Nature of Smectic Ordering at a Solid–Liquid-Crystal Interface and Its Influence on Layer Growth

J. S. Patel and Sin-Doo Lee[(a)]
Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701

J. W. Goodby
School of Chemistry, The University Hull, Kingston-Upon-Hull, HU6 7RX, Humberside, England

(Received 24 October 1990)

It is found that the layer normal of a chiral smectic-A liquid crystal is tilted away from an easy axis created by a unidirectional rubbing. The alignment angle of the tilted layer normal with respect to the easy axis approaches about 18°, which is substantially larger than what has been previously observed. This larger deviation cannot be described in terms of the surface electroclinic effect, and an alternative mechanism is proposed on the basis of molecular chirality and the degree of smectic ordering at the surface.

PACS numbers: 61.30.Eb, 61.30.Gd, 78.20.Jq

It is well known that liquid crystals (LCs) can be oriented on a rubbed surface in a unique direction because of the anisotropy in the surface forces created by the rubbing process.[1] It has been recently shown that surface interactions specific to an interface predominantly determine the nature of the surface-induced ordering.[2-4] In a nematic LC which is characterized only by orientational order, the molecules tend to lie parallel to the rubbing axis. However, in smectic LCs which are characterized by positional order as well as orientational order, the principal optic axis, lying along the layer normal, is often found to make an angle with respect to the rubbing axis.[5,6] Although the surface electroclinic (EC) effect[7,8] has been used for explaining this angular deviation, a complete picture of the phenomenon is still lacking.

In this Letter we report on the highly tilted alignment of the smectic layer with respect to the rubbing axis in some chiral smectic-A materials. It is found that the tilt angle Ψ of the smectic layer to the rubbing axis $\hat{b}$ is much larger ($\approx 18°$) than what has been previously observed. By measuring the magnitude of the EC effect in the material being examined, we show that the surface EC effect alone cannot explain the observed value of Ψ. We propose a new mechanism for this larger layer tilt in term of molecular chirality and the spatial variation of smectic ordering away from the surface.

We have measured the tilt angle Ψ of the smectic layer away from $\hat{b}$ in a chiral smectic-A compound, the R-enantiomers of 1-methylheptyl 4′-[{4″-dodecyloxyphenyl)propioloyl}-oxy] biphenyl 4-carboxylate (C_{12}1M7). The critical temperatures for the isotropic–smectic-A (I-Sm-A) and the smectic-A–smectic-C^* (Sm-A-Sm-C^*) transitions during heating are 94.2 and 82.4 °C, respectively. In higher homologs of this compound, a new smectic-A^* phase, which is a liquid-crystal analog of the Abrikosov phase of type-II superconductors, has been observed.[9] These materials are different from ordinary smectics in that they are highly chiral and thus produce highly twisted structures. As we shall see later, this is an important factor for explaining the large magnitude of Ψ in the compound studied.

Two sample cells were made of conductive indium-tin-oxide–coated glasses, and the thickness of the liquid crystal was controlled by using 15- and 3-μm spacers. The homogeneous alignment was obtained by coating both surfaces of the cell with poly-1,4-butyleneterephthalate polymer, followed by a unidirectional rubbing. The sample was filled in the isotropic state and cooled into the mesophase. In order to examine the effect of various surface conditions on the alignment, parts of the polymer coating were purposely removed in some areas by plasma etching in a vacuum chamber. The cell surface also has a surfactant-treated region for obtaining the homeotropic alignment.

The tilt angle Ψ of the optic axis from the rubbing axis $\hat{b}$ was found to be about 18° in both the thick (≈ 15 μm) and the thin (≈ 3 μm) cells. In the thinner cell two domains were observed in the region with both the top and the bottom surfaces rubbed. The growth of these two domains is probably due to two possible sites of nucleation which could be at either the top or the bottom surface. The optic axes in the two domains are symmetric with respect to the rubbing axis. On the other hand, only one domain was observed in the thicker cell. In this case, a relatively large difference in temperature between the top and the bottom surfaces results in a preferential growth of only one of the two domains from the cooler surface. By inverting the sample in the oven it was confirmed that nucleation always occurs on the top surface that is the cooler one.

An example of the alignment of the smectic-A sample of C_{12}1M7 on several different areas is shown in Figs. 1(a)–1(d), which were photographs taken between crossed polarizers. The rubbing axis $\hat{b}$ is parallel to the long side of the photographs as indicated in Fig. 1(a). Figures 1(a) and 1(b) show the results at 92.0 and 88.0 °C, respectively. In Figs. 1(c) and 1(d) the sample

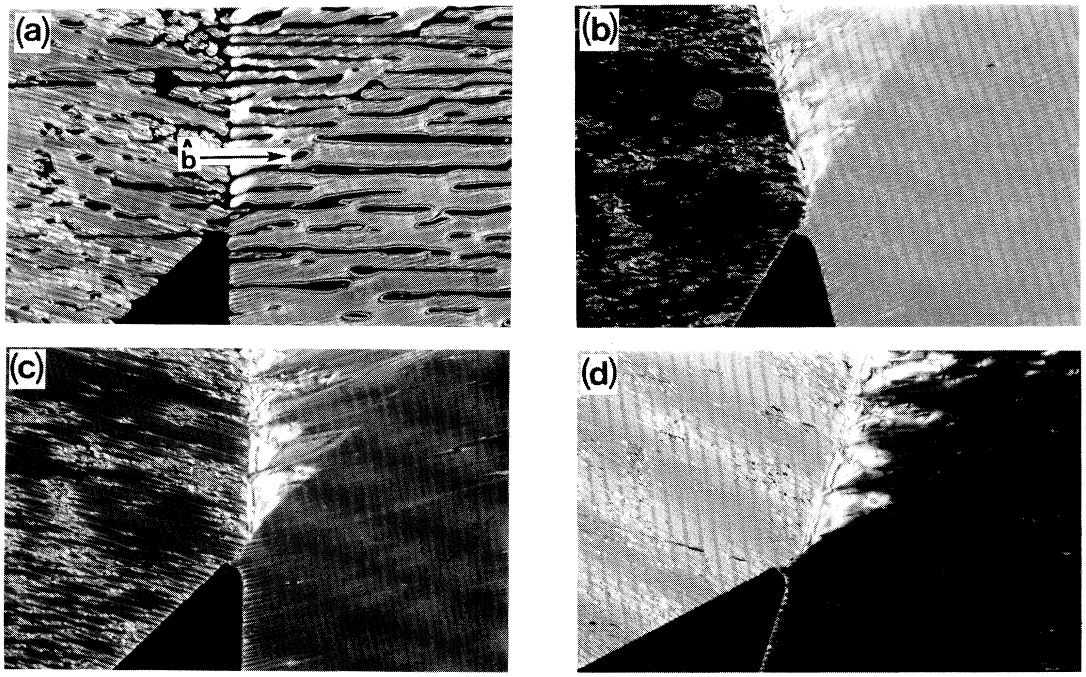

FIG. 1. An aligned sample of the smectic-A phase. (a) Only bottom aligning layer present, (b) both aligning layers present, (c) surfactant layers present, and (d) only top aligning layer present.

was rotated by approximately 18° clockwise and counterclockwise, respectively, so that the optic axis in the aligned region coincides with one of the polarizers and thus the maximum extinction was obtained. In the region in which only the top or the bottom surface was rubbed, the direction of the layer tilt with respect to $\hat{b}$ was determined by the rubbed surface on which nucleation took place. Since the nucleation starts on the cooler rubbed surface, the quality of the alignment is much better in the regions where these conditions are satisfied as shown in Figs. 1(c) and 1(d). The observed good extinction and the fact that optic axis does not line up with the rubbing axis indicate that the twist of the molecular director must be confined within a very thin boundary layer much less than the wavelength λ of the light (visible light in our case). This is because if the distance over which the twist occurs is large and comparable to λ, then wave guiding would occur provided the Mauguin condition is satisfied, i.e., $2\pi\Delta n/\lambda \gg q$, where Δn and q are the anisotropy of the refractive index and the wave vector associated with the twist. In this case extinction would be observed when the sample is aligned with the rubbing axis parallel to one of the polarizers.

We have measured the magnitude of the EC effect in a homogeneously aligned smectic-A sample to ascertain the validity of the mechanism for the layer tilt which is based on the surface EC effect. We then estimate the magnitude of the surface field required to produce the observed amount of the layer tilt with respect to the rubbing axis $\hat{b}$. Recall that in the EC response to an external electric field E applied parallel to the smectic-A layers, the molecules tilt by θ in a direction perpendicular to E, and the magnitude of θ is directly proportional to E.[10] The change in the molecular tilt θ leads to a change in the transmitted light intensity through the sample cell when viewed between cross polarizers, which enables us to measure the magnitude of θ as a function of E.

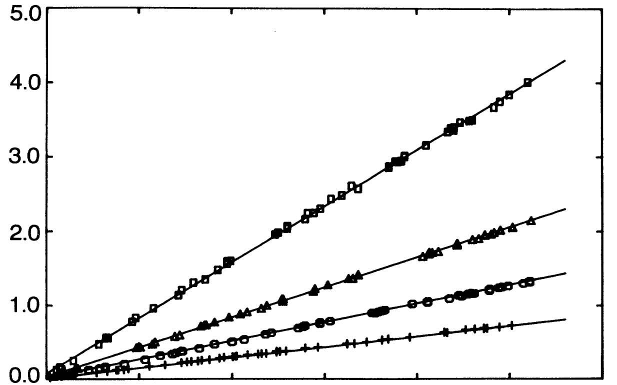

FIG. 2. The induced tilt angle θ vs applied field E. The square, triangle, circle, and cross symbols represent $T=86.0$, 88.0, 90.0, and 94.0 °C, respectively. The solid lines are the best linear fits.

In Fig. 2 we plot typical values of the induced molecular tilt θ as a function of the field strength E at several different temperatures. As shown in Fig. 2, the linear response is clear even at the I-Sm-A transition. As the Sm-A-Sm-C^* transition was approached, however, it was found that the EC response becomes increasingly nonlinear, which is similar to what has been reported previously.[11] The magnitude of θ reaches several degrees close to the Sm-A-Sm-C^* phase transition, although it is very small at the I-Sm-A transition. The magnitude of the molecular tilt θ at the strength of the surface polar field has been claimed to give an explanation for the layer tilt Ψ away from the rubbing axis $\hat{\mathbf{b}}$ in the Sm-A phase. However, the discrepancy between Ψ and θ is by a factor of 10 near the I-A transition.

In Fig. 3 we plot the temperature dependence of the linear EC effect. In the linear regime,[10] the molecular tilt angle θ is given by $(t\chi_p E/a')(T-T_c)^{-1}$, where χ_p^{-1} is the generalized susceptibility, a' is a temperature-independent constant, T_c is the critical temperature for the Sm-A-Sm-C^* transition, and t is the EC constant. Using this expression, we have $d\theta/dE = R(T-T_c)^{-1}$, where $R = t\chi_p/a'$, which gives a power-law divergence. The least-squares fit of the data is represented by the solid line in Fig. 3. As expected, there is a critical slowing down at the Sm-A-Sm-C^* transition. The fitted value of T_c is given by 82.6 °C which is consistent with microscopic observation. From the best fit, we found R to be about 2.6×10^{-8} mK/V. The value of R for $C_{12}1M7$ is about 4 times smaller than that for 764E aligned homogeneously on the similar substrate.[11] Note that the 764E material exhibits a strong nonlinear behavior of the induced molecular tilt. In this material, however, the tilt of the layer normal with respect to $\hat{\mathbf{b}}$ was found to be very small and essentially zero within experimental error. Thus, it is important to examine possible underlying mechanisms for the layer tilt, which distinguishes at least qualitatively between these two cases.

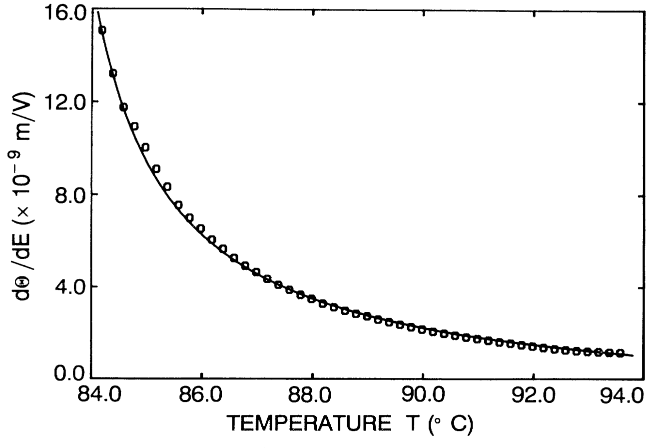

FIG. 3. The slope $d\theta/dE$ vs temperature T. The solid line is the best fit of the data by a form of $R/(T-T_c)+R_0$, with $R = t\chi_p/a'$ and $R_0 \approx 0$.

We first consider the EC coupling of the surface field and determine the magnitude of the resultant molecular tilt. Since no such measurement has been reported in the Sm-A phase so far, we get a crude estimate from the available data in the Sm-C^* phase. Recently, the polar surface field has been used to explain the twisted structure in ferroelectric LCs by Xue and Clark.[8] Using the evanescent-wave technique, they have shown that the molecules close to the surface are completely reoriented by applying an external electric field which overcomes the surface field. Furthermore, in the presence of polar surface interactions, the asymmetry in the switching characteristic was observed by changing the polarity of the applied field. The surface potential determined from this asymmetry was estimated as about 15 V for 3-5-μm samples, giving about 3-5 V/μm for the surface field strength E_s. Assuming that the value of this surface field E_s remains the same in the Sm-A phase and is of the same order of magnitude in our case, we can determine the molecular tilt θ at E_s and compare that with the layer tilt Ψ observed. In the compound studied, $C_{12}1M7$, the molecular tilt θ at $E = E_s$ is at most 2° which is much less than the angle Ψ ($\approx 18°$) of the layer tilt away from the rubbing axis. This clearly indicates that the surface EC effect alone cannot account for the observed large layer tilt.

We now propose an alternative way of explaining the larger layer tilt using a model based on molecular chirality and degree of the smectic ordering near the surface. In this model, the layer tilt is produced by a decrease in the smectic order close to the surface which allows for twisting via molecular chirality. Furthermore, this twist saturates at a certain distance ξ away from the surface. The distance ξ is determined by the thickness of the surface layer in which the smectic order varies spatially and reaches a limiting bulk value. This assertion that the smectic order parameter at the surface is different from the bulk may be supported by the fact[12] that in some materials, such as a series of alkylcyanobipenyl, the packing structure of the molecules in a monolayer film is found to be quite different from that in the bulk. Furthermore, we think that the smectic order parameter at the surface is smaller than the bulk value, thus allowing the molecules to twist close to the surface. This would be expected if the polymer chains, which provide the anisotropic potential for alignment, have nematiclike ordering induced by rubbing. Note that in this model the rate of twist will depend on the spatial variations of the smectic order parameter as well as the degree of the molecular chirality.

Consequently, the magnitude of the observed layer tilt in the bulk will be governed by the amount of twist at ξ with respect to the rubbing axis $\hat{\mathbf{b}}$. This behavior is similar to the deviation of the helix tilt from $\hat{\mathbf{b}}$ in the plane of the substrate near the isotropic-cholesteric transition.[13] In order to estimate the thickness ξ, we assume that the rate of twist within this layer remains constant and is on the order of the bulk value in the higher homologs of this compound. The pitch of the higher homologs in a bulk helical Sm-A^* phase was found to be about 0.5 μm.[14] From the measured value of $\Psi \approx 18°$ together with the pitch $p \approx 0.5$ μm for the material studied, the thickness ξ is then estimated as $p/20 \approx 250$ Å, which is incidentally of the same order as a typical smectic correlation length at a few degrees from the second-order transition.[15] It should be noted that, in contrast, the pitch of 764E mixture is compensated near the nematic–Sm-A transition; hence, it results in essentially no layer tilt. Depending on the nature of surface interactions specific to a LC-substrate interface, the degree of molecular chirality, and the range of the smectic correlation, the layer tilt angle will vary from zero to as much as 20° in the Sm-A phase. It might be interesting to examine the dependence of the pitch and the effect of the presence of a nematic phase on the magnitude of the layer tilt with respect to the rubbing axis.

In summary, we have observed larger layer tilt ($\approx 18°$) away from the rubbing axis $\hat{\mathbf{b}}$ in a chiral smectic-A LC, and proposed a new mechanism for the layer tilt on the basis of molecular chirality and the degree of surface ordering at the surface. The proposed model can explain the essential features of the experimental results. In addition, for $C_{12}1M7$, the thickness of the surface layer is estimated as about 250 Å which is of the order of the smectic correlation. It might be then concluded that molecular chirality, as well as the nature of surface smectic ordering at an interface, plays a crucial role in the growth of the tilted layer with respect to $\hat{\mathbf{b}}$ near the I–Sm-A transition.

---

[a] Present address: Optron Systems, Inc., 3 Preston Ct., Bedford, MA 01730.

[1] For a comprehensive discussion, see J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures* (Gordon and Breach, London, 1982).

[2] W. Chen, M. B. Feller, and Y. R. Shen, Phys. Rev. Lett. **63**, 2665 (1989); W. Chen, L. J. Martinez-Miranda, H. Hsiung, and Y. R. Shen, Phys. Rev. Lett. **62**, 1860 (1989).

[3] B. M. Ocko, Phys. Rev. Lett. **64**, 2160 (1990); B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielsen, and M. Deutsch, Phys. Rev. Lett. **57**, 94 (1986).

[4] S.-D. Lee, J. S. Patel, and J. W. Goodby (to be published).

[5] B. O. Myrvold, Liq. Cryst. **5**, 1139 (1989).

[6] K. Nakagawa, T. Shinomiya, M. Koden, K. Tsubota, T. Kuratate, Y. Ishii, F. Funada, M. Matsuura, and K. Awane, Ferroelectrics **85**, 39 (1988).

[7] J. Xue, N. A. Clark, and M. R. Meadows, Appl. Phys. Lett. **53**, 2397 (1988).

[8] J. Xue and N. A. Clark, Phys. Rev. Lett. **64**, 307 (1990).

[9] J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak, and J. S. Patel, Nature (London) **337**, 449 (1989); J. Am. Chem. Soc. **111**, 8119 (1989).

[10] S. Garoff and R. B. Meyer, Phys. Rev. Lett. **38**, 848 (1977); Phys. Rev. A **19**, 338 (1979).

[11] Sin-Doo Lee and J. S. Patel, Appl. Phys. Lett. **54**, 1653 (1989); **55**, 122 (1989).

[12] D. P. E. Smith, H. Hörber, Ch. Gerber, and G. Binnig, Science **245**, 43 (1989).

[13] S.-D. Lee and J. S. Patel, Phys. Rev. A **42**, 997 (1990).

[14] G. Srajer, R. Pindak, M. A. Waugh, J. W. Goodby, and J. S. Patel, Phys. Rev. Lett. **64**, 1545 (1990).

[15] See, for example, P. S. Pershan, *Structure of Liquid Crystal Phases* (World Scientific, Singapore, 1988).

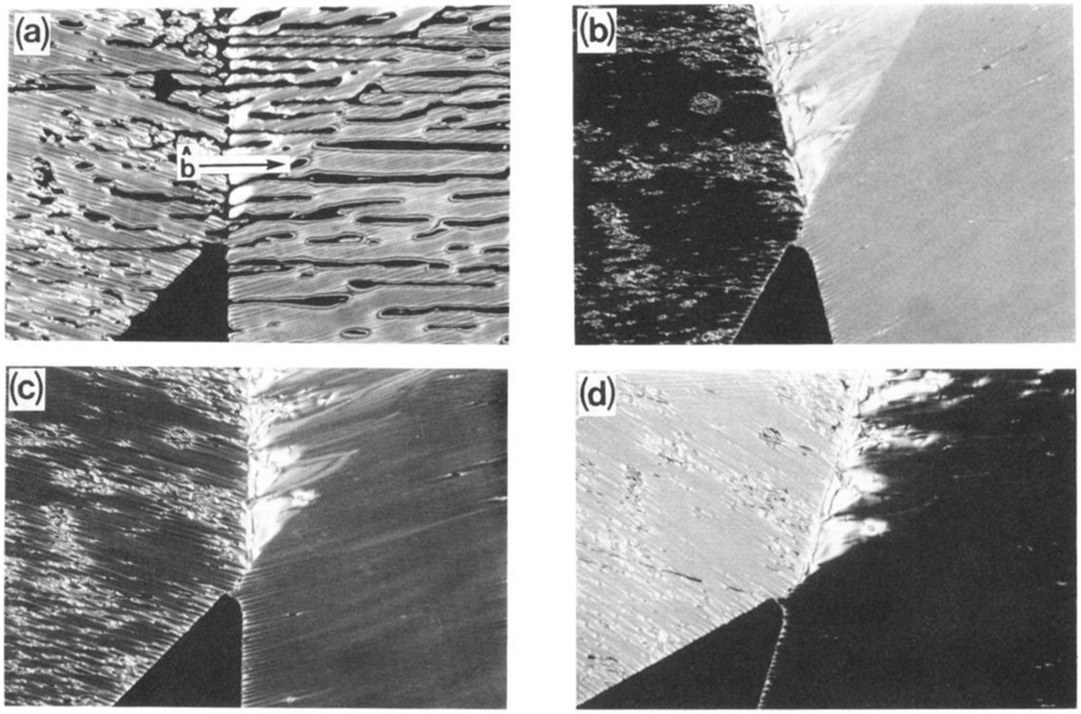

FIG. 1. An aligned sample of the smectic-*A* phase. (a) Only bottom aligning layer present, (b) both aligning layers present, (c) surfactant layers present, and (d) only top aligning layer present.