995, accepted 23 May 1995)

Résumé. — L'orientation de l'ancrage de différents cristaux liquides sur des surfaces de poly(tétrafluoroéthylène) (téflon) est mesurée par interférométrie optique. Un ancrage planaire est trouvé pour tous les composés essayés MBBA, 2OO6, 5CB et 7BPI, que les molécules soient polaires ou non polaires, en phase nématique ou smectique A. Ce résultat est cohérent avec la nature non-polaire du téflon qui n'est sensible qu'à l'interaction de London

Abstract. — The anchoring orientation of different liquid crystals in contact with poly(tetrafluoroethylene) (PTFE) treated surfaces is determined by means of optical interferometry The anchoring is found to be planar for all the compounds tested, MBBA, 2OO6, 5CB and 7BPI, consisting of polar and non-polar molecules, in the nematic or smectic A phase This result is consistent with the non-polar nature of PTFE, which is only sensitive to London-like interactions.

1. Introduction

For both fundamental reasons and display applications, there has been an increasing interest, for the last few years, in the study of the anchoring properties of liquid crystals onto solid substrates treated in different manners [1]. It has thus been found out that amphiphilic molecules such as lecithin [2] or silane [3] were convenient for producing homeotropic alignment, with the director oriented perpendicularly to the substrate. Moreover, the deposition of a thin layer of polymers such as poly(vinylalcohol), polyimid or nylon, induces the planar orientation, with possibly a small pretilt of a few degrees, the liquid crystal molecules being then almost parallel to the substrate [4]. The polymer, when deposited by solvent evaporation or by direct synthesis, has an isotropic structure. It is therefore not able to give any preferred orientation to the liquid crystal. This polymer deposition has therefore to be followed by some delicate rubbing in order to plow microgroves in it and to orient the polymer chains at its surface. Only few processes allow both operations, deposition and orientation of the polymer, to be performed at the same time: for instance the SiO-sputtering at oblique incidence [5], which is

rather costly, and more recently the photopolymerization of the alignment layer under polarized light [6] Here, we present an experimental determination of the pretilt anchoring angle ϵ of different liquid crystals on a poly(tetrafluoroethylene) (PTFE) film deposited and oriented in a one-step rubbing process initiated by Haller [7] and recently developed by Wittmann and Smith [8]. The anchoring angle ϵ is measured as a function of temperature by means of an interferometric method which allows for an accuracy of $\Delta\epsilon$ measurements of the order of 1°.

Different liquid crystal compounds with low and high polarizabilities, in the nematic and smectic A phases, are tested on the PTFE surfaces:

- The n-(4-methoxybenziliden)-4-butylaniline (MBBA), purchased from Aldrich, is purified and recrystallized in the laboratory in such a way that its melting temperature from the nematic to the isotropic phase reaches 44 °C. This very standard room-temperature compound is weakly polarizable, its molecule bearing a small dipole moment. MBBA should thus exhibit anchoring properties representative of a wide class of nematics. It is therefore interesting to study its behavior although the Schiff basis of the molecule makes it sensitive to hydrolysis.

- The 4-hexyloxyphenyl-4-ethoxybenzoate (2OO6), synthesized and purified in the laboratory [9], exhibits a nematic phase from 48 °C to 95.5 °C where the transition to the isotropic phase occurs. This compound with also a weak molecular dipole moment, should present electric interactions comparable to what they are in MBBA. Its anchoring properties should thus be similar to those of MBBA, but with less problems of degradation of the molecules with time, because of its higher thermal stability

- The 4-cyano-4'-n-pentylbiphenyl (5CB) from BDH-Merck, is a room-temperature nematic liquid crystal up to the transition to the isotropic phase at 35.5 °C. This molecule, in contrast with the two previous ones, has a strong electric polarization parallel to its main direction due to the cyano group. A well-known consequence of this cyano group is that the compound is mostly dimerized in the bulk, but its behavior is not so clear at the surfaces of the substrates. Recent STM studies have shown that the ordering of the cyanobiphenyl molecules in contact with a substrate depends upon the nature and the crystallographic structure of this substrate [10]. The 5CB molecules could thus interact in a different manner with the substrates compared to the nonpolar molecules of MBBA or 2OO6. This could lead to different anchoring properties on identical substrates.

- The 4-(3-methyl-2-chloropentanoyloxy)-4'-heptyloxy-biphenyl (7BPI) has been synthetized and carefully purified in the laboratory [11]. It exhibits the following polymorphism: crystal phase (44 °C) SmC* (56.0 °C) SmA (62 2 °C) isotropic phase. This compound, characterised by two asymmetric centers, has a smectic C* (SmC*) phase with a strong ferroelectric polarization $P_S = 230$ nC/cm^2 at a temperature 10 °C below the transition to the smectic A (SmA) phase. The ferroelectric SmC* phase is interesting for display applications provided that its anchoring to the plates leads to the bookshelf structure with the smectic layers perpendicular to the solid surfaces. This orientation has to be achieved in the SmA phase first before cooling down the sample into the ferroelectric phase. That is why we studied the anchoring properties of the PTFE surfaces on the SmA phase, and in fact we restricted our study to this phase without entering the SmC* phase because our experimental method for the tilt determination is not well adapted in this case.

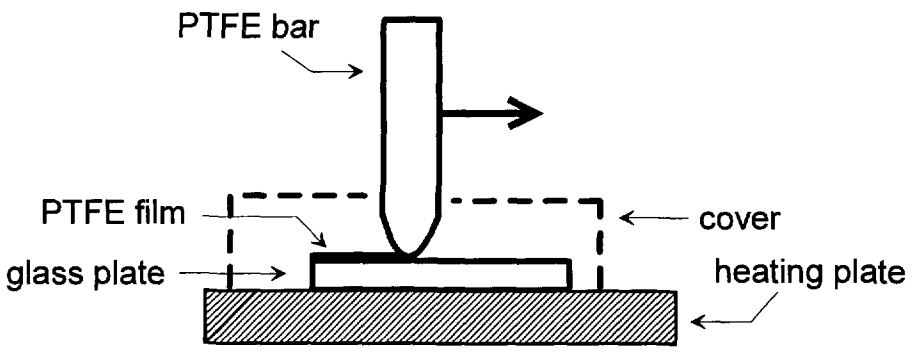

Fig. 1 — PTFE rubbing system The PTFE bar is pressed against the glass plate while slowly moved along it

2. Sample Preparation

Two kinds of glass surfaces, with and without an ITO layer, have been covered with a PTFE film. These glass plates, 1mm-thick and of 1×2 cm^2 size, are carefully cleaned and treated by slowly rubbing a PTFE-bar on them in a similar manner as promoted by Wittmann *et al.* [8]. The whole system (Fig. 1) is thermostated at about 150 °C. The PTFE-bar is slowly moved at 0 2 mm/s with a contact pressure of about 30 atm onto the glass plate.

The cells are made of two parallel plates with the same rubbing direction. Their spacing is obtained by introducing small silica balls from Colochrom at the corners (about 5 μm-diameter for non treated plates and about 20 μm-diameter for plates with an ITO layer). The cell is then placed within a press to adjust its parallelism by acting on four screws at the corners. The parallelism of the plates is optically controlled by looking at the equal-thickness fringes given by the interference of the reflected light from a fluorescent tube onto the internal surfaces. Generally we observe that the plates are not perfectly flat. We can nevertheless optimize the parallelism at the center of the cell, and arrange a fringeless area of typically 5 mm-diameter. The action on the screws is made soft by means of springs and small levers. However, the resulting strength onto each glass ball is really enormous so that the balls are partly driven inside the PTFE and ITO layers, and crushed. The thickness of the cell is thus reduced by a factor of about 2. The cell is then tightly glued with epoxy before being removed from the press.

The cell thickness is then measured before being filled with a liquid crystal. The method we use is again optical interferometry A He-Ne laser beam is diffused with different angles in the direction of the cell. These various rays are then reflected onto the internal surfaces of the cell and produce interference fringes similar to Michelson rings (Fig. 2). They obey the following relation:

$$2e \cos i_k = k\lambda_0, \tag{1}$$

where $\lambda_0 = 632.8$ nm is the wavelength of light, e is the cell thickness and i_k is the incidence angle of the light rays onto the cell, which interfer into the order k. By measuring the radius of the Michelson rings, we easily determine the cell thickness e with an accuracy of 0.1 μm. The measurement is performed on a small area of the cell, about 1 mm^2 size. When repeated in different places, this measurement allows us to index the equal thickness fringes observed in

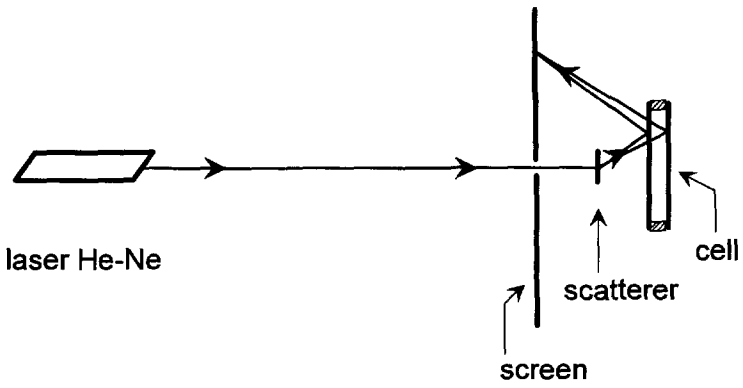

Fig. 2 — Interference set-up used for measuring the sample thickness.

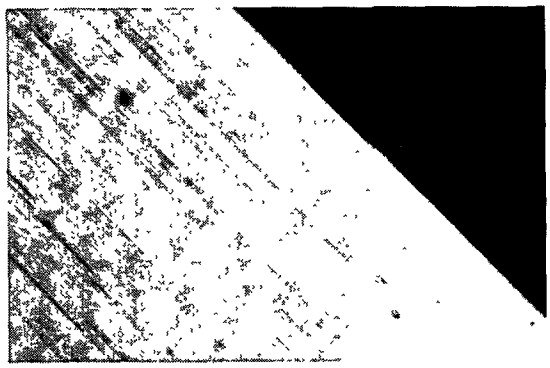

Fig 3 — Nematic sample of the 5CB compound between crossed polarizers. The orientation is uniform (the right upper corner is out of the sample and therefore black). The width of the photo corresponds to about 50 μm in the sample

the first part of the cell fabrication.

The cell is then filled by means of capillary forces, the liquid crystal in the nematic or isotropic phase flowing in the rubbing direction. Independently of the filling method and of further melting in the isotropic phase, the sample in the nematic phase typically appears under microscope between crossed polarizers, as shown in Figure 3. It is reasonably homogeneous with uniform extinction when rotating the microscope stage, except along some narrow stripes parallel to the rubbing direction. In these places, the anchoring of the nematic phase is different, probably because the PTFE film has been scratched during rubbing by hard microscopic dusts encrusted inside the PTFE stick. Neither these stripes nor the PTFE film can be optically observed before introducing the liquid crystal into the cell. This is consistent with recent evaluations using AFM techniques [12] which indicate that the PTFE film thickness deposited by this method is very thin, of the order of 10 to 50 nm. Sometimes the sample exhibits a few faint lines separating places of slightly different tints. These lines are roughly oriented

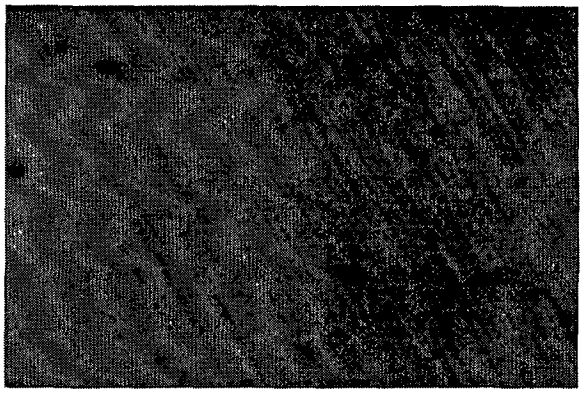

Fig. 4. — SmA sample of the 7BPI compound between crossed polarizers The orientation is uniform with faint stripes parallel to the rubbing direction. The width of the photo corresponds to about 50 μm in the sample.

perpendicular to the rubbing direction. They correspond to steps in the PTFE film where the thickness changes abruptly. The steps are produced by the stick-slip mechanism possibly associated with and amplified by vibrations in the PTFE-bar.

In the case of 7BPI, the liquid crystal is introduced in the isotropic phase and slowly cooled down into the SmA phase. The sample appears then between crossed polarizers to be uniformly oriented in the so-called bookshelf geometry, i.e., with the smectic layers perpendicular to the plates. Stripes parallel to the rubbing direction, typical of this orientation, are observed (Fig. 4), together with the stick-slip lines perpendicular to the rubbing direction as in the nematic cells.

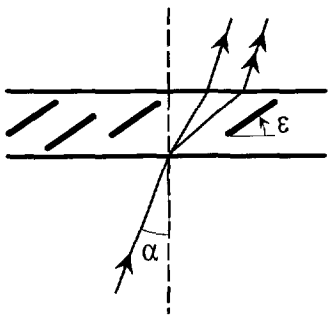

Fig 5 — The molecules are uniformly tilted by ϵ within the sample. The average direction of the light going through the microscope is in the same plane as the molecules, at the incidence angle α to the sample.

3. Anchoring Angle

At the minimum of energy, the sample is uniformly oriented in its whole bulk so that the anchoring angle ϵ imposed at the surfaces propagates and tilts the nematic director everywhere (Fig. 5). The tilt angle ϵ may therefore be determined through an integration method, for instance by measuring the path difference δ between the ordinary and extraordinary optical rays crossing the whole sample of thickness e. In normal incidence and to the first order in Δn, this path difference is given by

$$\delta = \Delta n \; e \; \cos^2 \epsilon, \tag{2}$$

where $\Delta n = (n_e - n_o)$ is the difference between the extraordinary and ordinary optical indices of the nematic for white light, i.e., for the average wave length $\lambda = 0.55$ μm. The path difference δ is experimentally determined using a rotating compensator mounted in a Laborlux Leica microscope. This simple system allows for the determination of δ up to 3 μm within the accuracy $\Delta\delta \sim 10$ nm. Unfortunately, as equation (2) shows, the determination of ϵ with this straightforward method becomes inaccurate when ϵ is small or close to $\pi/2$. The error on the tilt measurements is then $\Delta\epsilon \sim \Delta\delta/2\epsilon$, or $\Delta\epsilon \sim \Delta\delta/2(\pi/2 - \epsilon)$, respectively. We then measure the path difference δ across the sample for several oblique incidences of light. Such an experimental method is in fact a kind of conoscopy restricted to a few incidence angles. It has been commonly used in liquid crystals for a long time.

Practically, the oblique incidence of light is realized by tilting the sample by an angle $\alpha = 19°$ inside the thermostat (Fig. 5). This tilt angle is limited by the available room inside the thermostat. As we shall see, this choice of α is sufficient to achieve the determination of the anchoring angles within an accuracy $\Delta\epsilon \sim 1°$. Larger tilt angles α would restrict the width of the focussed zone leading to more difficult measurements of δ. δ may be expressed in the following manner

$$\delta = e[n_o \cos i_o - n \cos i], \tag{3}$$

where i_o and i are, respectively, the angles of the ordinary and extraordinary light waves within the sample and arising from the same ray at the incidence angle α in the air. They are given by the refraction relations:

$$\sin \alpha = n_o \sin i_o = n \sin i, \tag{4}$$

where n refers to the optical index of the extraordinary wave at the incidence angle i:

$$\frac{1}{n^2} = \frac{\cos^2(i - \epsilon)}{n_e^2} + \frac{\sin^2(i - \epsilon)}{n_o^2}, \tag{5}$$

with $C = \left[\frac{1}{n_o^2} - \frac{1}{n^2}\right]^{1/2}$ and $C_o = \left[\frac{1}{n_o^2} - \frac{1}{n_e^2}\right]^{1/2}$, this equation becomes

$$C = C_o \cos(i - \epsilon) = X \cos i + Y \sin i, \tag{6}$$

where we have set down:

$$\begin{cases} X = C_o & \cos \epsilon \\ Y = C_o & \sin \epsilon \end{cases} \tag{7}$$

The experimental measurement of δ allows us to calculate i and n, and then C, by combining equations (3) and (4). We thus find the linear relation (6) between X and Y, with two unknowns C_o and ϵ. At this stage, we may directly take the optical indices of the liquid crystal from the literature, and calculate C_o, and then deduce the anchoring angle ϵ with equation (7). However,

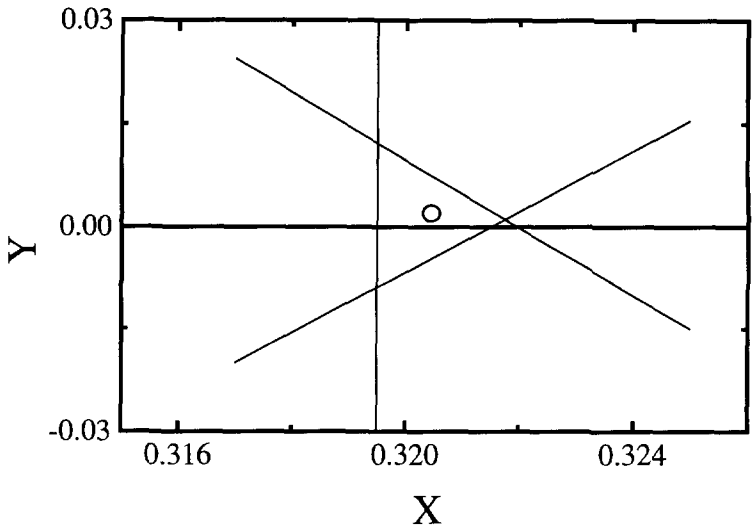

Fig 6 — The thin straight lines correspond to the 3 linear relations (6) for a typical measurement, see text. The open circle corresponds to the most probable values of the parameters X and Y

this simple method is generally impossible because the optical indices of many liquid crystals are not yet published. This method is also inconvenient when the impurity concentrations, generally unknown, are different in the two experiments. The reason is that $C_o \sim \left[\frac{2\Delta n}{n^3}\right]^{1/2}$ is essentially a function of the birefringence Δn, which is strongly dependent upon the impurity concentrations via the order parameter S (the variations of n_o are relatively smaller; we may take $n_o = 1.5$) It is thus better to determine C_o and ϵ in the same experiment by comparing measurements at different tilt angles α. On performing measurements with $\alpha = +19°$, $-19°$ and $0°$ at the same place on the same sample, we get three independent linear relations between X and Y, which allow us to determine C_o, i.e., Δn, and ϵ. Moreover the consistency of the three measurements should bring a confirmation of the results.

In Figure 6 are shown the 3 linear relations (6), Y as a function of X, corresponding to typical measurements performed for the 3 different tilts in the same place of the MBBA-cell. The straight lines do not cross exactly at the same point because of small experimental errors. The most probable result is given by the barycenter of the triangle that they form.

4. Experimental Results

The anchoring angle ϵ is measured algebraically with our interferometric method. Since the cell fabrication is symmetrical, both signs should appear with an equal probability. The anchoring angle ϵ, as measured in a 6.1 μm-thick cell of MBBA with PTFE-treated plates as a function of the temperature difference from the isotropic phase transition ΔT, is displayed in Figure 7. In this figure we do not exactly find the forecast symmetrical behavior because of a small systematic error. All the measurements, performed every two degrees in several places of the sample, are included in the segment: $|\epsilon| = 0.9 \pm 0.6°$, except close to the isotropic transition where the error bar increases. The birefringence results Δn, which are a secondary

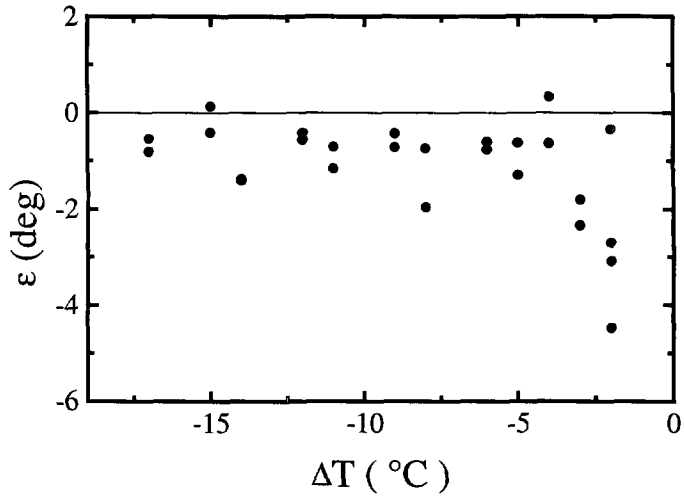

Fig. 7. — Pretilt angle ϵ of MBBA on the PTFE treated surfaces *versus* $\Delta T = T - T_{Iso}$, for different places in the sample The data close to the isotropic phase transition are less accurate

outcome of the measurements, are displayed *versus* ΔT (Fig. 8). They are consistent within a small error ~ 0.01 with the tabulated values, sketched as a solid line [13]. This provides an indirect confirmation of the validity of our pretilt measurements which indicate that the anchoring of MBBA is planar on the PTFE treated plates in the whole temperature range, within experimental errors, systematic and statistic, that are worth about 1°.

Comparable results are obtained with 2O06 and 5CB. Figures 9 and 10 show the pretilt angle ϵ and the birefringence Δn as measured in 2O06 *versus* the temperature difference from the isotropic phase transition ΔT. Figures 11 and 12 similarly yield the measurements of $|\epsilon|$ and Δn *versus* ΔT for 5CB. In the latter case, the pretilt angle is found within a larger error bar, $|\epsilon| = 1.2 \pm 1°$, probably because of more numerous defects within the sample, which makes the measurements difficult. Nevertheless, all the measurements clearly show that the anchoring of the nematic liquid crystals is planar with a quasi-zero pretilt, independent of the permanent dipole moment of the molecules

Figure 13 depicts the measurements of the pretilt angle ϵ *versus* ΔT for 7BPI in the SmA phase. Again, the anchoring of liquid crystal is found to be planar on the PTFE surfaces with a good accuracy. Let us notice here that a symmetric chevron structure could take place in the SmA phase. The chevron structure is produced by the shrinking of the smectic layers when the temperature is decreased from the temperature of the isotropic to smectic-A phase transition T_{Iso}. However, this layer shrinking is weak as indicated by the X-ray measurements of the layer thickness d *versus* ΔT (Fig. 14). Therefore, the angle θ of the chevron, which is given by the relation:

$$\cos\theta = \frac{d(T)}{d(T_{Iso})}, \tag{8}$$

is small ($\theta < 4°$), if however the chevron really builds up. Naturally, the chevron angle θ increases when the sample is cooled down to the SmC* phase, and typical defects in the shape of hairpin, due to chevron reversals, appear [14]. If the sample is heated up to 0.5 °C inside

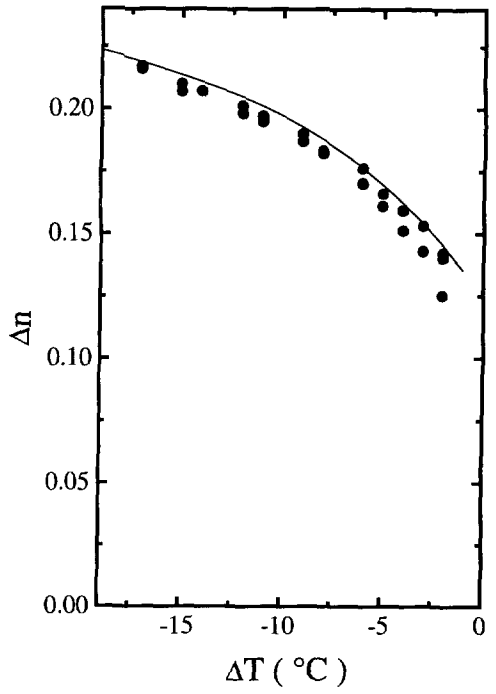

Fig. 8. — Birefringence Δn of MBBA *versus* $\Delta T = T - T_{\mathrm{Iso}}$. The solid line displays the data published in reference [12].

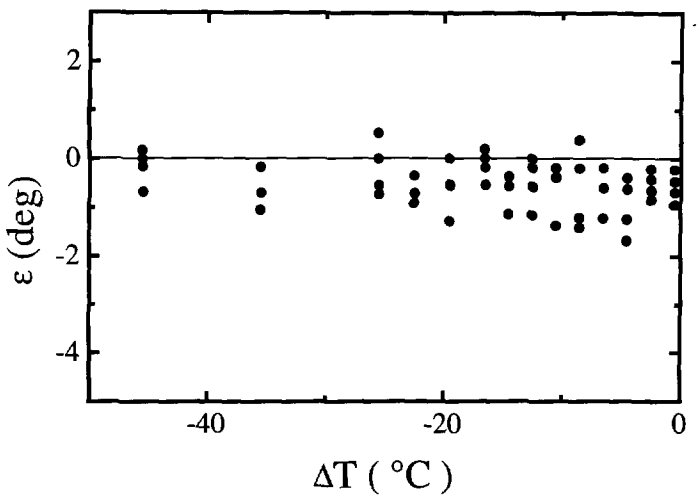

Fig. 9 — Pretilt angle ϵ of 2006 on the PTFE treated surfaces *versus* $\Delta T = T - T_{\mathrm{Iso}}$, for different places in the sample.

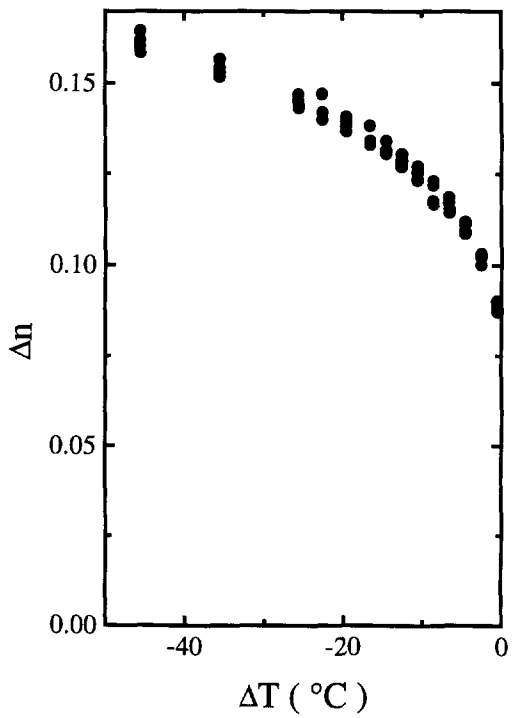

Fig. 10. — Birefringence Δn of 2OO6 *versus* $\Delta T = T - T_{\mathrm{Iso}}$

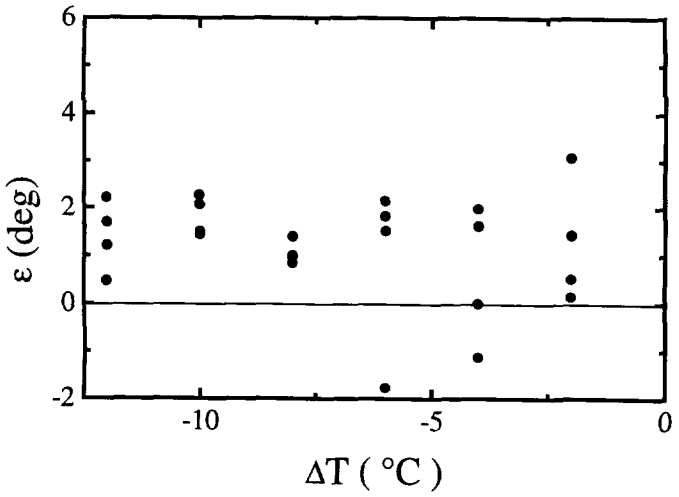

Fig. 11. — Pretilt angle ϵ of 5CB on the PTFE treated surfaces *versus* $\Delta T = T - T_{\mathrm{Iso}}$, for different places in the sample.

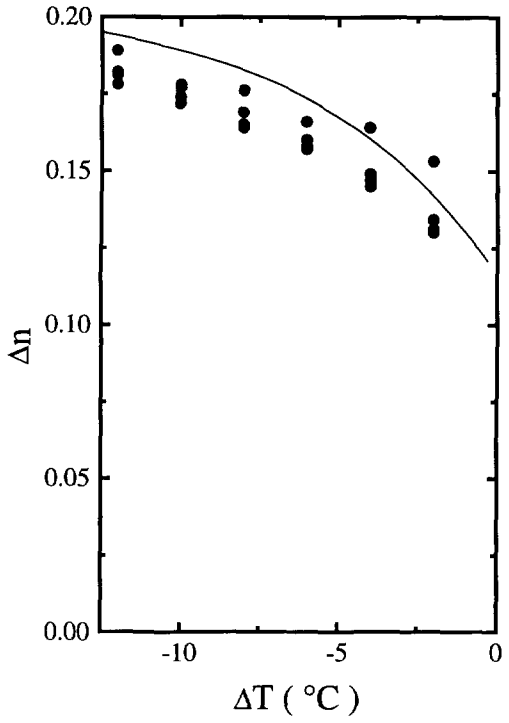

Fig. 12. — Birefringence Δn of 5CB *versus* $\Delta T = T - T_{\text{Iso}}$ The solid line displays the data communicated by BDH-Merck

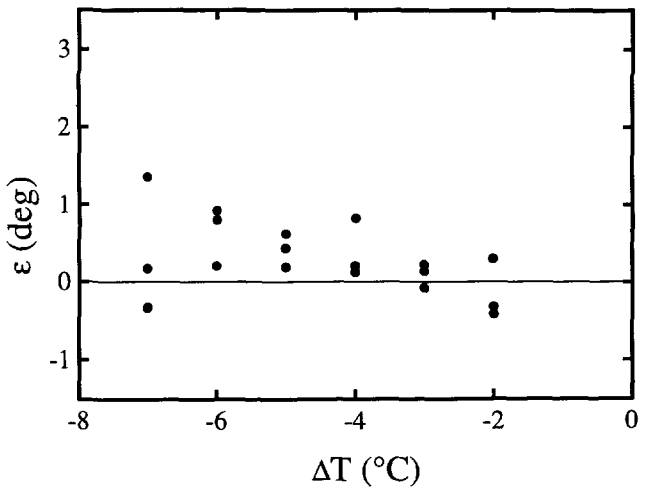

Fig 13 — Pretilt angle ϵ of 7BPI in the SmA phase obtained on the PTFE treated surfaces *versus* $\Delta T = T - T_{\text{Iso}}$, for different places in the sample.

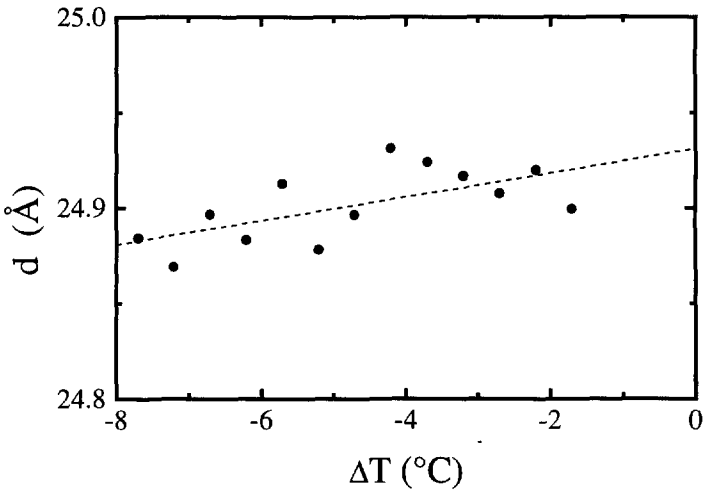

Fig 14 — Layer thickness d *versus* $\Delta T = T - T_{Iso}$, obtained by X-ray diffraction.

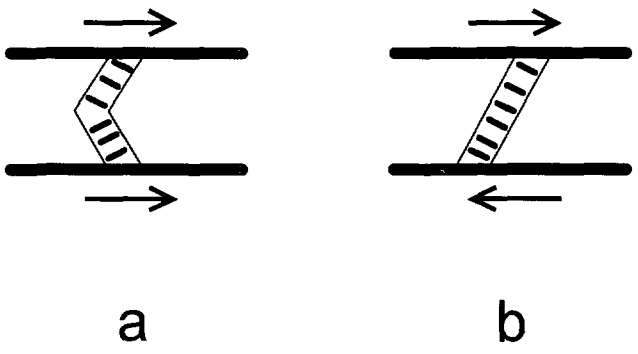

Fig 15 — Structure of the sample in the case of a non-zero pretilt. a) In the parallel configuration, b) In the antiparallel configuration

the SmA phase and cooled down into the SmC* phase, the chevron defects first disappear and then reappear mostly at the same places as previously. This half-memory effect of the chevron direction corroborates the previous remark that the chevron angle θ is small in the SmA phase. The chevron structure therefore introduces only negligible errors in the tilt measurements. Moreover, the chevron being essentially symmetrical due to its formation mechanism, such errors should compensate in a first order approximation. More exactly, we may notice that the anchoring to the plates with non-zero pretilt leads to two different orientations in the cell at the transition temperature T_{Iso}, according to the parallel (Fig 15a) or antiparallel (Fig. 15b) configuration which is given to the cell. Since the occurrence of the chevron, and its direction, appear to be rather undetermined at the SmA-SmC* phase transition, we may

discard the parallel configuration in our experiment. Thus, at the transition temperature T_{Iso}, the structure of the chevron should be quasibookshelf as shown in Figure 15b. When the temperature is then decreased, a slight chevron may superpose to the quasibookshelf structure, breaking it and introducing a negligible difference between the measured average tilt angle and the pretilt angle at the solid surfaces.

5. Conclusion

In summary, anchoring is found to be planar on the PTFE-treated surfaces independently of the molecular formula and the phase, nematic or smectic, of the liquid crystal in contact. This observation is consistent with the recent measurements of the anchoring angle of commercial mixtures on PTFE-treated surfaces [15]. This behavior may be understood from the non-polar nature of PTFE . The PTFE-surfaces are only sensitive to the London interaction which is an attractive interaction, larger for the hard cores of the molecules than for the aliphatic tails, since the cores are more polarizable than the tails. The cores of the molecules should therefore prefer to come as close as possible to the PTFE-surfaces and thus to orient parallel to them. This mechanism explains the planar anchoring effectively observed.

The optical determination of the pretilt angle that we have used here cannot be extended to the SmC* phase because in this phase, the molecules can easily rotate along a cone and change their direction accross the sample The average angle measured with our integration method should not correspond then to the pretilt angle close to the anchoring surfaces. In this case, local and more sophisticated methods, such as surface plasmons or guided optical wave analyses, have to be used [16]. However, taking the generality of our results into account, we may extrapolate and we believe that the anchoring also remains planar in the SmC* phase.

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