

Optical studies of the liquid crystal *B2* phase formed by banana-shaped molecules

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Null-transmission ellipsometry and depolarized light microscopy have been performed on free-standing films of three achiral banana-shaped compounds in the *B2* phase. Our results support a two-layer unit cell previously proposed to explain the observed antiferroelectricity in thin films and bulk samples. We have studied thicker films than previously reported and have found no deviations in the film structure from the earlier findings. Moreover, we can determine the layer spacing, the molecular tilt from the layer normal, and the three principal indices of refraction in the molecular reference frame.

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I. INTRODUCTION

The discovery of ferroelectric [1] and antiferroelectric [2] ordering in chiral, rod-shaped liquid crystals created a lot of excitement in condensed matter physics. However, it was generally assumed that chirality in the molecule was necessary to break the mirror symmetry and create ferroelectric or antiferroelectric ordering. Watanabe *et al.* [3] proposed that antiferroelectric and ferroelectric smectic phases may appear in systems consisting of achiral molecules if the molecules are packed with C_{2v} symmetry. This packing is possible with banana-shaped molecules due to their shape. Molecules of this type have been synthesized in various laboratories [4] and have been found to form many unusual mesophases that may be analogous to certain unconventional superconducting states [5]. Niori *et al.* [6] first observed ferroelectric ordering in the *B2* phase of such compounds. Link *et al.* [7] performed electro-optical studies with a small applied electric field ($E \sim 10$ V/cm) on films in the *B2* phase from two to ten layers in thickness and bulk samples with a much larger field ($E \sim 5$ V/ μm). They proposed the models shown in Figs. 1(a)–1(d) to explain their observations.

Link *et al.* [7] observed only one layer structure in free-standing films [Fig. 1(a)] while they found two zero-field states in bulk samples [Figs. 1(a) and 1(c)] [8]. Subsequently, Kats and Lajzerowicz [9] formulated a Landau theory for the banana phases. From their theory, they proposed that the air-film interface stabilized the structure seen in thin films. To determine if there is a thickness dependence to the layer structure and to obtain the optical tilt and the principal indices of refraction, we have studied films of thickness up to 54 layers in three compounds showing the *B2* phase using null-transmission ellipsometry (NTE). The layer spacing was measured by x-ray diffraction. Depolar-

ized reflected light microscopy (DRLM) was employed to check the switching behavior of the thin films.

Figures 1(a)–1(d) show the layer arrangements of the *B2* phase as reported by Link *et al.* [7]. There exists no long-range positional ordering within each layer. The molecules are tilted by an angle θ from the layer normal. Within each layer all the molecules are aligned, so a vector \mathbf{b} that points along the bend of the molecule can be defined [Fig. 1(e)]. Two things differentiate the various structures. The first is whether the tilt orientation of adjacent layers is parallel (synclonic) or antiparallel (anticlinic). The second is whether \mathbf{b} in adjacent layers is parallel or antiparallel. The polarization of each layer is perpendicular to the tilt plane and either parallel or antiparallel to \mathbf{b} . For the layer structures shown in Figs. 1(a) and 1(c), films with even N have no net polarization while films with odd N have a net polarization because there is one layer whose polarization is not canceled. Here N is the number of layers in the film.

II. EXPERIMENTAL METHOD

We have studied three compounds. The phase sequences for $C_{8,12}$ and $C_{9,12}$ [10] [see Fig. 2(a)] are isotropic (*I*)

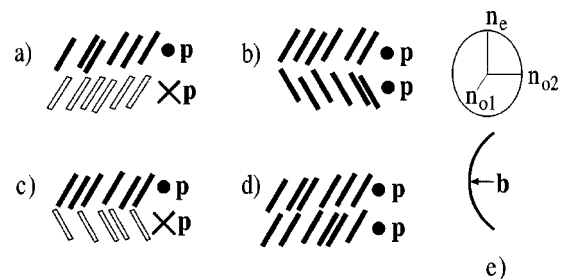


FIG. 1. (a)–(d) show cartoons of the layer arrangements proposed by Link *et al.* [7] for the *B2* phase. The polarization \mathbf{p} of each layer is perpendicular to the tilt plane and parallel to the bow orientation. The molecules are drawn solid when the bend points into the page, and hollow when the bend points out of the page. (e) defines the vector \mathbf{b} as pointing along the bend of the molecule. Above the molecular cartoon is the corresponding ellipsoid of refraction showing n_{o1} , n_{o2} , and n_e .

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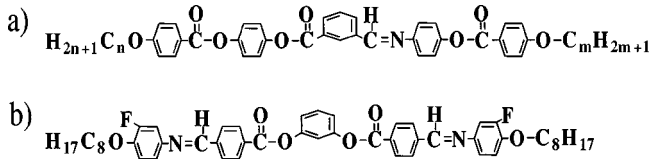


FIG. 2. (a) and (b) show the molecular structure for the homologous series $C_{n,m}$ and 8OF, respectively. The bends in the molecules are provided by the center benzene rings. The molecules are drawn straight to save space.

(128 °C)– $B2$ (113 °C)–crystal (Cr) and I (133 °C)– $B2$ (112 °C)–Cr, respectively. 8OF [Fig. 2(b)] has the phase sequence I (154 °C)– $B2$ (147 °C)– $B3$ (118 °C)–Cr. With two imino linkages and a high temperature $B2$ phase window, the 8OF compound degraded quickly. This occurred on the order of about 4 h in our system, so we studied it in a degraded state [11]. The I – $B2$ transition temperature was allowed to decrease from 154 °C to 145 °C before the sample was replaced. The $C_{n,m}$ compounds have a lower $B2$ phase window and only one imino linkage, so degradation of these compounds was less pronounced. The $C_{n,m}$ compounds were studied at 125 °C while 8OF was studied in the middle of the $B2$ temperature window.

We studied compounds in their $B2$ phase using the free-standing film geometry. Films, unlike bulk cells, provide uniform alignment of the layers. The films were drawn across a 4 mm diameter hole in a glass cover slip. The hole was surrounded by either two or four electrodes. The field was large enough to orient films with a net polarization without inducing flow or distorting the zero-field layer structure. The films were drawn in a temperature-regulated sealed environment with an argon exchange gas.

NTE [12] was used to acquire the optical properties of the samples. Our NTE approach has been described in recent papers [13,14]. The ellipsometric parameters Δ and Ψ are measured by using the polarizer-compensator-sample-analyzer configuration with a resolution of 0.001°. Our NTE experimental runs were done with an electric field of 5 V/cm. We used a four-electrode plate that allowed us to smoothly control the direction of the electric field. A film was pulled in the $B2$ phase range and allowed to become uniform in thickness, at which time we began to take ellipsometric data while rotating the electric field within the plane of the film with a step size of 8°. This procedure allowed us to acquire Δ and Ψ at various film-structure orientations, providing that the film had a net polarization. Several rotations were conducted to check that the data were reproducible. If the field did not cause the film to align, data were taken while the film structure slowly reoriented because of thermal fluctuations. We lose orientation information by this approach, but can still plot Ψ versus Δ to get a characteristic shape that depends on the layer arrangement in the film. Such films need not yield data points for a complete rotation.

In our DRLM [15] experiment, N was determined by measuring the intensity of a laser beam reflected by the film at near normal incidence. It is known that for $N \leq 10$ the reflected intensity is proportional to N^2 [16]. By pulling a series of thin films, it is possible to determine N . In our

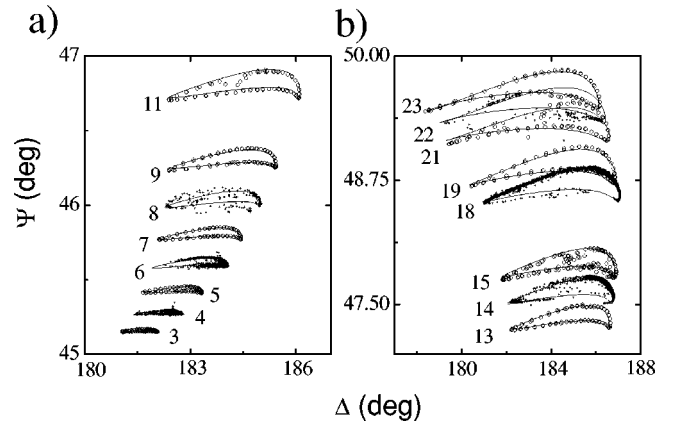


FIG. 3. The Ψ versus Δ data are shown here for $C_{9,12}$ films in the $B2$ phase with N from 3 to 11 and 13 to 23 layers in (a) and (b), respectively. Next to each plot N for that film is given. For clarity, data from films with odd N are shown with circles and from films with even N with crosses. The simulations are shown with solid lines.

DRLM studies a two-electrode film plate was used because we were interested only in how the film responds to an electric field. We used a square electric field of 22 V/cm with a frequency of 0.3 Hz. We could see if the film reoriented when the electric field direction changed.

III. DATA ANALYSIS

In contrast to some previous ellipsometric experiments on liquid crystals [17], a biaxial ellipsoid of refraction, instead of uniaxial, was used to approximate the optical properties of each layer because the banana-shaped molecules are strongly biaxial. The principal indices of refraction in the molecular reference frame are shown in Fig. 1(e). n_e is along the long axis of the molecule (\hat{n}), n_{o2} is along \mathbf{b} , and n_{o1} is perpendicular to \mathbf{b} and \hat{n} .

The Ψ versus Δ curves are simulated as a function of film orientation using the 4×4 matrix method [18]. The following parameters are necessary to make a fit: the three indices of refraction (n_e , n_{o1} , and n_{o2}), the layer spacing (d), θ , and N . A layer structure is also necessary to simulate the film. We probe the optical tilt angle, which is typically different from the tilt angle found by x-ray diffraction [19].

We could measure N exactly for thin films. To determine N for one film it was necessary to pull a series of films. Each film gives a characteristic Ψ and Δ curve upon rotation which is a function of both the biaxiality and the optical thickness. When averaged over one rotation, Ψ and Δ depend primarily upon the optical thickness and therefore N . The average Ψ and Δ change in discrete steps due to quantization of N with an N -dependent trend (see Fig. 3). N was estimated independently from the color of white light reflected off the film [20].

We observed that films with odd N oriented in the applied electric field while films with even N did not. A two-layer antiferroelectric structure is the simplest explanation of this behavior. Using DRLM this even-odd behavior was ob-

served in films for $N=2-8$ layers; it was difficult to determine N exactly for $N>8$ from the simple reflectivity method described earlier, and thereby address the even-odd behavior for thicker films [21]. We confirmed the even-odd behavior in the NTE system where N is easily measurable. We pulled almost all the films from in the ranges $N=2-23$ for $C_{9,12}$, $2-20$ for $C_{8,12}$, and $2-6$ for 8OF [22]. However, it was difficult to pull thicker films. This means there are large gaps between the different N values for thick films. This, together with the fact that we could not measure the optical parameters with extremely high precision, meant we could only determine N for thicker films with a precision of ± 1 (see the discussion below). We were thus unable to confirm the even-odd effect in films thicker than $N=23$ and 20 for $C_{9,12}$ and $C_{8,12}$, respectively. We did observe that some thick films (up to 54 layers for $C_{9,12}$) oriented with the field while others did not.

Because N for thin films was found by the method described above, and d was obtained from x-ray diffraction, we were left with four fitting parameters (θ , n_e , n_{o1} , and n_{o2}). These remaining optical parameters can be found by numerical modeling the data by minimizing the mean squared deviation of the model from the data. Numerical fitting using the 4×4 matrix method was done only on films with odd N . Only these films aligned with the field, thereby making it possible to simulate Ψ and Δ as a function of the orientation of the film and compare the data to the simulations. Afterward, we can simulate the Ψ versus Δ plots for the films of even N using the optical parameters from the odd N data, and compare the data to the simulation. We found that only one set of optical parameters gave the best fit.

To determine if the structure is synclinic or anticlinic a comparison between NTE data and simulation is necessary. If the range of allowed values for the indices of refraction is unrestricted, the simulations fit well for both synclinic and anticlinic layer structures. However, for the anticlinic layer structure, the simulations have n_e increasing systematically from 2.3 to 4 and n_{o1} decreasing from 1.1 to 0.6 as N increases from 3 to 23 layers for $C_{9,12}$. Not only is this not a reasonable value for a liquid crystal compound, the principal indices of refraction in the molecular frame should not change greatly with film thickness. The optical parameters in a simulation with a synclinic layer structure film are approximately constant, except for a small systematic variation as a function of N , which will be investigated in the future [23]. These observations imply that the synclinic structure is an accurate description of our data, while the anticlinic structure is not.

Using NTE we have observed that the tilt plane is aligned perpendicular to the electric field in films of odd N , thereby implying that the polarization is perpendicular to the tilt plane. This observation implies that \mathbf{b} is also perpendicular to the tilt plane [24].

For $C_{9,12}$, we found $d=37.90 \pm 0.05$ Å, $\theta=39^\circ \pm 3^\circ$, $n_e=1.665 \pm 0.01$, $n_{o1}=1.483 \pm 0.007$, and $n_{o2}=1.534 \pm 0.002$. The error bars on the optical parameters are the standard deviations of the values for simulations of different N , while the error bar on d is from the x-ray results. The

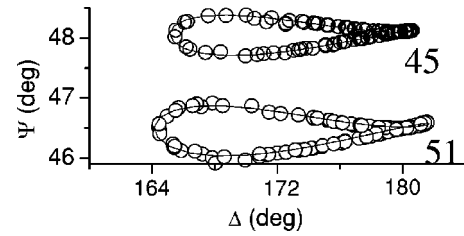


FIG. 4. Ψ versus Δ data are shown here for thicker films of $C_{9,12}$ in the *B2* phase. Next to each plot N for that film is given. The data are shown with circles and the simulations are shown with solid lines.

results of these fittings are shown in Figs. 3 and 4 and are discussed below. For $C_{8,12}$, $d=36.97 \pm 0.05$ Å, $\theta=37^\circ \pm 3^\circ$, $n_e=1.68 \pm 0.02$, $n_{o1}=1.49 \pm 0.02$, and $n_{o2}=1.54 \pm 0.01$. For 8OF, $d=39.4 \pm 0.2$ Å, $\theta=22.8^\circ \pm 2^\circ$, $n_e=1.768 \pm 0.03$, $n_{o1}=1.503 \pm 0.006$, and $n_{o2}=1.547 \pm 0.002$.

Figures 3(a) and 3(b) show the data and simulations for $C_{9,12}$ films with N from 3 to 11 and 13 to 23, respectively. The data were noisier for even N because the electric field did not provide uniform domains, while the simulations assumed a uniform domain sample [25]. The two-layer film data are not shown because they were very noisy, although it was clear that the film did not respond to the electric field. The simulations for the films of even N are produced by allowing the optical parameters to vary within the error bars quoted above and are in good agreement with the data.

Figure 4 shows Ψ versus Δ data for two thicker $C_{9,12}$ films which align due to the electric field. To find N we used the values of θ , n_e , n_{o1} , and n_{o2} found from thinner films and the bulk value of d . The optical parameters are then allowed to vary to give the best fits shown with solid lines. Very good fits were obtained with $N=45$ and 51 . We acquired data from another thick film which did not respond to the electric field. Unfortunately, during the 16 h run conducted on this film, the orientation of the film structure did not change much and gave only a small section of the Ψ versus Δ curve. However, from the acquired data our simulation yields $N=54$, which is consistent with the film color. These thick film results support the film structure shown in Fig. 1(a).

To determine if the indices of refraction we have found are reasonable, a comparison to rodlike molecules is necessary. These compounds have been studied extensively, and their indices of refraction are well known. Two layers of tilted rodlike molecules with anticlinic tilts can be compared to a single untilted layer of banana-shaped molecules. Let the tilt of the molecules in the rodlike layers be ϕ , the index of refraction along the long axis of the molecule be n_{re} , and the index of refraction perpendicular to the long axis of the molecule be n_{ro} . If we ignore the off-diagonal components of the ellipsoid of refraction, then the following equations for the indices of refraction in the layer frame for the rodlike molecules can be found. The index of refraction along the layer normal is $n_{l1}=n_{re}\cos^2(\phi)+n_{ro}\sin^2(\phi)$, the index of refraction along the c director is $n_{l2}=n_{ro}\cos^2(\phi)+n_{re}\sin^2(\phi)$, and the index of refraction perpendicular to the layer normal and the c director is $n_{l3}=n_{ro}$. The rodlike indices of refraction

tion in the layer reference frame n_{l1} , n_{l2} , and n_{l3} should correspond to n_e , n_{o2} , and n_{o1} of a layer made of banana-shaped molecules.

In this comparison ϕ should be equal to the bend angle of the banana molecule, which is typically 30° . A typical rod-like liquid crystal compound *p*-decyloxybenzylidene-*p*-amino-2-methylbutyl cinnamate (DOBAMBC) has the indices of refraction $n_{re} = 1.68$ and $n_{ro} = 1.48$. With these values we obtain $n_e = 1.63$, $n_{o2} = 1.53$, and $n_{o1} = 1.48$. These values are in reasonable agreement with what was found for $C_{9,12}$ and $C_{8,12}$. The agreement is not as good for 8OF. This may be due to unusually large indices of refraction for 8OF or because the results for 8OF are based upon the data for only a few films.

In our DRLM system we pulled one $N=1$ $C_{9,12}$ film. Further investigation may yield information on the role of steric interlayer interactions in the $B2$ phase. One-layer films are extremely rare, and we did not have the opportunity to study one in the NTE system.

IV. CONCLUSION

We have studied films of thickness up to $N=54$. After considerable effort, we found it to be nearly impossible to pull thicker films for these compounds. Even with such thick films no transition into a bulk layer arrangement with antclinic tilts was detected. However, it has been observed that the two surfaces of a film can remain coupled for $N > 100$ [17]. It may be necessary to study much thicker films to

resolve this issue. This would require a compound with which it is easier to pull thick films.

In conclusion, we have studied films of thicknesses up to 54 layers in three compounds using NTE and DRLM. We have simultaneously acquired the three indices of refraction and the optical tilt angle using NTE, which has not been possible for this phase by other techniques. The measured values of the indices of refraction are in reasonable agreement with those of rodlike molecules. The following three observations based upon our data were confirmed in the $B2$ phase of these compounds. First, the simplest explanation of the even-odd behavior seen in films is that \mathbf{b} is antiparallel in adjacent layers. Second, our data support a synclinic layer structure. Third, the polarization is perpendicular to the tilt plane and is either parallel or antiparallel to \mathbf{b} . All three observations agree with what was found by Link *et al.* [7] in very thin films. We did not observe a bulk structure that is different from the surface in films up to 54 layers.

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- [22] Our sample of 8OF (~ 40 mg) was used up so a more exhaustive study of this compound could not be done.
- [23] The large error in θ may be due to θ or d changing with N .
- [24] NTE is insensitive to 180° rotations in molecules about any of their principal axes because the ellipsoid of refraction remains unchanged upon such an operation. Therefore the orientation

- of \mathbf{b} must be inferred from the polarization direction.
- [25] The results for the films of even N are often those of more than one domain. This was unavoidable because of the large amount of time required to allow the domains to reorient on their own.