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Anomalous anisotropy of the elastic constants in the induced smectic O film

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Surface tension is known to induce smectic O (S_O) films at the free surface of isotropic droplets of 1-methylheptyl terephthalylidene-bis-4-aminocinnamate (MHTAC). The S_O film has its molecules disposed in a herringbone fashion, with the layers parallel to the free surface. It constitutes a model of a 2D polar nematic liquid crystal without any contact to solid substrates. The film is oriented uniformly when applying a uniform electric field, except along disclination walls. By measuring the width of the disclination walls in the two configurations with the electric field parallel and perpendicular, we determine the anisotropy of the elastic constants in the induced S_O films. We find the ratio of the 2D bend to splay elastic constants K_b/K_s to be $\simeq 0{\cdot}25$ which is anomalously small when compared to the corresponding 3D ratio $(K_2+K_3)/2K_1$ usually found for the bulk nematic phase. This experimental result is comparable to measurements performed with 2D suspended S_C films with, however, a different physics.

1. Introduction

Contrarily to ordinary crystals which exhibit surface melting, the surface of liquid crystals freezes first [1]. Under the action of surface tension, the molecules at the free surface of an isotropic liquid crystal droplet tend to constitute a smectic layer which again favours the formation of a second layer and so on. Surface tension is thus able to induce a smectic film at the free surface of isotropic liquid crystal droplets, at a temperature higher than the smectic to isotropic transition temperature of the bulk. Generally this process stops after the film has grown a few layers. In 1-methylheptyl terephthalylidene-bis-4-aminocinnamate (MHTAC), the induced film may grow up to several hundred smectic layers depending on the chosen temperature, completely wetting the isotropic phase [2]. It constitutes, in a simple manner, a perfect smectic sample free from solid contacts, with the layers parallel to the isotropic surface.

The other interesting property of MHTAC is that it produces a smectic O (S_O) phase below 158°C. As previously shown, this exceptional phase resembles very much the smectic C (S_C) phase with the molecules positionally disordered in the layers and tilted with reference to the layer normal ($\Psi = 50°$) [3]. The main difference from S_C is that in S_O the tilt of the molecules occurs in alternate directions from one layer to the other one, forming a *herringbone* structure (see figure 1). This particular structure is evidenced by the physical properties of the film which depend on the parity of the number of its layers, and by the antiferroelectricity with alternate in plane polarization, which is measured in chiral S_O^* films [4]. A similar structure has almost simultaneously been claimed for the smectic C_A phase of 4-(1-methylheptyloxycarbonyl)phenyl

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4′-octyloxybiphenyl-4-carboxylate, on the basis of rather indirect arguments [5], and with, perhaps, a doubling of the antiferroelectric period [6].

Because the molecules are tilted, the S_O film is birefringent and observable under a polarizing microscope. Moreover, the electric polarization which naturally exists at the interface with air [7] is tilted also. Its projection **P** on to the film couples to a horizontally applied electric field **E** and thus allows external action on the orientation of the film (see figure 1). This projection **P** of the electric polarization, parallel by symmetry to the horizontal projection of the molecules, defines the director **n** of the S_O-film. Here, since the induced S_O films are very thin, the orientational fluctuations of the wavevector non-parallel to the layers may be neglected. The S_O-films, therefore, constitute model systems for the 2D polar nematic liquid crystal, with a true unit vector as the director. The elasticity of the film is governed by the elastic constants K_s and K_b, respectively, for splay and bend deformations. Since S_O is similar to S_C as far as in plane properties are concerned, these elastic constants may be written as $K_s = NDK_1 \sin^2\Psi$ and $K_b = ND(K_2\cos^2\Psi + K_3\sin^2\Psi)\sin^2\Psi$, where $D = 3{\cdot}0$ nm is the layer thickness, K_1, K_2 and K_3 are the usual Frank elastic constants, and N is the number of the layers in the film [8]. As already mentioned, a permanent electric field **E** applied to the film orients it uniformly except along disclination walls [4]. Measurements of the width of these walls yield the ratios K_s/P and K_b/P, and thus the anisotropy of the elastic constants of the film.

The Frank elastic constants and their ratios have been extensively measured for the nematic phases of different compounds as a function of temperature, using Freedericks transitions [9–10] or Rayleigh light scattering [11–12]. With both methods, the alignment of the samples has to be as perfect as possible, with strong anchoring [10] and negligible stray light [12]. Moreover, delicate corrections to finite size effects have to be applied when using light scattering methods [12]. Though of interest also, measurements of the elastic constants for tilted smectics are much less common [13]. In this paper, we take profit from our particular system which does not suffer the usual drawbacks from solid boundaries, to perform the first measurement of the anisotropy of the elastic constants for the S_O phase of racemic MHTAC in the vicinity of the isotropic phase. We combine for that purpose measurements of the width of the disclination walls oriented parallel and perpendicular to the applied electric field **E**.

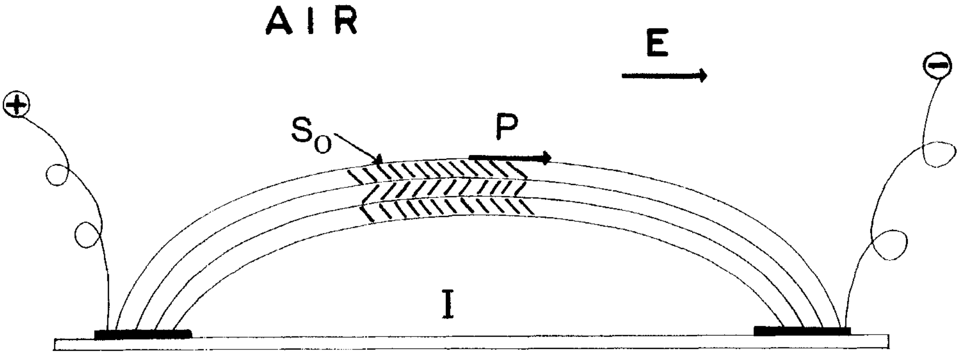


Figure 1. Induced S_O film at the free surface of an isotropic MHTAC droplet less than 1 μm thick. The distance between the electrodes is 2 mm. Note the alternating structure of the S_O phase. Note also that to simplify matters, we have not drawn here the vertical component of the electric polarization at the surface of the film.

2. Theoretical

We first consider a disclination wall perpendicular to the applied electric field **E**, **E** being oriented along the x axis (see figure 2). The density of elastic energy may be written as

$$f_K=\tfrac{1}{2}K_s(\operatorname{div}\mathbf{n})^2+\tfrac{1}{2}K_b(\mathbf{n}\wedge\mathbf{rot}\,\mathbf{n})^2=\tfrac{1}{2}K(1-\eta\cos 2\varphi)\left(\frac{\partial\varphi}{\partial x}\right)^2$$

where the director $\mathbf{n}=(\cos\varphi,\sin\varphi,0)$, and $K_b=K(1-\eta)$ and $K_s=K(1+\eta)$. Neglecting the induced polarization and the space charge $\nabla\cdot\mathbf{P}$, which is reasonable for our rather small electric fields and relatively large wall widths [14], the density of electric energy is simply

$$f_E=-PE\cos\varphi.$$

When minimized, the total free energy of the film yields the Euler–Langrange equation

$$(1-\eta\cos 2\varphi)\varphi''+\eta(\sin 2\varphi)\varphi'^2-A\sin\varphi=0, \tag{1}$$

the term $A=EP/K$ implicitly depending on the number of layers N, since P is a constant and K is proportional to N [4]. Let us remark also that the structure of the disclination wall remains independent of the electric field if a scaling factor $E^{-1/2}$ is applied on the x axis, and that $\varphi(x)$ is an even function, indicating that the wall is symmetrical from its centre as is consistent with the symmetry of the particular case considered here. Equation (1) may be solved by means of classical transformations. Multiplying by φ' and integrating, we get

$$(1-\eta\cos 2\varphi)\varphi'^2=2A(1-\cos\varphi), \tag{2}$$

where the integration constant is chosen such that φ' and φ tend to zero when x goes to infinity. Putting $v=\cot\varphi/2$, this equation immediately transforms to

$$\frac{v'^2}{1+v^2}=\frac{A}{1-\eta}\,\frac{1}{1+(8\eta/1-\eta)[v^2/(1+v^2)^2]}. \tag{3}$$

Restricting our attention to the part of the wall around its centre, where $3\pi/4<\varphi<5\pi/4$, i.e. such that $v^2<0{\cdot}17$, we may write equation (3) to a first order approximation in v^2 as

$$v'^2=\frac{A}{1-\eta}\left(1+\frac{1-9\eta}{1-\eta}v^2\right),$$

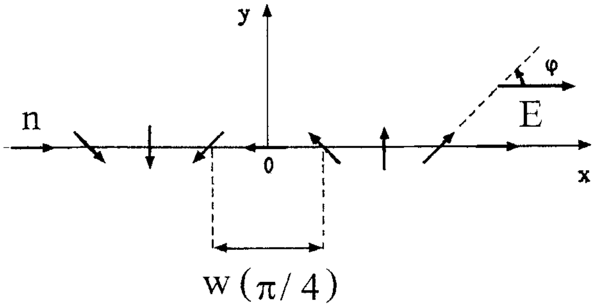


Figure 2. 2π rotation of the director **n** in a disclination wall perpendicular to **E**. The wall width $w_\perp$ is defined as the distance between the places nearest to the wall centre, where **n** is at $\pi/4$ to the wall direction.

which integrates readily and yields the width $w_\perp$ of the central part of the wall from $\varphi=3\pi/4$ to $\varphi=5\pi/4$

$$w_\perp=\frac{2(1-\eta)}{[A(1-9\eta)]^{1/2}}\sinh^{-1}\left[\left(\frac{1-9\eta}{1-\eta}\right)^{1/2}\tan\frac{\pi}{8}\right]. \tag{4}$$

We now consider the other symmetric case, where **E** is oriented along the y axis, i.e. parallel to the disclination wall. The energy density keeps the same form as in the perpendicular case, except for the electric part which becomes $-PE\sin\varphi$. Equation (1) thus remains identical, but with an opposite sign on η, while φ is changed into $\varphi+\pi/2$. The width $w_\parallel$ of the central part of the wall, defined as the place where $5\pi/4<\varphi<7\pi/4$, is then

$$w_\parallel=\frac{2(1+\eta)}{[A(1+9\eta)]^{1/2}}\sinh^{-1}\left[\left(\frac{1+9\eta}{1+\eta}\right)^{1/2}\tan\frac{\pi}{8}\right]. \tag{5}$$

When the anisotropy of the elastic constants is weak, η is small and a first order approximation in η may be taken. We then deduce

$$\frac{w_\parallel}{w_\perp}=1+\eta\left(\frac{8\sin(\pi/8)}{\sinh^{-1}\tan(\pi/8)}-7\right). \tag{6}$$

In figure 3 is represented the ratio $w_\parallel/w_\perp$ versus η as given from equation (6), together with the exact result obtained from numerical integration of equation (2). This last result allows direct comparisons to the measurements.

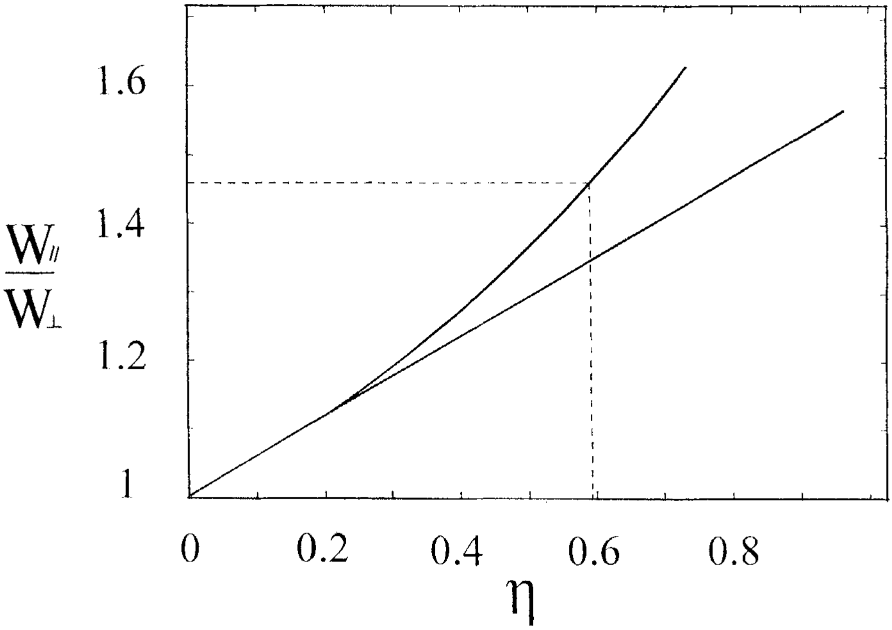
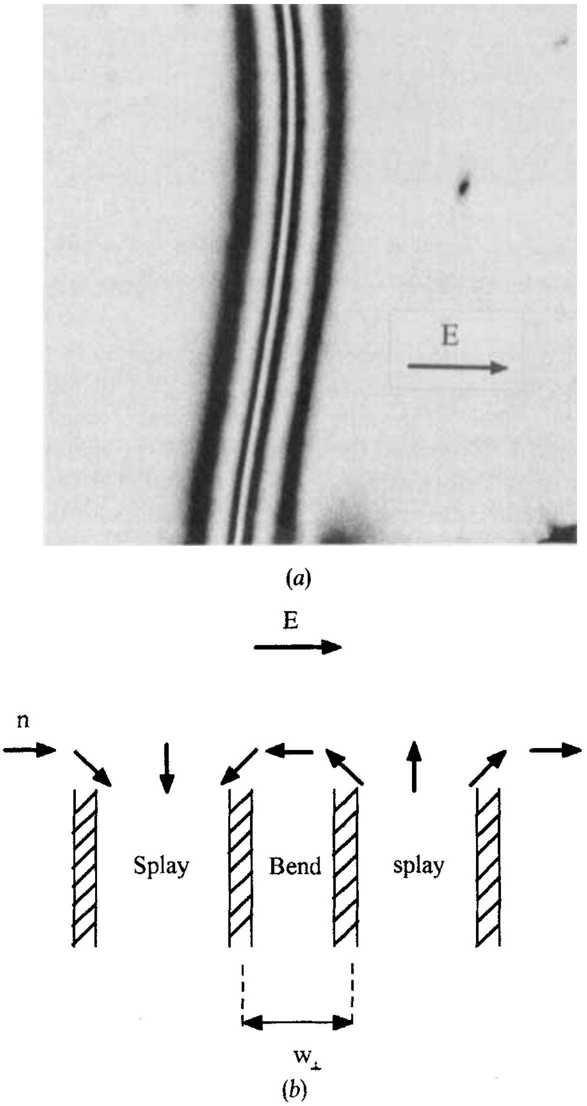


Figure 3. Wall width ratio $w_\parallel/w_\perp$ calculated as a function of the elastic anisotropy coefficient η. Both the first order approximation (equation (6)) and the exact result from numerical calculation are shown. This last calculation yields $\eta=0{\cdot}59$ from the experimental wall width ratio $w_\parallel/w_\perp=1{\cdot}46$ (dashed lines).

3. Experimental

The sample and experimental set-up are as described in [4]. A small quantity of racemic MHTAC is deposited on a clean glass plate between two evaporated gold electrodes, and is precisely thermostated inside an Instec stage (see figure 1). The surface induced S_O-film and the disclination walls that it produces when an electric field is applied [15] are then observed between crossed polarizers with a Laborlux Leica microscope. The film thickness is determined from birefringence measurements, using a rotating compensator [8].

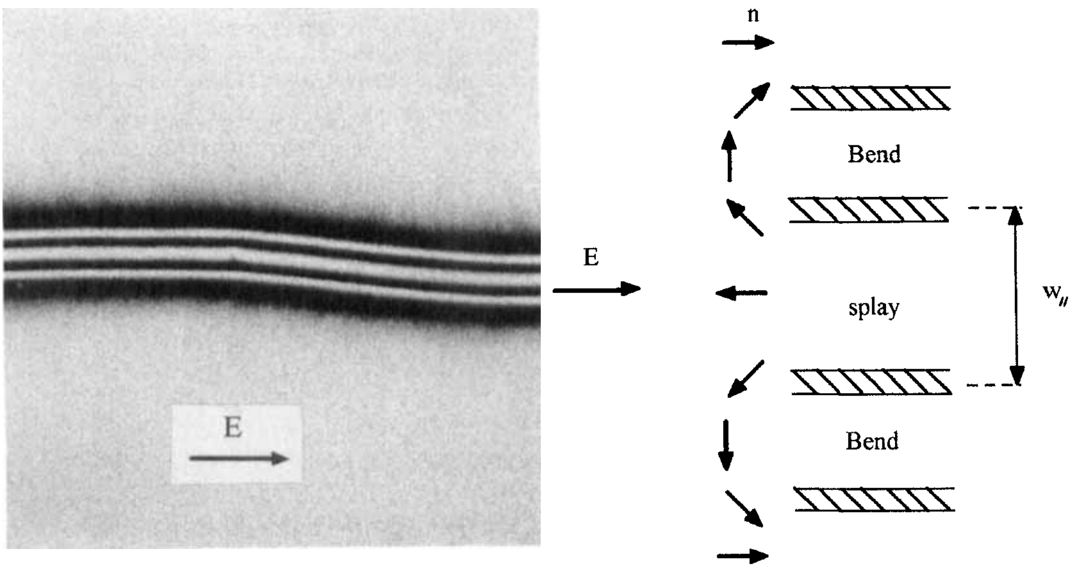
Typical disclination walls perpendicular and parallel to the electric field are shown in the photographs of figures 4 (*a*) and 5 (*a*), respectively. The polarizers are oriented at



(*a*)

(*b*)

Figure 4. (*a*) Photograph of a disclination wall perpendicular to E in a S_O film approximately 20 layers thick. The polarizers are crossed and oriented at $\pi/4$ to the wall direction. (*b*) Sketch of the photograph depicting the distortion in the wall and giving the location of the black fringes when the polarizers are crossed and oriented at $\pi/4$ to **E**.



(a) (b)

Figure 5. (a) and (b), legend as for figure 4, but the wall is now parallel to E.

$\pi/4$ from the wall direction, and therefore the black fringes on the photographs mark the places where the director is tilted by $\pi/4$ with respect to the wall direction (see figures 4(b) and 5(b)). Clearly, the walls are symmetrical, consistent with the above discussion on equation 1. Moreover, the central part of the wall in figure 5(a), which essentially involves splay deformations, is more expanded than that in figure 4(a), which corresponds to bend deformations. This gives evidence for the elastic anisotropy $K_s > K_b$, i.e. roughly $2K_1 > K_2 + K_3$, using the Frank elastic constants.

More quantitatively, the wall widths $w_\parallel$ and $w_\perp$ are measured as defined above, from the distance between the two central fringes of the wall, for different E values. As shown in figure 6, the quantities $w_\parallel^{-2}$ and $w_\perp^{-2}$ are found to depend linearly on E, which is consistent with the prediction of equation (1). However, slight deviations from linearity are observed in the range of the small values. These deviations are due to elastic distortions produced by accidents in the film, e.g., defects or dust, in the vicinity of the place where the measurement is performed. In order that such deviations be negligible, the energy density of the corresponding elastic distortion must remain much smaller than that of the measured wall, say, two orders of magnitude smaller. This condition is reached when the cause, dust or defects, of the parasite distortion is one order of magnitude farther from the place where the measurement is performed than the width of the wall itself. This condition is naturally more difficult to fulfil in the range of the small E values where the walls become very large. On the other hand, the large E values have other drawbacks. They produce narrow walls that are measured with a large relative uncertainty, probably superimposed upon by some systematic error due to the tendency we have to give them a minimum width when measuring them. Also, the high voltage measurements heat up the S_O-films and can destroy them. In order to avoid such problems, the measurement procedure has to be as fast as possible, i.e. the photograph has to be taken immediately after the electric field is applied and stabilization of the wall is reached.

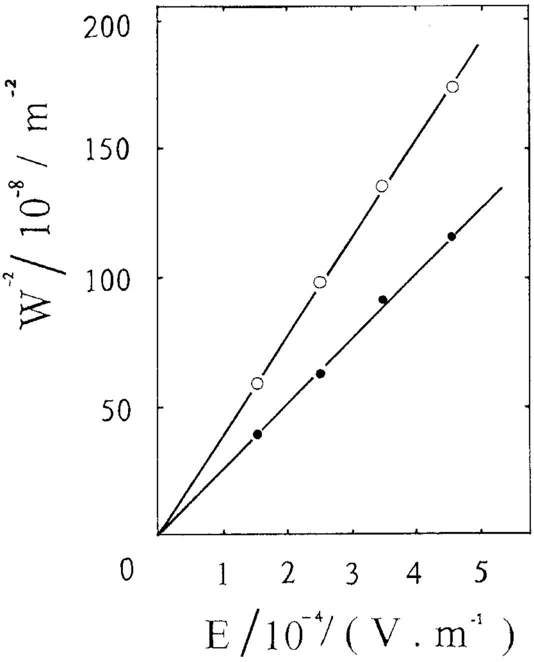


Figure 6. Inverse squared wall width $w_{\|}^{-2}$ (dots) and $w_{\perp}^{-2}$ (open circles) versus electric field **E**.

Measurement of the ratio $w_{\|}/w_{\perp}=1{\cdot}46\pm0{\cdot}09$ is found to be independent of the electric field values within the error bar, in agreement with the remark on equation (1) and with equation (6) itself. This result, compared to theory, allows the determination of the anisotropy coefficient $\eta=0{\cdot}59\pm0{\cdot}08$ (see figure 3), and therefore yields the anisotropy of the 2D elastic constants $K_b/K_s=0{\cdot}26\pm0{\cdot}07$ in a surface induced S_O-film of 20 layers.

4. Discussion and conclusions

Only few measurements of the orientational elastic constants have been performed for smectic phases, but following a remark in [13], the in plane distortions in the tilted and disordered smectic liquid crystals have similar elastic constants to the nematic phase. It is therefore reasonable to compare our experimental elastic anisotropy $K_b/K_s=0{\cdot}26$ to the corresponding anisotropy $(K_2\cos^2\Psi+K_3\sin^2\Psi)/K_1\simeq(K_2+K_3)/2K_1$, available in the literature for the nematic phase. In general, the ratio $(K_2+K_3)/2K_1$ is found to be larger than unity [9], increasing roughly as the length to width ratio L/W of the rigid part of the molecule [10]. In the case of the long MHTAC molecule, $L=3{\cdot}0$ nm and $W=0{\cdot}55$ nm, i.e. $L/W=5{\cdot}5$, and the extrapolation in figure 10 of [10] indicates a ratio $K_3/K_1\simeq5$. Taking a typical value $K_2/K_1\simeq0{\cdot}6$–$0{\cdot}7$, we thus estimate $(K_2+K_3)/2K_1\simeq3$, which is one order of magnitude larger than our experimental result. Our experimental elastic anisotropy may then be tentatively explained by noting that the general trend for K_3/K_1 in the nematic phase is to decrease with increasing temperature towards unity, until the bulk nematic to isotropic phase transition is reached, while the K_2/K_1 ratio remains about constant. The temperature in our induced films being a little bit higher than this bulk transition temperature, we may thus expect K_3/K_1, and consequently $(K_2+K_3)/2K_1$, to be smaller than the predicted values. However, the experimental and theoretical results in [10] show that this temperature correction is insufficient to explain alone a reduction factor of about one order of magnitude.

The consequences of the particular geometry of the experiment on the anisotropy of the elastic constants K_b/K_s, that is the 2D character of the free floating films, should also be considered. As observed by Rosenblatt *et al.*, for freely suspended films [16], the electrostatic interactions between the surface dipoles produce a strong enhancement of K_1, but leave K_2 and K_3 unperturbed. A similar electrostatic effect should also exist in the induced films, and could explain the low value of K_b/K_s that we observe. There is, however, a marked difference, because the induced S_O-films have only one dipolar surface, the air–S_O interface [4], instead of two in the symmetric suspended S_C films. The electrostatic interactions should thus result in a constant correction to K_s, independent of the film thickness, and should then lead to a K_b/K_s ratio strongly dependent on the film thickness, since the uncorrected 2D elastic constants K_s and K_b are proportional to the film thickness. Preliminary measurements, however, do not show such a thickness dependence of K_b/K_s. We may, therefore, discard the renormalization of the elastic constants from the electrostatic interactions between the surface dipoles to explain our results.

A renormalization of the elastic constants, proportional to the film thickness, could, however, arise from flexoelectricity. Let us briefly examine the effects of the leading terms in the interaction energy involving the flexoelectric polarization. The major coupling term, with the applied electric field E, remains constant when integrated between two black fringes. It is, therefore, unable to modify the position of the fringes and consequently to change the measured elastic constants. The other leading term, coupling the flexoelectric polarization to the surface dipoles, should produce dissymmetry in the walls perpendicular to E, and two different shapes for the walls parallel to E according to their sense of rotation, but none of these complications are observed here. We may, therefore, conclude that flexoelectricity does not play a significant role in our experiment and cannot explain our observed anisotropy of the elastic constants.

We are finally left with the possibility that the novel S_O phase behaves differently from the classical nematic and S_C phases. More experiments are naturally needed to ascertain this point, for instance with S_C induced films.

It is a pleasure to acknowledge useful discussions with G. Durand.

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[7] The electric polarization at the interface with the isotropic droplet which could be due to ordoelectricity, can be neglected. Its amplitude is at least one order of magnitude smaller than the contribution arising from the other interface, since no parity effect is observed in the measurements of the total polarization of the film versus its number of layers [4]. Let us recall also that the electric polarization of the interface with air probably arises from the reduced polarizability of the aliphatic tips of the molecules in contact with air, resulting from the reduced dielectric constant of their surroundings compared to those in the bulk. Another contribution could also come from the average electropositivity of the molecule. This chemical property always makes the liquid crystal slightly positively charged, as is demonstrated from the slow drift of the droplet towards the negative electrode.

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