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X-ray Diffraction and Torsional Viscosity Investigations of Laterally Linked S_C* Liquid Crystal Dimers

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The mechanism by which a tristable, laterally linked, S_C* liquid crystal dimer reorients under the application of an electric field has been investigated by a combination of X-ray diffraction studies and torsional viscosity measurements. A new experimental liquid crystal cell has been developed that allows direct measurement of layer spacing as a function of applied field at controlled temperature. The distance between smectic layers is consistent with the dimer naturally arranging in a "U" conformation. No significant change in layer spacing of the dimer was observed upon the application of an electric field for all temperatures and field strengths accessible. The torsional viscosity of the tristable phase of the dimer is similar to previously characterized tristable compounds. These results are consistent with the hypothesis that electrically induced switching of the optically pure dimer occurs by conventional, conical Clark−Lagerwall-type switching seen in other ferroelectric and antiferroelectric materials.

Introduction

Dimeric liquid crystals show interesting possibilities for use in flat panel display devices. Namely, twin liquid crystals possessing chiral tilted smectic phases (S_C*) have been studied because of their attractive mechanical and electrooptic properties.[1,2] These dimers are most commonly formed from "monomeric" units linked in a head-to-tail fashion. We have synthesized S_C* liquid crystal dimers with the monomeric units covalently joined through a lateral spacer.[3] Twin molecules of this architecture were first reported by A. C. Griffin and co-workers.[4,5] More recently, Tschierske et al. reported a series of laterally connected twins and investigated the influence of structural variations on phase behavior.[6]

We recently reported the synthesis and electrooptic properties of laterally linked dimeric liquid crystals possessing chiral centers on each monomeric half twin.[3] The twins exhibit an interesting and uncommon electrooptic response. A mesophase that exhibits tristable switching was found to exist at a temperature higher than that in which bistable switching occurs. In materials such as MHPOBC [4-[[(1-methylheptyl)oxy]carbonyl]-phenyl 4′-(octyloxy)-biphenyl-4-carboxylate] that possess a tristable S_C*_α phase,[7] this mesophase exists at a higher temperature than the bistable S_C* phase, which in turn, exists at a higher temperature than the antiferroelectric S_C*_A phase. However, the S_C*_α phase occurring in MHPOBC and related compounds exists over only a one or two degree temperature range and the tristable switching has no threshold. The tristable nature of our dimers differs in that the phase is stable over a range of ∼10 degrees, and the switching is characterized by the presence of a threshold.

A variety of switching mechanisms can be proposed to describe the interesting field-induced response of these twins. The most obvious mechanism is one in which the dimer arranges in the common antiferroelectric herringbone ordering, as shown in Figure 1. This state would exist at zero applied field, between the two ferroelectric states that are induced by positive or negative voltage across the cell.

An alternative switching mechanism can be proposed that could explain the tristable nature of the phase. A field-induced conformation change of the dimer from a dipole opposed state to one of two dipole aligned states would result in the three states. This reorientation is shown in Figure 2. This conformation change is not unlike that seen by Griffin and co-workers in their study of a Schiff's base ligated twin.[4] Griffin found, on the basis of small-angle X-ray diffraction and space-filling molecular models, that his twin mesogen could exist in two S_C conformations ("S" and "U") with distinctly different layer spacings. The conformation is dependent on the thermal history of the material but is not subject to field-induced change because of symmetry.

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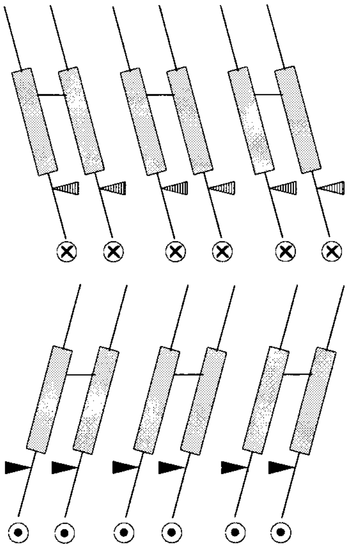

Figure 1. Herringbone ordering of the *R*,*R* dimer that could give rise to a tristable electrical response.

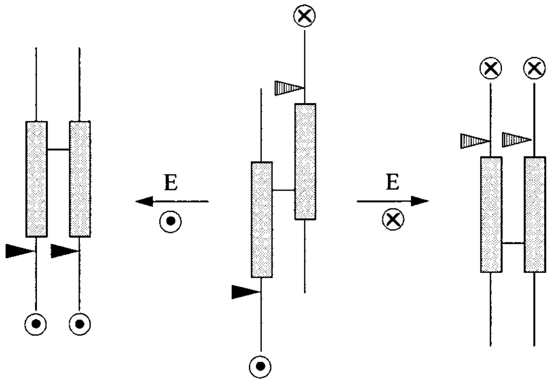

Figure 2. Proposed field-induced conformational change. Dipole cancellation is shown by the center molecule shown in its "S" conformation. Application of an electric field resulting in dipole alignment of the molecule through a conformation change is shown by the outer molecules ("U" conformation). E is the electric field directed either into or out of the page.

In our case, the conformation change could be driven by the application of an electric field. This reorientation is similar in many respects to the manner in which polymers with pendant hyperpolarizable chromophores respond to the poling fields used to induce noncentrosymmetric alignment in second order, nonlinear optical materials.[8] The "neutral", dipole-opposed state shown in Figure 2 arises in the "S" conformation. This would not be the expected state for an optically pure dimeric material that arranges in a manner similar to its monomeric counterpart as shown in Figure 3. An optically pure monomeric mesogen arranges in a tilted smectic phase as shown in Figure 3a. To maintain a similar packing arrangement with aligned dipoles for joined mesogens requires the twins to exist in a "U" conformation (Figure 3b). To obtain the dipole opposed "S" conformation (Figure 3c) required for a field-induced conformation change, a new packing arrangement unlike that of the corresponding monomer would be required. This packing arrangement that would produce dipole cancellation is analogous to the "S" conformation in Griffin's analogues. If it exists, it could give rise to a field-induced conformation change. Griffin's findings indicate that such a conformation change is likely to be accompanied by a change in layer spacings, a change that is measurable by X-ray diffraction.

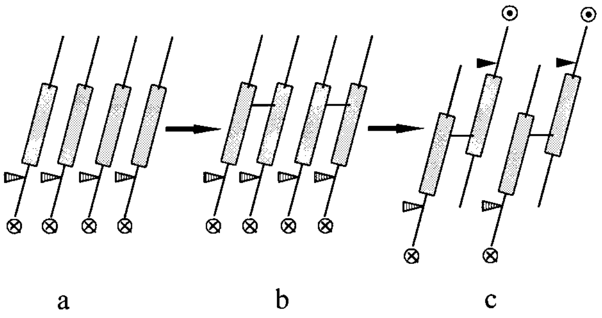

Figure 3. (a) Packing arrangement for an optically pure, monomeric S_C* material; (b) "U" conformation resulting in dipole alignment formed when two monomers are linked within the same packing arrangement; and (c) "S" conformation in which the dipoles of each half of the molecule are in direct opposition.

X-ray diffraction is a valuable tool for understanding the orientation and structure of liquid crystalline materials. It is commonly used to measure the layer spacing of liquid crystals at controlled temperatures.[9-13] However, few reports have been made of investigations involving the use of this technique in conjunction with the application of an external electric field.[14-16] We have developed a new liquid crystal cell that allows examination of materials by reflection X-ray diffraction under controlled electric fields. When used in conjunction with a temperature-controlled stage and a variable voltage source, smectic layer spacings can be investigated as a function of both field and temperature. The cell is comprised of two electrodes, between which liquid crystal material is sandwiched, as shown in Figure 4. The bottom electrode is a glass substrate with a patterned indium tin oxide (ITO) electrode. The top electrode is a thin, polished beryllium foil that allows transmission of Cu Kα radiation. Comparison of the layer spacings of S_C* liquid crystals obtained with and without an applied field provides insight into the mechanism by which these materials switch.

To complement our X-ray studies, we have undertaken a series of torsional viscosity measurements. Torsional viscosity provides a measure of the resistance of a material to bulk reorientation. Surface-aligned ferroelectric materials realign in an electric field through a collective molecular motion. The torsional viscosity (η_t) related to this reordering is described by the equation, $\eta_t = \tau P_s E$, where τ is the switching speed, P_s is the

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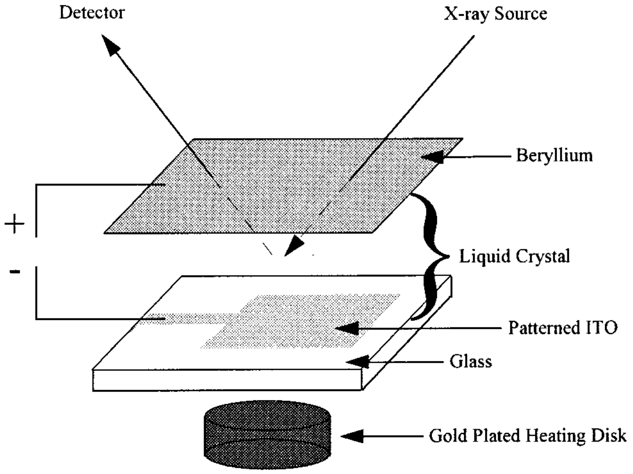

Figure 4. Experimental design of the liquid crystal cell used to obtain X-ray diffraction patterns at elevated temperatures and under an applied field.

spontaneous polarization, and E is the electric field.[17] In conventional ferroelectric liquid crystal materials, an applied field causes the molecular director to precess halfway around a cone, resulting in an energetically degenerate second state possessing an opposite tilt, with respect to the layer normal. This type of switching is referred to as Clark−Lagerwall switching and has been well-characterized.[18] Molecular reorientation by this mode of switching proceeds with no change in the smectic layer spacing. However, an electric field-induced reorientation of the dimer, for example, from an "S" to a "U" conformation, would involve reorganization of the lamellar structure. Such a phenomenon requires disruption of the smectic layers, which is expected to result in a higher resistance to switching, and thus, would be expected to exhibit higher torsional viscosity.

We have reported the unusual electrooptic properties of a S_C* twin liquid crystal.[3] Here we report X-ray and torsional viscosity measurements that provide insight into the mechanism by which field-induced switching occurs in these molecules.

Experimental Section

The structures and polymorphism of the dimer **1**, monomer **2**, and MHPOBC **3**, are shown in Figure 5. The complete synthesis and phase characterization of these materials and the equipment used in electrooptic studies have been previously reported.[3,19,20] The torsional viscosity measurements were performed using Displaytech parallel rubbed cells with a thickness of 4 μm.

Ambient-temperature X-ray diffraction studies were performed on unoriented powder samples on glass slides using Cu Kα radiation supplied from a Philips PW1729 generator operating at 40 kV and 40 mA. The diffracted radiation was collected via a Philips APD 3520 scanning detector. High-temperature X-ray analyses were done on a Scintag X_1 diffraction system with a $\theta-\theta$ powder diffractometer fitted with a solid-state Si(Li) detector. The diffraction system was equipped with a Research Instruments heater controlled by a Micristar temperature processor. Studies performed without an electric field were done at 30 kV and 15 mA with the unoriented sample placed on a cover slip. Experiments done under an electric field were performed at 45 kV and 40 mA with the sample contained in the special cell arrangement. Voltage waveforms were generated using a custom written LabView (National Instruments) operating program and the signal to the cell was amplified by a Kepco BOP 500M bipolar operational amplifier.

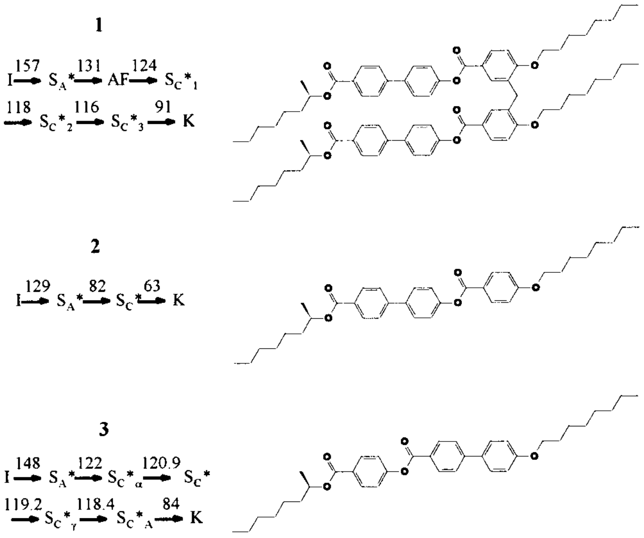

Figure 5. Molecular structure and phase assignments of the laterally linked dimer **1**, its corresponding monomer **2**, and MHPOBC **3**. All temperatures are in Celsius.

The design of the liquid crystal cell used in the electric field experiments is shown in Figure 4. It consists of an indium tin oxide (ITO)-coated glass slide (25 × 25 × 1 mm, $R < 100\ \Omega/\mathrm{cm}^2$, Delta Technologies, Ltd.) in which the ITO film has been patterned by standard lithographic techniques to form the bottom electrode. The top electrode is a beryllium foil (1 × 1 × 0.015 in., Brush Wellman Co.) that allows 88% transmission of Cu Kα radiation. The liquid crystalline material is introduced between the electrodes by capillary action while in the isotropic state. This provides a cell with an thickness of ~20 μm, as determined by optical microscopy of the cell cross section. It should be noted that because of the surface roughness of the beryllium foil, the cell thickness can vary by as much as ±3 μm, as measured by a Tencor Alpha-step 200 profilometer.

Spartan simulations were used to calculate the molecular configurations using the Merck Molecular Force Field.[21] Dreiding models were used to estimate end to end distances for the dimer in the "U" and "S" conformations.

Results and Discussion

X-ray Analysis. The dimer **1** is shown in Figure 5 in a "U" conformation. Rotation of a "monomeric" half of the molecule through the methylene linking unit results in an "S" conformation of the dimer. The relative minimum energy geometries of these two conformers was determined by Spartan molecular modeling. This simulation predicts a maximum end to end distance for the "U" conformation to be 35 Å, while the "S" conformation is predicted to have a maximum end to end distance of 42 Å. Although the simulation calculates nearly degenerate energy values for the two conformations (208−210 kcal/mol for "U" and 211−218 kcal/mol "S"), there exists a high-energy barrier associated with

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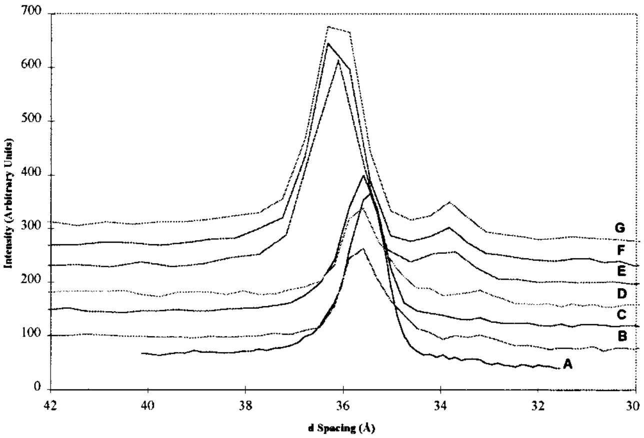

Figure 6. X-ray diffraction pattern of the dimer under the application of varying electric fields at 103 °C: (A) no applied field; (B) 100 V, 16 Hz square wave; (C) 150 V, 1 Hz square wave; (D) 180 V, 5 Hz square wave; (E) 200 V, dc field; (F) 300V, dc field; and (G) 300 V, 50 Hz square wave.

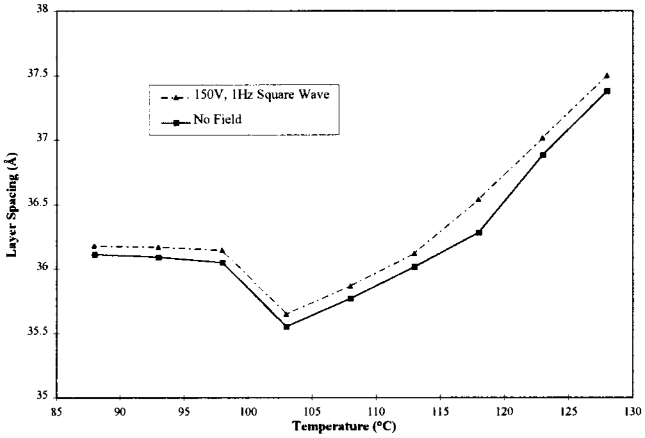

Figure 7. Comparison of the layer spacing of the dimer with and without an applied field throughout the entire temperature regime at which the molecule exhibits tilted smectic phases.

the transition from one conformation to the other. Using Dreiding models, the end to end distance of the "U" conformation was determined to be 35 Å, while the end to end length of the "S" conformation measured 46 Å.

X-ray diffraction patterns from the dimer were recorded in the S_C* phase under fields of varying strength. The results can be seen in Figure 6. For all field strengths, the layer spacing is 35.9 ± 0.3 Å. This value correlates well to the predicted 35 Å end to end length of the "U" conformation. A smaller intensity peak becomes evident at voltages above 200 V (cell thickness ~20 μm) at a *d* spacing of 34 Å and appears to be coupled with a slight increase in the layer spacing. The origin of this phenomenon is not understood, but is likely due to a minor change in the packing of the material in response to the high fields.

Layer spacings were also obtained with and without a field throughout the entire S_C* range of the dimer. The results of this study are shown in Figure 7, a plot of layer spacing as a function of temperature. A predictable increase in layer spacing is observed with increasing temperature in the S_C* range of the material consistent with a decreased tilt angle. A slight increase in layer spacing is observed upon the application of the field at all temperatures. However, the magnitude of the change is substantially less than that expected for a major conformational change.

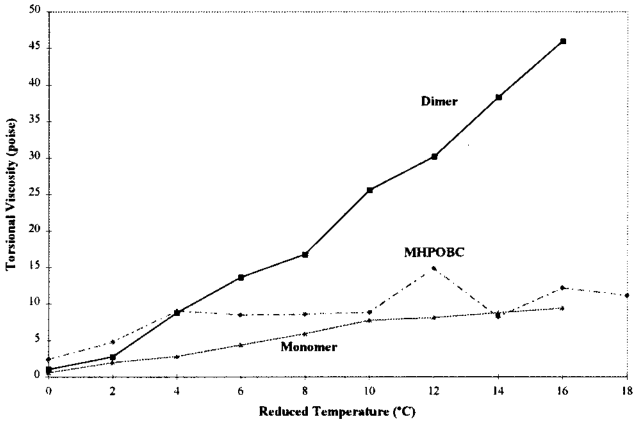

Figure 8. Torsional viscosity of the dimer, monomer, and MHPOBC, as a function of reduced temperature. Reduced temperature is defined as $T_c - T$, where T_c is the S_A*−S_C* transition temperature. Polarization and switching speed measurements were obtained at 17.5 V/μm.

Torsional Viscosity Study. We compared the dimer to its corresponding monomer and MHPOBC using torsional viscosity as a probe of the resistance of a material to electric field-induced reorientation. The torsional viscosity was calculated from polarization and response times which were previously described.[3] Figure 8 shows the torsional viscosity of the three compounds as a function of reduced temperature. At temperatures near their Curie points, η_t of the three materials is nearly equal and reduction in temperature leads to an increase in η_t. The monomer and MHPOBC are constitutional isomers and, as expected, have similar torsional viscosities over the entire temperature range investigated, while the bulkier twin compound shows a much stronger dependence of viscosity on temperature.

The electrooptical properties of the dimer, monomer, and MHPOBC have been studied in detail.[3,19,20,22−24] Both the monomer and MHPOBC are reported to undergo conventional Clark−Lagerwall-type switching. The torsional viscosity of the dimer is similar to that of both the monomer and MHPOBC at low values of reduced temperature. This is consistent with a common switching mechanism for all three materials. The torsional viscosity of the dimer increases with decreasing temperature at a much faster rate than the monomer and MHPOBC. The monotonic increase in the torsional viscosity of the dimer as a function of temperature is not representative of a change in the mechanism of switching, i.e., from Clark−Lagerwall-type switching to switching involving a conformational change. Were such a transition to occur, the torsional viscosity would be expected to undergo a sharper, step-function-like increase at the point where the transition occurred. This behavior is not evident in the data, even at the highest fields we could apply (highest field applied prior to "shorting out" the cell), as shown in Figure 9. Instead,

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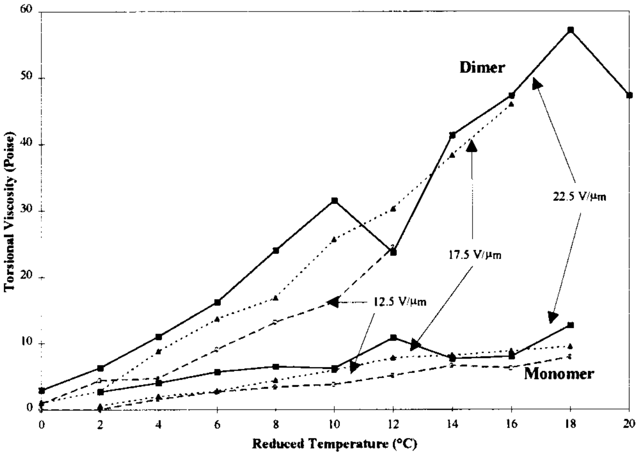

Figure 9. Torsional viscosity of dimer and monomer at varying applied fields. Note: values for MHPOBC are omitted for clarity, but they are similar to the values of the monomer for all applied fields.

the slope is nearly constant and simply correlates with the decreased response times at lower temperatures typical of S_C* materials. The slow response time of the dimer is expected due to the increased bulkiness of the molecule compared to the two smaller mesogens.

Conclusions

The mechanism by which a laterally linked dimeric liquid crystal aligns in an applied field has been investigated using X-ray diffraction and torsional viscosity studies. No significant change in layer spacing occurs when a field is applied over the entire S_C* range. The torsional viscosity of the dimer is similar to both the monomer and MHPOBC at temperatures just below the Curie point and steadily increases with decreasing temperature. Previously reported polarized optical microscopy of this material showed that when switching was observed by application of a dc field, no morphological change in texture could be distinguished.[3] These data are consistent with the conclusion that layer integrity is maintained in these materials and that reorientation of the dimer occurs by conventional Clark–Lagerwall-type switching and not by any realignment involving a large conformational change.

Layer spacing measurements indicate the ligated twin exists in the "U" conformation. This being the case, a dimer of such architecture containing either *R*,*R* or *S*,*S* stereocenter pairs would not be expected to undergo a conformational change. However, a meso dimer possessing *R*,*S* chirality should be ideally suited for such a field-induced conformation change. The dipoles should directly oppose in the meso dimer in a manner similar to a racemic, monomeric S_C material (see Figure 10). The driving force for Clark–Lagerwall switching in these molecules has been effectively removed, leaving the opportunity to achieve a field-induced conformation change by applying the high fields used in other poling type applications. Testing this hypothesis is the focus of our current efforts. Modifications to the design of the molecule, including the incorporation of functionalities with higher polarizabilities and lengthening the tethering unit between mesogenic cores, are envisioned to reduce the activation barrier for such a field-induced conformation change.

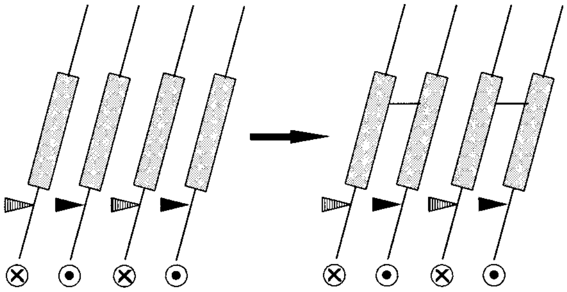

Figure 10. Packing arrangement of a racemic S_C* material (left) and the "U" conformation with the same packing arrangement for an *R*,*S* dimer resulting in dipole cancellation.

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