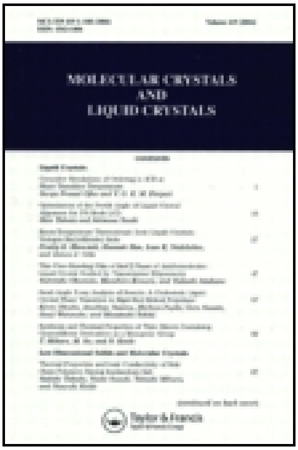

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First Truly Ferroelectric Liquid Crystal

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FIRST TRULY FERROELECTRIC LIQUID CRYSTAL

PHYSICAL PROPERTIES OF THE FIRST TRULY FERROELECTRIC LIQUID-CRYSTAL PHASE AND A PROPOSED ANTIFERROELECTRIC LIQUID-CRYSTAL PHASE

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The first ferroelectric liquid crystalline phase (in 8SI* (ΔS–(+)–(4–(2'-methylbutyl) phenyl-4'-n-octylbiphenyl-4 carboxylate) is reported and its physical properties are discussed. The close connection between the phase sequences of 8SI* and its racemate are established. Both compounds show a number of smectic phases above the newly discovered ferroelectric phase and its analogue in the racemate. These phases (C,I and G') are tilted in the racemate 8SI and tilted with a helicoidal structure in 8SI*. In the truly ferroelectric phase, X, the director of the molecules can be oriented in a bistable way in an electric field. Furthermore when the field is turned off the director orientation remains unchanged. This behavior is fundamentally different from that in *bulk* smectic phases which support the helix structure in the absence of external forces. A model for 'racemates' in higher smectic phases like G, G', H' etc as well as a the newly discovered ferroelectric phase is presented. The response of cholesteric blue phases of 8SI* to an external field is discussed in an appendix.

PACS: 61.30Eb,Gd, 64.70Ew, 77.8

I. INTRODUCTION

Ferroelectricity, a phenomenon well established in solid state physics, has not been discovered so far in liquid crystals, the stable phases which mediate the liquid to solid transition in many organic compounds. So far only helielectric, chiral smectic liquid crystals have been reported. In smectic liquid crystals, which have

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attracted increasing attention over the last few years,(1,2) the elongated molecules which exhibit these phases, are arranged in a layered structure.

In a smectic A phase, the simplest type of a smectic, the molecules are completely disordered within the layers thus forming a two-dimensional fluid whereas a density wave exists in the direction of the layer normal. If all molecules are tilted with respect to the layer normal in a uniform fashion but otherwise the degree of fluidity inside the layers is unchanged, one calls such a phase smectic C. Increasing the degree of order (or reducing the fluidity) within the layers leads to tilted phases like smectic F, I, G, G′, H, H′ and to various nontilted smectics: crystal B, hexatic B, E etc.(3-5)

Whereas in C there is 2-dimensional fluidity within a layer, in F and I the molecules are restricted to move only along the lines of a 2-dimensional grid set in the layers. This is our physical notion of "long range bond orientational order"(6) which accounts for the large heat of transition (≈ 1 cal/gm) at the C to I (or F) transition. In the G, G′ and H phases, X-ray measurements show long range correlations for the centers of mass of the molecules(3-5) within a layer. The molecules are localized at the intersection of the grid lines but rotate freely about their long axis in G and G′ and in a hindered fashion in H and H′. That is to say, there is still a considerable amount of motion in the system. There is practically no heat of transition observed at the I (or F) to G′ (or G) even though it is presumably at these transitions that long range positional ordering sets in. On the other hand, between the solid phases and the liquid crystal solid-like phases, heats of transition are about 10 cal/gm suggesting that correlation between layers is still be building up in the G, H′ and H phases.(7)

If a compound is composed of chiral molecules or if one adds a chiral agent to a compound forming tilted smectic phases, the resulting smectic phases have a helicoidal structure, i.e. the director which characterizes the preferred direction of the molecules, rotates in a helical fashion(8–10) with a pitch typically 4-6 μm. These chiral analogues of the tilted smectic phases are known to exist for C, I, F, G′ and some G phases. They are then usually called C*, I*, F*, G′* and G* where the asterisk indicates the spiral structure. As has been pointed out by Meyer *et al.*(8) a permanent polarization which locally twists in a plane perpendicular to the axis of the helicoidal structure of the director, results from the combination of layering, tilt and molecular chirality. This occurs even if the units forming chiral phases are dimers of strongly polar molecules.(11) Because of the rigid coupling between director orientation and polarization there is no net polarization on a scale much larger than the pitch: it globally averages to zero.

Here we present a detailed discussion of the first truly ferroelectric liquid crystal(12) we observed in 8SI* and its analogue in the racemate 8SI. Unlike the higher temperature chiral phases (C*, I* and G′*), there is no spiral structure for the director in smectic X, and within a layer, the tilt direction of the director assumes only a finite number of orientations. Application of an electric field allows for a reorientation of the director from one of these states to another if the field is above a certain threshold value corresponding to the energy barrier between each state. This feature differs from chiral smectic phases which exhibit no threshold due to the complete degeneracy between different orientations in these phases. (12,13) In addition, X possesses a net permanent polarization in the absence of any external forces including surface forces, a feature very different from the bulk C* phase even if the latter is 'unwound'.(13)

So far, only two classes of in-plane ordering have been observed for tilted phases. In both cases, the in-plane ordering is rectangular(3–5,15) and they are distinguished by how the director tilt is oriented relative to the rectangular lattice. When the director tilt is along the short side of the rectangle, the phases are called I, G′, and H′; when along the longer side, they are F, G and H. It is really not known how a helix structure would modify these ideas. Subsequent to our announcement of the existence of X in 8SI*, recent x-ray observations(14) indicate its in-plane structure to be of the G-type. A truly ferroelectric smectic has also been observed(16) in another compound where the in-plane structure is known(15) to be similar to H′. Thus it seems that liquid crystal phases in which there is a net polarization and no spiral structure are not peculiar to a unique structure. We proposed(12) the hat symbol be used to designate these phases. For example, the X phase in 8SI* should now be called $\hat{G}$. G* indicates a spiral structure and G does not usually exhibit a polarization, thus neither of these designations are correct.

The newly discovered ferroelectric liquid crystalline phase naturally raises the question: what does its analogue in the racemate look like both on a macroscopic and a microscopic scale? We will propose that the analogue of X is basically an antiferroelectric liquid crystal phase with macroscopic regions of opposite net polarization.

The paper is organized as follows. In section II we present our experimental results for 8SI and 8SI*: X-ray determination of the layer spacing, differential scanning calorimetry, microscopic observations of bulk samples and freely suspended thin films and response to an external a.c. and d.c. electric field. In section III we give a discussion of our results and a comparison with the behavior of similar systems. In an appendix, we include an interpretation of the electric response of the two cholesteric blue phases of 8SI*.

II. EXPERIMENTAL RESULTS

A. Transition Temperatures and Heats of Transition

The transition temperatures of 8SI and 8SI*(17) were determined using DSC (differential scanning calorimetry) and observations in the polarization microscope. In detail, we find the sequences:

a) for 8SI*

$$\mathrm{Xtal} \xleftarrow[1.8]{40.9} \mathrm{X} \xleftrightarrow[-]{61.7} \mathrm{G'^{*}} \xleftrightarrow[-]{66.5} \mathrm{I^{*}} \xleftrightarrow[1.0]{70.3} \mathrm{C^{*}} \xleftrightarrow{81} \mathrm{A} \xleftrightarrow[1.1]{136.4} \mathrm{Chol} \xleftrightarrow[0.4]{141.4} \mathrm{Iso} \quad \begin{matrix}(^{\circ}\mathrm{C})\\ (\mathrm{cal/gm})\end{matrix}$$

$$T_{\mathrm{melt}} = 48.2^{\circ}\,\mathrm{C}(8.5\ \mathrm{cal/gm})$$

b) for 8SI

$$\mathrm{Xtal} \xleftarrow[1.7]{40.1} \mathrm{X} \xleftrightarrow[-]{62} \mathrm{G'} \xleftrightarrow[-]{65} \mathrm{I} \xleftrightarrow[1.1]{68.7} \mathrm{C} \xleftrightarrow[-]{83.8} \mathrm{A} \xleftrightarrow[1.1]{135.1} \mathrm{Nem} \xleftrightarrow[0.5]{140.6} \mathrm{Iso} \quad \begin{matrix}(^{\circ}\mathrm{C})\\ (\mathrm{cal/gm})\end{matrix}$$

$$T_{\mathrm{melt}} = 59^{\circ}\,\mathrm{C}\ (9.0\ \mathrm{cal/gm}).$$

The transition temperatures of the racemate for the transitions isotropic-nematic, nematic-A, A-C and C-I agree within 1° C with those given previously by Goodby and Gray[17] whereas those for 8SI* have not been published before. At lower temperatures, i.e. below the I phase we find, however, two additional smectic phases, namely G'^* and $\tilde{X}$, the analogue of X in 8SI*. This is in contrast with the findings of ref 17, where only one phase (H) was reported to occur below the I phase.

By inspection of the transition temperatures of 8SI and 8SI*, it is clear that there is a close correspondence between the data for all phases - except for two cholesteric blue phases which do not exist in the racemate.

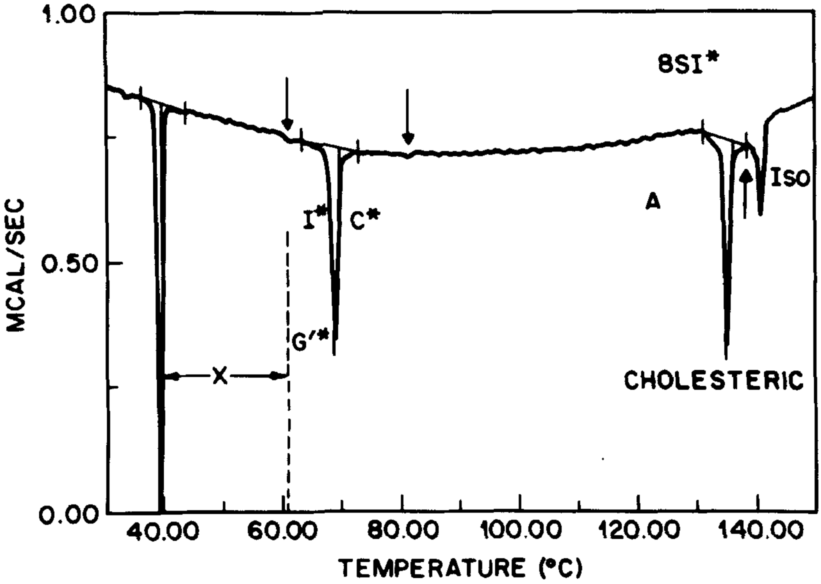


Fig. 1: DSC cooling trace for 8SI*

The DSC traces were taken on a Perkin Elmer DSC IV and are shown on cooling in figure 1 for 8SI* and in figure 2 for its racemate. In both cases there is a large heat of transition at the $I \rightarrow C$ (or $I^* \rightarrow C^*$) transition indicating a major change in the degree of freedom inside the layers, a change which is very subtle to see in the light microscope. Although the transition $G'^* \rightarrow X$ and $G' \rightarrow \tilde{X}$ cannot be extracted beyond doubt from the DSC traces and one has thus to rely on optical measurements (to be described below) a small step might be identified on the DSC trace. The heat of transition for both the G'* → I and G' → I transitions is too small to be observed and one relies solely on texture changes in the light microscope to identify this transition. On cooling through X, the transition to a crystal phase takes place at 40.2° C with a heat of transition of 1.8 cal/gm. This is considerably less than 8.5 cal/gm observed at the melting transition (48.2° C) but larger than any of the heats of transitions at the higher temperature transitions. In this sense then, we consider all phases of 8SI* and 8SI above 40° C "liquid crystalline" as opposed to simply "crystalline".

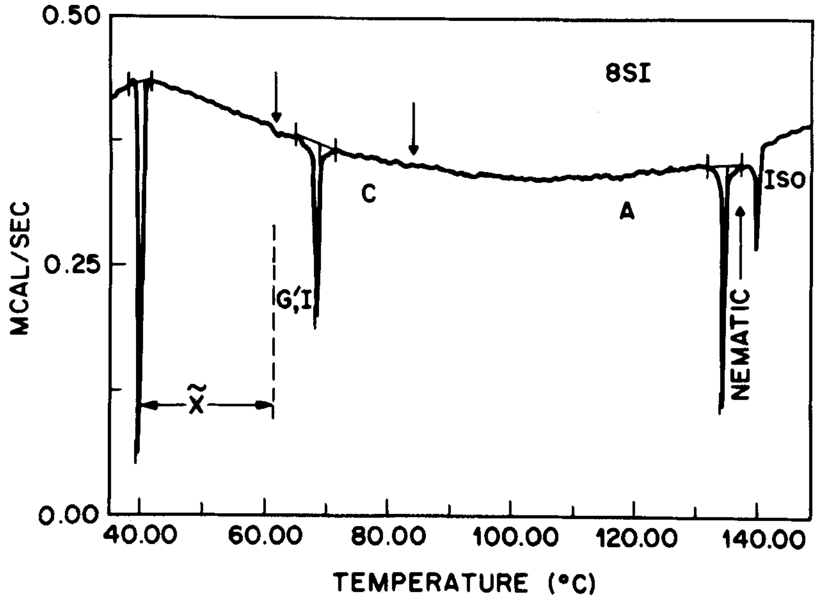


Fig. 2: DSC cooling trace for 8SI clearly showing a similar sequence of transitions as for 8SI*

Intuitively, the magnitude of the heat of transition associated with change from one phase to another gives a measure of the difference in ordering between the two phases. For example, typically, 0.5 cal/gm is observed at nematic-isotropic transitions which differ by orientational order whereas 2 cal/gm is more typical of a smectic A-isotropic transition in which both orientational order and 1-d periodicity are involved. At the melting transition in 8SI*/8SI the difference between X (and $\tilde{X}$) and the stable solid phase is 9 cal/gm whereas only 1 cal/gm separates them from the fluid C* (and C) phase. (G′)* is so "fluid" it supports the helix structure with a relatively tight pitch (4-5 μm). This suggests that the correlation between layers is not fully developed. Somehow the rectangular structure rotates from layer to layer in (G′)* whereas in X the rectangles are presumably oriented from layer to layer. The strength of coupling between the director tilt and the in-plane structure is still relatively weak and changes between (G′)* and X in 8SI* to the G structure. We will show later, laboratory strength, but large, electric fields can change the orientation of the director in the X phase.

Another characteristic of transitions between solid phases and liquid crystal solid-like phases is hysteresis. Very little to no hysteresis is observed at liquid crystal-liquid crystal transitions whereas, there is very often large differences in solid-liquid crystal phase transition temperatures upon heating and cooling. The transition temperatures at the X-(G′)* and (G′)*-I* transitions and their analogues in the racemate are the same on heating and cooling whereas the X-solid transition is not reversible in this way.

We note that there is a 10°C difference between the melting transition in the racemate and the chiral species but all liquid crystal transitions, involving X and $\tilde{X}$

occur at very similar temperatures.

B. X-ray Measurements

The layer spacing in the smectic phases was determined by X-ray diffraction using a Rigaku rotating anode and a linear detector. We have plotted our results as a function of temperature in figure 3a for 8SI and 8SI*. In the C* phase, the layer spacing first decreases to 28.9Å corresponding to a tilt angle of 16° and then increases again before leveling off in the A phase (zero tilt) at 30Å. The fully extended length of the molecule evaluated in the all trans configuration of the space filling model is 33Å. When heated from the crystal phase to the I* → C*

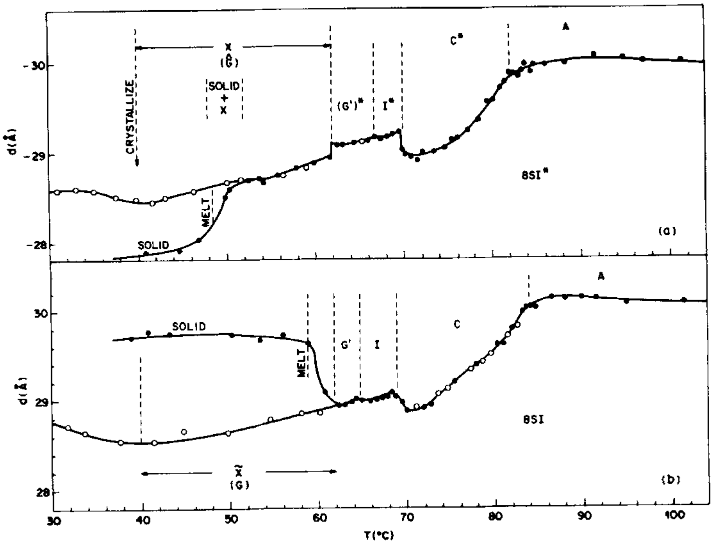


Fig. 3a: Layer spacing as a function of temperature in 8SI* and 8SI.

transition the layer spacing increases monotonically from 28.9Å to 29.2Å. These observations differ drastically from those made for 90SI(18) where the layer spacing decreases at both the I ↔ G′ and G′ ↔ H′ transitions in a discontinuous way.

Again we note the extraordinary similarity between 8SI and 8SI* in the liquid crystal phases but the 2Å discrepancy between the solid structure of 8SI and 8SI*.

Fig. 3b shows qualitative changes in the scattered x-ray intensity as a function of scattering angle in the wide angle regime. The vertical axis in Fig. 3b is normalized by the maximum number of counts in the interval shown. The horizontal axis is the same for all temperatures and spans the interval $(7Å)^{-1}$ on the left to about $(4Å)^{-1}$ on the right. In general, to obtain the spectra, a minimum of two hours counting time was required.

The fluidity of the C* phase is evidenced by the broadness of the peak. Progressively cooling to the crystal phase, the peak narrows and the intensity in the "wings" drops. In the crystal phase, additional structural features can be resolved.

A crude measure of the in-plane order is estimated from the peak width at half the maximum intensity relative to this same quantity in the C* phase. In the phases C*, I*, (G′)*, X and crystal we find 1.0, 0.35, 0.27, 0.23 and 0.20 respectively. The last number represents the instrumental resolution. The narrowing of the peaks is a measure of the progressive enhancement of correlations between planes as the temperature decreases, in agreement with the first results of Doucet et al. for smectic G and more ordered smectic phases.(7)

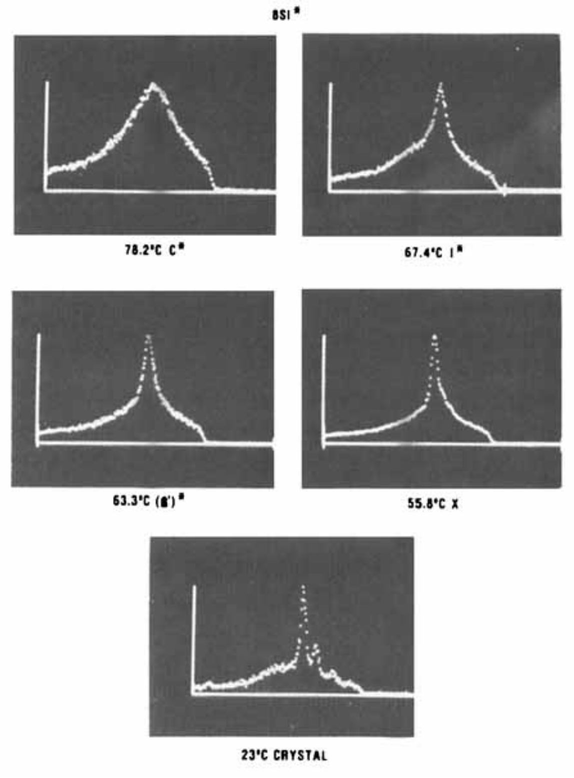


Fig. 3b: Photographs of the x-ray scattering intensity versus scattering angle in the wide angle region showing growth of in-plane ordering in the various phases of 8SI*.

C. Optical Microscope Observations

1. *Free Standing Films*

Chiral smectic phases are optically uniaxial, because of the helix structure, whereas the X phase turned out to be biaxial. To observe this we looked at a free standing film of 8SI* in the microscope. All our films were drawn in the smectic A phase (100° C) and showed the same degree of optical extinction in the C*, I* and G′* phase between crossed polarizers. Only changes in fluidity marked these transitions upon heating and cooling. The transition G′* $\rightleftarrows$ X not only shows a change in fluidity but also the sudden appearance of birefringence colors just below 62° C and the film lost its smoothness (see Fig. 4a and b). From this we infer the biaxial nature of this phase. We distinguish between the colours of optical rotatory power and biaxiality by rotating the film between crossed polarizers. In the former case there is no change in color nor in intensity of transmitted light whereas in the latter there is. Thus X is biaxial in our films.

In the racemate, 8SI, the transitions become visible as a change in fluidity in the vicinity of the various transition temperatures and as an (apparent) increase of the rigidity of the textures observed. In Figure 4 we show a photomicrograph of the X and $\tilde{X}$ phase at 54° C and 42° C respectively. This illustrates another physical characteristic which prompts us to consider X and $\tilde{X}$ liquid crystal as

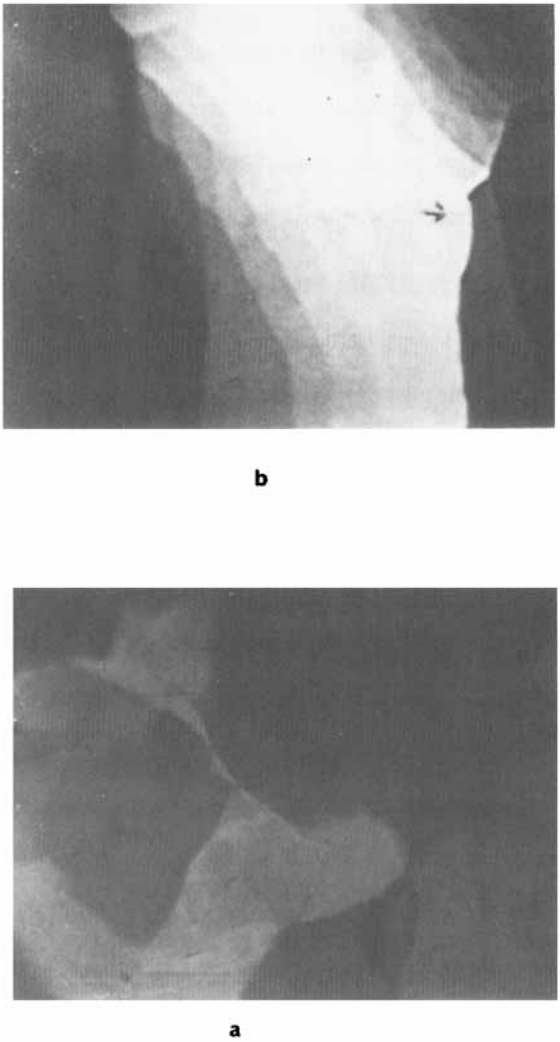


Fig. 4: Photomicrographs of a) X phase at 54° C and b) $\tilde{X}$ phase at 42° C in a thick freely suspended thin film. The fact that these phases are stable as freely suspended film is additional evidence of their liquid crystallinity.

opposed to solid crystal phases. Freely suspended films of X and $\tilde{X}$ are stable. When the sample crystallizes, the film breaks. Solid phases such as graphite and mica exist as sheet like structures since there is very weak coupling between layers. The difference then between a liquid crystal X and a solid phase may be in the strength of the correlations between layers.

In a bulk sample, X easily escapes observation if cooling is done rapidly. It is only after several hours that the X phase untwists spontaneously giving a hint of the achirality of the phase. For its analogue $\tilde{X}$ in the racemate, this problem does not exist, since both G′ and $\tilde{X}$ are tilted and biaxial and thus birefringent in the thin film geometry.

2. *Electro-optic Response*

The most elegant and clearcut way of distinguishing the I*, G′* and C* phases on the one hand and the X phase on the other is certainly the different electrooptic behavior of these phases. In 8SI*, X possesses a net permanent polarization (whereas its counterpart in 8SI does not) and can be switched in a bistable way in an electric field. The existence of a permanent polarization in smectic X was demonstrated by applying a dc electric field across a 52 μm thick sample (see e.g., Fig. 5). In order to obtain well-ordered samples; 8SI* and 8SI were rapidly cooled from the isotropic phase to the A phase in a magnetic field of 10 Kgauss parallel to the electrode surface. This technique with slow cooling gives well-ordered smectic phases of relatively thick samples (~ 50μ) provided there is a smectic A-isotropic transition. Cooling 8SI* rapidly enabled us to "short-circuit" the narrow cholesteric phase (and blue phases) and smectic A batonnets were formed in the isotropic melt. These coalesced to form monodomains on the order of 400–500 μm (see Fig. 6) in the usual way.(19) We did not treat the glass plates with any surfactant.

First of all, we studied the response when a dc electric field was applied across a 12 μm thick sample of 8SI* held between transparent electrodes. We refer to this sample configuration as a switching sample. Reversing the field resulted in a reorientation of the director at an angle of about 45 degrees to its previous orientation giving rise to good contrast between the two states. When the field was turned off, the sample returned to its equilibrium configuration of the uniformly twisted state. When a rectangular voltage pulse was applied to the chiral smectic phases of 8SI*: C*, I* and G'*, walls moved as a solitary wave as discussed previously in some detail(12) i.e., the chiral phases of 8SI* show the 'soliton switch' behavior(12) and the switching time is found to be proportional to $1/\sqrt{V}$ and to γ, where V is the applied voltage and γ the orientational viscosity. Our results for the switching time are summarized in Figure 7. As expected G'* shows the longest switching time, which is no surprise due to its larger viscosity.

At 66° C, we observed in the polarizing microscope that 15V cleared the sample of the surface lines shown in Fig. 6. When the field was turned off, the director configuration relaxed to the helicoidal structure (in seconds or less)[13] and surface lines reappeared in about a minute. Figure 6 shows the state of the sample at this point when the surface lines are about 4.6 μm apart. With time, more lines appear. Cooling in steps of 1° C to 62° C, we repeated this experiment and found qualitatively the same behavior: the helicoidal structure reappeared (in seconds or less) and the surface lines grew back (in 1 or 2 minutes). At 61° C something

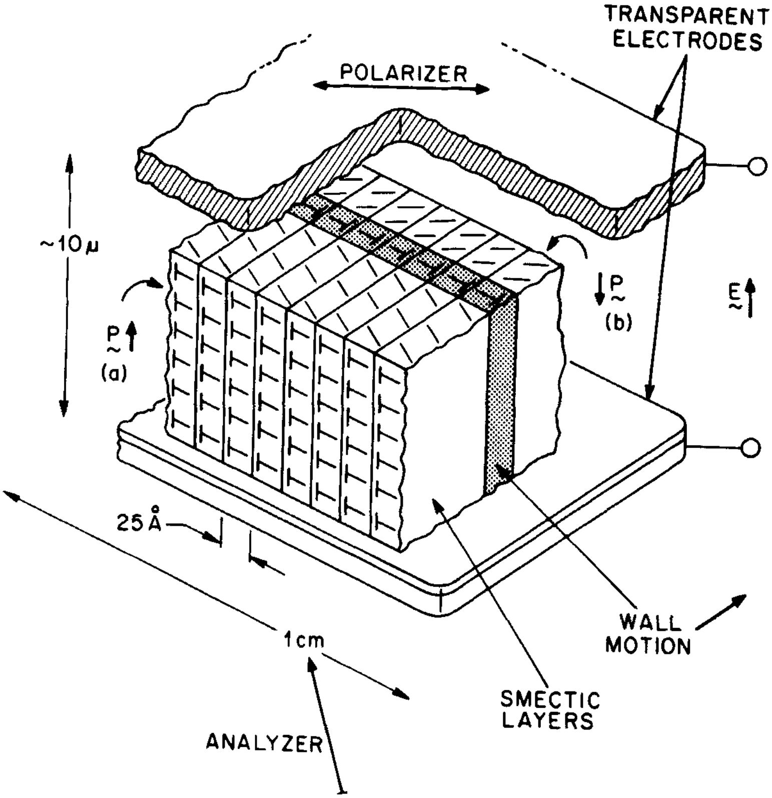


Fig. 5: Schematic of the two states of well-ordered smectic X phase, which occurs at lower temperatures than the G* liquid crystal phase which has been characterized as a crystal. The detailed in-plane structure of X is similar to G in 8SI*. **P** is the polarization which is "up" for one state (a) and "down" for the other (b). In an applied field, X switches from state (a) to (b) via wall motion parallel to the layers. The nail-head indicates the end of the director behind the page.

different happened. The director re-oriented slowly (~secs) in a 12V dc field but no change was observed at the end of an hour after the field had been switched off (state (a) in Fig. 6). When the sign of the field was reversed, the director re-oriented to state (b) in Fig. 6 and again, when the field was switched off, no change occurred.

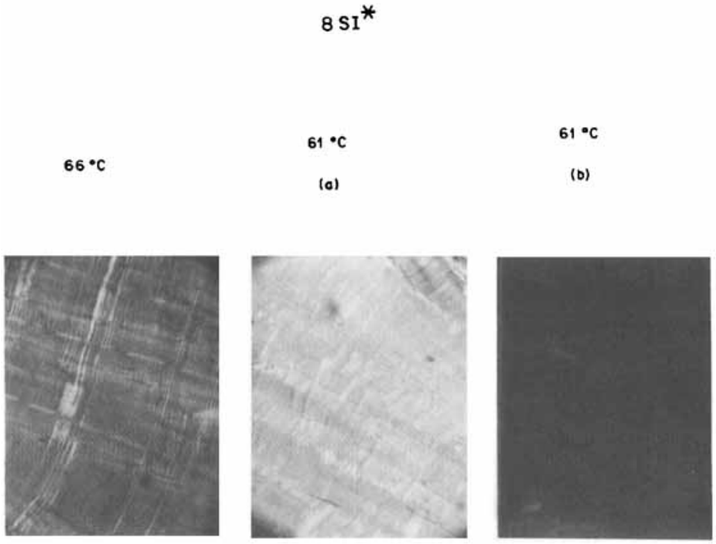


Fig. 6: Optical micrographs of 8SI* at at 66° C and 61° C for states (a) and (b). The sample is viewed through the transparent electrodes of Fig. 5.

Unlike the phases above 61° C, there was now a threshold voltage, V_C, to re-orient the director. For example, at 58° C, no change was observed for fields less than 50 volts/ 12μ. In the vicinity of V_C, $((V-V_C)/V_C \approx 50\%)$, we measured with a stop-watch the times to change from state (a) to state (b) across a fixed area of the sample (about 500 μm^2) somewhat larger than shown in Fig. 6. The stop watch was started once the field was reversed and stopped when the domain wall

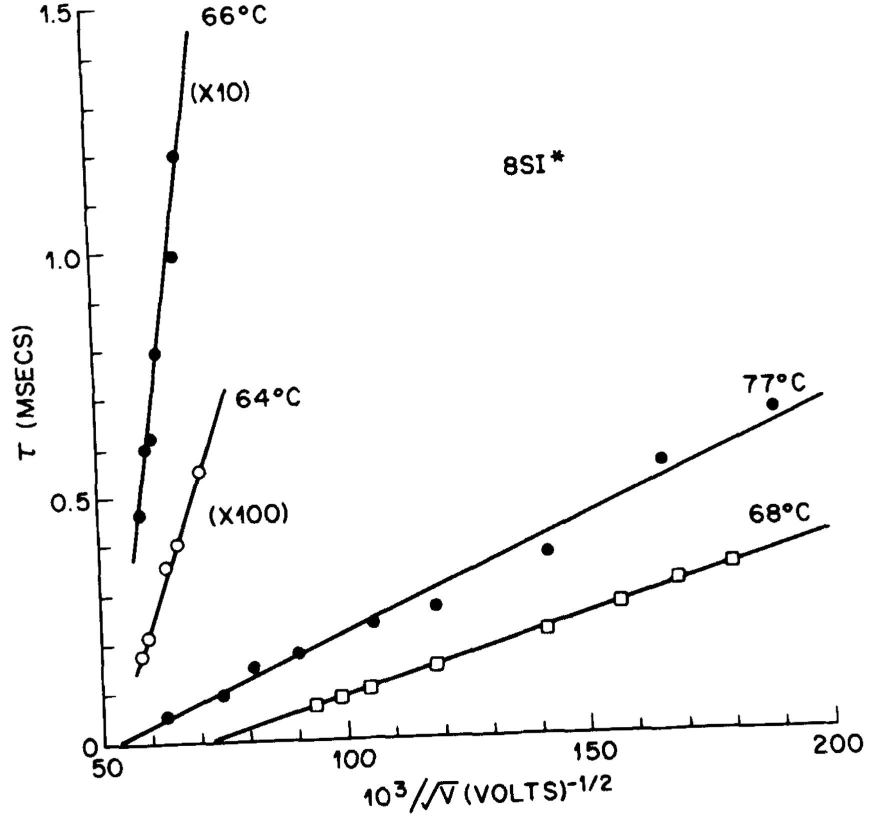


Fig. 7: Switching time τ, as a function of $1000/\sqrt{V}$ for the C*, I*, G′* phases of 8SI*. In order to obtain the switching times for 66° C and 64° C, multiply the ordinate scale by 10 and 100 respectively. These curves were obtained by measuring the change in contrast as a function of time when the field is switched from +V to -V within 0.5 μ secs. The total switching time τ has an elastic contribution arising from the repulsive interaction between walls. If the field is released, the walls take ~1 sec to relax back to the uniform twisted state. In these experiments, the field is reversed rapidly and the walls are pushed to their new location, before elastic relaxation can take place but not before some intial elastic repulsion has already started the switching process. This reduces τ a constant amount, $\tau_{\text{repulsive}}$, at constant temperature. τ is plotted here as $\tau = -\tau_{\text{repulsive}}$ (msecs) $+ b$ (msecs Volts$^{1/2}$)$/\sqrt{V}$. At $T = 77°$ C (C* phase), 68° C (I*), 66° C ((G′)*) and 64° C ((G′)*), the values for $\tau_{\text{repulsive}}$ and b are (0.26, 5.0), (0.24, 3.2), (3.2, 6.35) and (14.8, 287) respectively.

had traversed the area under examination. Provided we were within 50% of V_C so that the switching times, τ, were fairly long, we found that $V \ln \tau$ (with V in volts and τ in seconds) was constant to better than 7% For example; at 55.5° C, we found for V = 140, 160 and 180 volts, $\tau = 33.1, 27.5$ and 18 seconds respectively, giving an average $V \ln \tau = 514 \pm 20$ [volts ln secs]. In Fig. 8 we plot this parameter (with the observed spread as an error bar) as a function of temperature. Interestingly, we find a straight line which extrapolates to zero at 61.4° C.

It is important to note that in order to make these observations, fairly well-oriented samples are necessary other wise it is hard to see any contrast. The change from state (a) to state (b) proceeds by wall motion in the layers (sketched in Fig. 5) and some degree of co-operativity may be necessary to effect this transition. When the domains are small (less than 50μ, say) it is in fact difficult to observe any change in X with field.

The kind of wall motion we observed in X is different from that of C*, I* and G'* phases where wall motion proceeds perpendicular to the layers in what we have called the "soliton-switch".(13) The electrooptic response in phases equipped with the helicoidal structure proceeds without a threshold field and, in the absence of external forces, without bistability since in these phases, the allowed director orientation is infinitely degenerate on the surface of a cone. For example, once the field is turned off, a field oriented C* phase will relax to some other configuration, as determined by surface forces, say. In X, we propose that the director can assume only a discrete set of orientations on the cone surface thus accounting for its threshold behavior in a natural way, independent of the detailed crystallographic structure. Furthermore, Fig. 8 shows that $\tau = \exp\left\{C|T_C - T|/V\right\}$ where C is a positive constant where the free parameter, T_C, is identical, within the accuracy of our measurements, to the $G'^* \rightleftarrows X$ transition temperature. Qualitatively, one might interpret this relation as evidence of the existence of an activation energy to start director re-orientation. The factor 1/V effectively reduces the activation energy.

To get some additional insight into the meaning of the term "racemate" for the more ordered smectics, we also prepared a 50 μm switching sample of 8SI

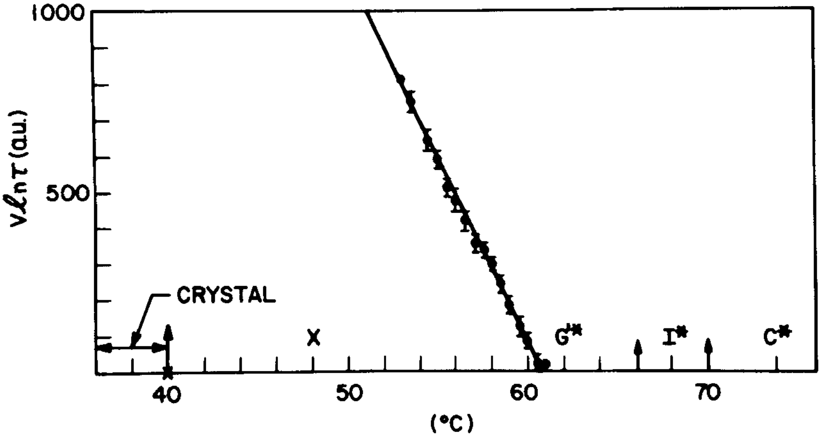


Fig. 8: Vlnτ as a function of temperature in the X-phase of 8SI*.

which was oriented by cooling slowly through the isotropic to nematic transition in a magnetic field of 10 kG. In the C, I and G′ phase we did not observe any switching. However regular arrays of birefringent lines spaced between 2 and 4 μm apart appeared in these phases. Furthermore we observed rather complicated electrohydrodynamic instabilities depending on frequency and applied voltage. In the analogue of the X phase, this picture changed and we were able to observe motion parallel to the layers at very large voltages (e.g., 600V across 50 μm). When the field was switched off, the configuration stayed without any perceptible change. From the high voltage necessary to induce any motion however, it is clear that the permanent polarization in $\tilde{X}$ is either very small or zero.

III. DISCUSSION OF RESULTS

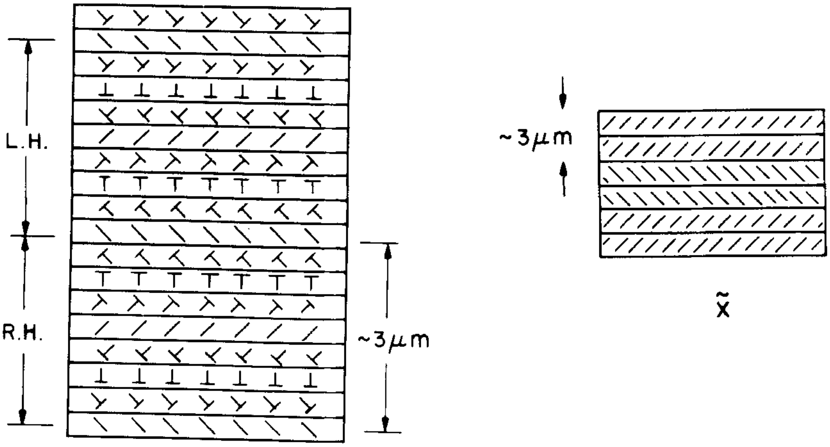
Our results for switching times in the chiral smectic phases of 8SI* show that the soliton switch mechanism proposed recently(13) has a rather broad range of applicability. It applies at least for C*, I* and G′* phase — where the range of applicability might only be restricted by electrohydrodynamic instabilities which dominate the switching behavior or by the fact that the soliton is not well formed as is the case e.g., in large pitch chiral smectics. By inspection of Figure 7 we notice, however, a number of additional interesting features. First of all the absolute magnitude of the switching time in the C* and I* phase of DOBAMBC (p-decyloxybenzylidene-p‘-amino 2methylbutyl cinnamate) is longer than it is in 8SI*. On the other hand the polarization of DOBAMBC(10) is an order of magnitude larger than that of 8SI*. These two facts together with the relation $\left(\tau \sim \frac{\gamma}{\sqrt{V}}\right)$ lead to the conclusion that the director viscosity in 8SI* is about an order of magnitude smaller than that of DOBAMBC. The molecular structure of the two compounds is so similar that this seems unlikely so, a tentative hypothesis is that the enhanced viscosity of DOBAMBC is due to the onset of electrohydrodynamic (EHD) instabilities during the switching process. Certainly, one observes motion in DOBAMBC for relatively large fields when $E > 4\pi P/\epsilon_a \sin\theta$. These instabilities arise because of the competition between the polarization and the dielectric anisotropy to orient the director in an applied field. In 8SI* both these effects are in the same direction and we do not observe EHD instabilities, whereas in DOBAMBC, these two effects compete giving rise to EHD and longer switching times. In fact in sufficiently large fields, EHD can lead to an *increase* in switching times with increasing voltage!

We found that 8SI* possesses a truly ferroelectric liquid crystalline phase which is biaxial, without a helix structure and can be switched in a bistable way. Furthermore X possesses a net permanent polarization and a finite threshold for switching. These facts together with the law for the switching time given above, (Fig. 8), lead us to propose that the finite threshold is due to the existence of an activation energy barrier which must be overcome to start the director re-orientation (unlike the phases with a helix, the director in X has only two equivalent directions). The activation energy is greater, as one cools further into the X-phase. The prefactor $1/V$ in the exponent for τ also has a simple qualitative and intuitive interpretation: a larger applied voltage reduces the activation energy barrier and thus yields faster switching. It seems to be important to stress that all features are independent of the detailed crystallographic structure within the plane of the layers. Our model is compatible with both, long range translational order inside the plane or long range bond orientational order rigidly coupled to the tilt degree of freedom.

In concluding the discussion of the X-phase of 8SI*(12) we mention that we have found X in other compounds: e.g., in C92M4(S-(+)-(4-(2'methylbutyl)benzoate4'-nonyloxybiphenyl))(20) and in the liquid crystalline phase of HOBACPC (p-hexyloxybenzilidene p'-amino-2chloropropyl cinnamate) which appears below 50° C(15) i.e., below the Smectic IV phase of Jain and Wahl.(21) In MORA12 (s-4-(6methyl)octylresorcylidene-4'-dodecylaniline) below 24.5° C we have found an additional liquid crystal phase which shows true bistability.(22) In this case, however, the switching mechanism is not completely clear. From our preliminary experiments we would conclude that switching proceeds both perpendicular and inside the layers simultaneously.

Although we believe the main interest in X is a fundamental one and with the long intrinsic switching times of currently available materials, immediate utilization of X seems unlikely, however, coupled with a higher temperature, sub-micro-second switching but not bistable C* phase, X could be useful for electrooptic storage rather like the smectic A valve.(23) In the C* phase of 8SI*, we observed switching times typically on the order of 10 μseconds (see Fig. 7).

The results on the racemate clearly indicate that there is a very close correspondence in the phase sequence between 8SI and 8SI*, an observation which is also true for the magnitude of the heats of transition. From the results of the electrooptic experiments discussed in the last section, the question of the structure of $\tilde{X}$, the counterpart of X arises. Here we conjecture (in agreement with all experimental observations made so far) that $\tilde{X}$ is an antiferroelectric liquid crystal, i.e. regions with non zero net polarization alternate in a regular manner. This model is capable of accounting for the strange electrooptic response we observed. The thickness of the domains with one preferred direction of the net polarization would be of the same order of magnitude as the distance between the regular arrays of lines observed in 8SI. We speculate that these arrays of lines in phases like I and G′ which exist with a helix structure in 8SI* correspond to regions of opposite screw sense of the helices in 8SI. This hypothesis needs to be tested by other, independent techniques. In Figure 9 we give a sketch of our model.



G′. I

$\tilde{X}$

Fig. 9: Sketch of the model

It is interesting to note that Doucet et al.(15) came to similar conclusions when studying the racemate of HOBACPC. These authors observed that chiral HOBACPC exhibited Bragg spots in an electric field. These spots were on a hexagonal lattice oriented perpendicular to the director. In the racemate they did not observe such spots and from that concluded that left and right handed layers were interleaved in the racemate.

CONCLUSIONS

We observed the first truly ferroelctric liquid crystal phase in 8SI*. This phase is characterized by a high degree of 2-d (in-plane) order. Unlike phases in which there is a helicoidal structure as well as layers, there are only two equivalent orientations for X relative to an in-plane rectangular lattice. We propose this as the reason for the inherent bistability of X.

As evidence of its liquid crystallinity, as opposed to crystallinity, we have presented 1) the absence of a heat of transition between it and an accepted liquid crystal phase (I*) compared to the 8.5 cal/gm the stable solid phase gives up when it melts to X. 2) The absence of hysteresis between X and $(G')^*$ and the presence of hysteresis between X and the solid phase. 3) The formation of stable freely suspended films in both X and $\tilde{X}$ whereas the onset of crystallization usually ruptures films. 4) The solid phases of 8SI and 8SI* exhibit a difference of 2Å in their characteristic lengths whereas the magnitude of the layer spacing of the canonical liquid crystalline phases of 8SI and 8SI* are identical. This structural similarity is also observed in X and $\tilde{X}$. Whereas chirality results in structural differences in solid phases, as first pointed out by Pasteur, structural clues of chirality are absent in fluid phases.

The ferroelectric nature of X is demonstrated by its behavior in an applied field where it is observed to switch in a bistable manner. Furthermore, we observed a threshold field below which no director response was observed. When τ was the time to switch with an applied voltage V, the function $V\ell n\tau$ was found to be a constant at constant temperature and decreased linearly with increasing temperature to be zero at the X-(G')* transition temperature. We interpreted this to mean that V lowered the barrier between the equivalent orientations of X relative to a 2-d in-plane lattice.

The polarization of X is about three orders of magnitude smaller than in solid ferroelectrics like $BaTiO_3$. The total energy associated with the usual ferroelectric ordering caused by the interaction between polarization and the local internal electric field caused by the polarization itself, is small in 8SI*.(24) This interaction energy is $-\frac{1}{2}(\mathbf{p}_s\cdot\mathbf{E})$ and **E** is of the order of the saturation polarization ($\approx$100 esu in X).(21) Thus per unit cell, $\mathbf{p}_s \cong 100\times 20\text{Å}\times 10\text{Å}\times 5\text{Å} = 1.4\times10^{-19}$ esu and $\frac{1}{2}(\mathbf{p}_s\cdot\mathbf{E}) = 0.7\times10^{-19}\times100 = 1.4\times10^{-17}$ ergs which is much smaller than kT_c when T_c is around room temperature.

The ferroelectric nature of X results because of the strong coupling between molecular asymmetry, the director **n** and the 2-d in-plane lattice. The very small values for the saturation polarization indicate that there is still a fair amount of rotational degrees of freedom associated with X.

We called the analogue of X in 8SI $\tilde{X}$ and proposed that its structure is a macroscopic segragation into alternating left and right handed sheets: thus alternating regions of "up" and "down" polarization states. The analogue of the spiral states in 8SI are alternating layers of right and left handed helices. Evidence for this are the striped appearance of these phases in the polarizing microscope as well as the complicated response of the racemate in applied electric fields.

We thank J. W. Goodby for providing us with 8SI and 8SI*.

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Appendix: Blue Phases of 8SI*

The electric field response of the two blue phases of 8SI* is also of some interest.[A1,A2] In 8SI* we find that an external field applied to blue phase I induces the transition to the cholesteric phase whereas an electric field applied to blue phase II seems to favor a transition to the isotropic phase.

We propose the following intuitive explanation for these observations. We imagine BPI to be formed of a cubic array of objects made of isotropic liquid sitting in an infinite cluster of cholesteric which is not endowed with a unique twist axis. BPII is then the converse: cholesteric objects sitting on a cubic lattice inside an infinite cluster of isotropic liquid. This picture is in spirit similar to the model proposed previously,[A1] it avoids, however, a too detailed specification of the objects sitting on a cubic lattice, a question which is anyway, at present, out of reach experimentally. The effect of an electric field on BPII in the above picture basically amounts to a breakdown of the cubic lattice of cholesteric units which become isotropic via ohmic heating. In the case of the response of BPI the electric field breaks the spatial isotropy of the twist direction thus stabilizing a uniaxial cholesteric phase as opposed to the isotropic blue phase.

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