Helielectric-ferroelectric transition mediated by a tilt-suppressing intermediate phase in liquid crystals

H. R. Brand,* P. E. Cladis, and P. L. Finn

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 5 June 1984)

In the newly synthesized compound MORA12 [S-4-0-(6 methyl)octylresorcylidene-4'-dodecylaniline], we observed a novel intermediate phase (which we call P^*) between two tilted smectic liquid-crystal phases, C^* and X. The C^* phase has a helicoidal structure whereas the X phase does not. In the P^* phase the layer spacing increases continuously from 32.3 Å to nearly 37 Å in a 10 °C temperature interval. This is a large temperature dependence of a lattice parameter which we attribute to the onset of hexagonal (as opposed to rectangular) in-plane ordering for which there is no easy axis for tilt: The tilt angle decreases as the degree of hexagonal in-plane order increases. The X phase is a true ferroelectric phase with a bistable electro-optic response whereas P^*, being helielectric, is not bistable. Furthermore, for fields larger than 1 V/μm, the switching times in C^* and P^* increased with increasing voltages.

In MORA12,[1] we observed a novel intermediate phase (P^*) between two tilted smectic phases,[2] C^* and X. The smectic-C^* phase has a helicoidal structure where the director spirals about the layer normal with a pitch of 2—3 μm.[3] There is no helix in the X phase. Only the C^* phase of this compound has been previously discussed.[1,3] We point out here for the first time that MORA12 also exhibits P^* and X phases. The purpose of this paper is to describe some of their unusual physical properties. X is a truly ferroelectric phase[4] with a bistable response to an applied electric field and P^* is a helielectric phase in which the layer spacing increases continuously from 32.3 Å to 37 Å in a relatively small interval of temperature (10 °C).

Liquid crystals are classified as being smectic if they have a layer structure in contrast to, e.g., nematic liquid crystals which typically exist at higher temperatures and show only orientational order. A typical layer spacing is 20—35 Å. Here we are concerned with those smectic liquid crystals in which the preferred direction along which the molecules orient (called the director) is inclined relative to the layer normal, i.e., tilted smectic phases. As a reference for the reader, we summarize here our view of the various tilted phases.[4] In the smectic-C phase, there is two-dimensional (2D) fluidity in the plane of the layers. Smectic phases I and F are characterized by "bond orientational" order in the plane of the layers. We interpret this to mean that in-plane translational motions are restricted to the lines of a centered rectangular grid. In G' (sometimes called J) and G, the in-plane translational order is now discrete: the molecules are localized on a 2D centered rectangular lattice but rotate freely about their long axis. In H' (sometimes called K) and H, these rotations freeze out so that although the in-plane order is still 2D rectangular, the molecule at the center of the rectangle is distinguishable from the ones at the corners. In I, G', and H', the tilt is to the short side of the rectangle whereas in F, G, and H it is towards the long side. Cooling from C to H, there is an increase in the degree of

layer registry but the Debye-Waller factor, even in the H and H' phases, it still much larger than it is in solid crystals.

In more fluid tilted smectic phases formed by chiral molecules, the director spirals about the layer normal giving rise to a helicoidal structure with a pitch typically 1—5 μm. The in-plane structure of these phases is the same as that mentioned above. Phases with the helix structure are denoted C^*, I^*, or F^*, as the case may be. These phases are helielectric: there is a polarization, P, normal to the plane spanned by the director and the layer normal, which twists uniformly in space so that globally $\langle P \rangle = 0$ in the absence of an electric field. These phases are not bistable.

In the more ordered tilted smectic phases formed by chiral molecules, the helix structure is suppressed and they are truly ferroelectric.[4] There is a spontaneous polarization, $\langle P \rangle \neq 0$ even in the absence of a field. In these cases we call the phase[4] $\hat{G}$ or $\hat{H}'$, if we know that their in-plane structure corresponds to G or H', respectively, and X, if we do not know details of the in-plane structure. These phases are bistable.

We will argue that tilt is, in general, stabilized by a rectangular in-plane lattice whereas hexagonal lattices favor orthogonal or untilted phases. Thus the dramatic decrease in tilt angle observed throughout the P^* phase is evidence of the onset of hexagonal, rather than rectangular, in-plane symmetry. Furthermore, we will argue that there is no stable orthogonal phase below P^* because of the tendency of MORA compounds to form molecular chains with the long molecular axis inclined to the chain axis. This kind of superstructure naturally packs as a tilted, nonhelicoidal smectic liquid crystal. In order to be consistent with the most recent assignment of code letters for the smectic phase[5] of chiral compounds, we call this new phase P^*.

The molecular structure of MORA12 is shown in Fig. 1. Fully extended, MORA12 is about 38.5 Å. It exhibited the following sequence of transitions:
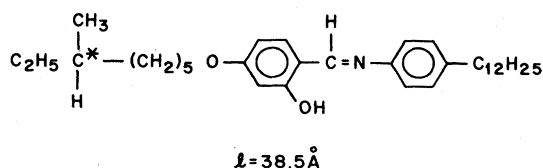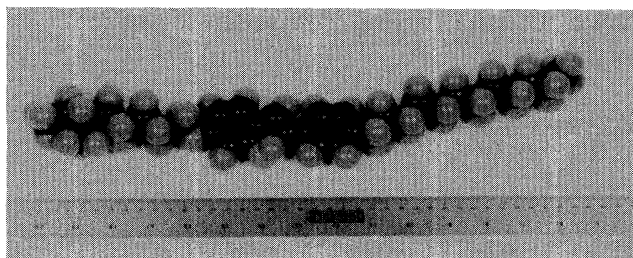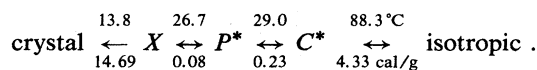
©1985 The American Physical Society

FIG. 1. The molecular structure of MORA12.

$$\text{crystal} \underset{14.69}{\overset{13.8}{\leftarrow}} X \underset{0.08}{\overset{26.7}{\leftrightarrow}} P^* \underset{0.23}{\overset{29.0}{\leftrightarrow}} C^* \underset{4.33 \text{ cal/g}}{\overset{88.3\,°C}{\leftrightarrow}} \text{isotropic}.$$

The melting point is 38.5 °C; the heat of melting is 22.17 cal/g.

Figure 2 shows the differential scanning calorimetry (DSC) traces carried out on a Perkin-Elmer DSCIV. 6.18 mg of material were used. The sharpness of the peaks and
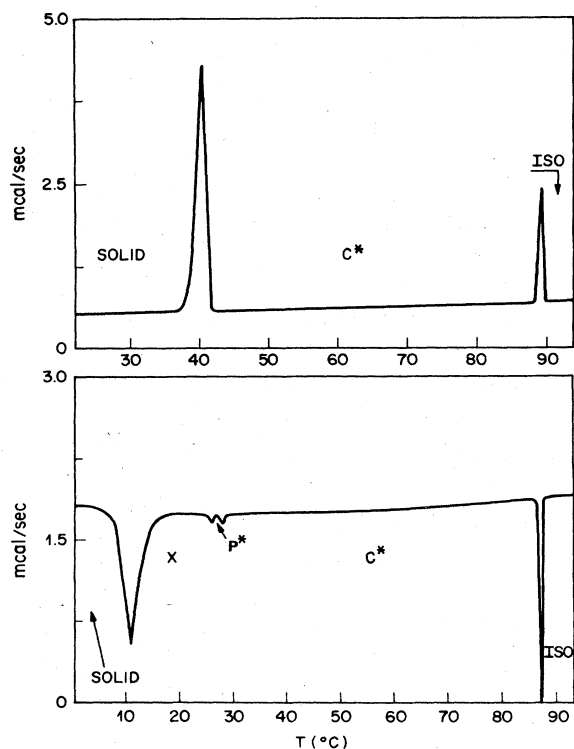

FIG. 2. DSC curves for MORA12, scan rate 3°/min, sample weight 6.2 mg. (a) heating on top, (b) cooling on bottom.

the values for the melting temperature (38.49 °C, 3.5 °C higher than previously reported[1]) are testimony of the high purity of this compound. The magnitude of the heat of transition at the C^* to isotropic transition is about twice that usually observed at the A to isotropic transition and is about the same as in MORA8, the only other compound known to show a C^* to isotropic transition.[1]

Both P^* and X are monotropic phases. The heat of transition at the C^*-P^* transition is about one fourth that which usually occurs at the C^*-I^* transition (~ 1 cal/g) and the 0.08 cal/g between P^* and X is about the same order of magnitude as is observed at a $(G')^*$-I^* transition.[4] Thus, between X and C^*, there is a difference of only 0.36 cal/g, whereas the 14.7 cal/g between X and the crystal phase tells us there is a larger difference in the degree of ordering between these two phases than between X and a fluid liquid-crystal phase like C^*.

The layer spacing of MORA12 as measured using a Rigaku rotating anode and a linear detector versus temperature is shown in Fig. 3. Entering the C^* phase from the isotropic phase, the layer spacing decreases from 31.9 Å to 31.3 Å and reaches a minimum at $\simeq 73$ °C. This corresponds to a maximum tilt (the angle between the direc-
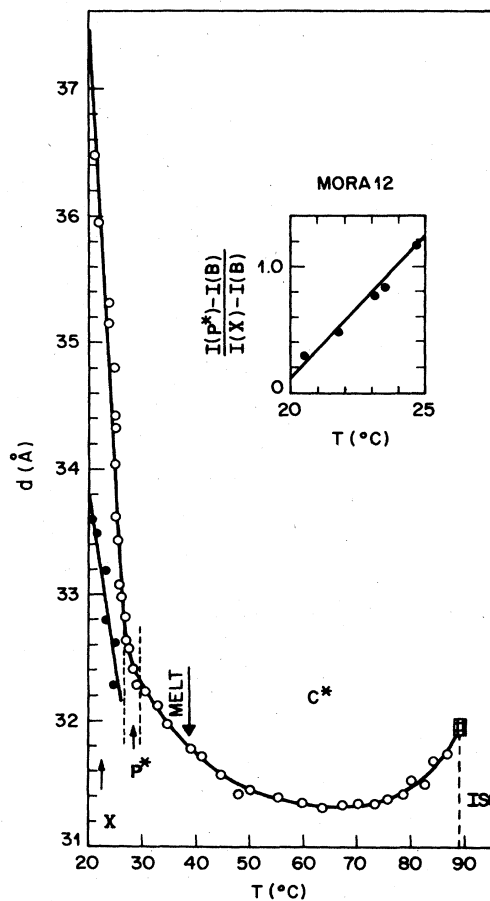

FIG. 3. Layer spacing as measured by x-ray scattering as a function of temperature. The molecular length of the molecule in the stereo model is 38.5 Å. Inset: ratio of the intensity of P^* to X peaks in the coexistence region. $I(B)$ is the background intensity.

tor and the layer normal) of about 26°. Below 73 °C, the layer spacing increases to 32.3 Å at the transition to P^*.

Since there is no smectic A phase, we determined the tilt angle in the C^* phase of MORA12 by optical means. A 12-μm-thick sample was prepared between transparent electrodes. The smectic phase was oriented with the layer normal in the plane of the electrodes. In this geometry, the two director orientations in the chiral phases associated with the two polarization states also lie in the electrode plane with an angle of 2θ, θ being the tilt angle, between them. Applying an electric field of 90 V/12 μm aligned the director in one of these states. The sample was rotated between crossed polarizers so that this state appeared black in the optical microscope. When the field is reversed, the director realigns in the second state and the sample appears bright. Optical extinction is obtained once again when the sample is rotated 2θ. In this way, the tilt angle of MORA12 can be determined. It was found to be 34° at 60 °C. Figure 3 gives the measured layer spacing, $d=31.36$ Å at 60 °C. Thus if l is the molecular length, the relation $\cos\theta=d/l$ gives $l=37.8$ Å, in rather good agreement with the fully extended length (38.5 Å) shown in Fig. 1.

The stable range of P^* is less than 5 °C and it coexists with the X phase for another 5 °C. In Fig. 3, the layer spacing increases about 1 Å in the stable range of P^*. At 25.1 °C, the single peak corresponding to the layer spacing is replaced by two peaks: an intense one centered about 34 Å and a weak one centered around 32 Å. Decreasing the temperature results in the growth in intensity of the wider angle peak (shorter length) and reduction in intensity of the smaller angle peak (longer length). This is shown as an inset in Fig. 3 and is easily interpreted as phase coexistence of P^* and X. The maximum length reached in the P^* phase is 36.5 Å which is close to the fully extended length of MORA12 ($\simeq$38.5 Å see Fig. 1), and there is no longer a helix structure. We checked the possibility that the P^*-X two-phase region extends above 25 °C by taking a long (14 h) x-ray exposure at 27.5 °C. An extrapolation of the Fig. 3 inset indicates the expected relative magnitude of the smectic X to smectic P^* peak to be $\frac{1}{2}$ the value at 24 °C but in fact, no evidence of any additional structure to the P^* peak (at even $\frac{1}{10}$th the expected peak height) was found. This serves to further distinguish P^* from X and C^*.

Subtle texture changes are observed in the optical microscope at the C^*-P^* transition (29.4 °C) similar to a C^* to I^* transition, where it will be recalled, there is hardly any change in layer spacing associated with the onset of rectangular in-plane ordering in the I^* phase. On the other hand, at 25 °C, a dramatic change is observed at the P^*-X transition. The temperatures quoted here are from observations made with a Mettler FP5 hotstage and are in reasonable agreement with the transition temperatures found in Figs. 2 and 3. No evidence of a P^*-X two-phase region is observed in optical microscope samples below 25 °C. In addition, we found that the liquid-crystal phases of MORA12 were immiscible with those of other well-known Schiff-base compounds. Thus P^* is not obviously I^*, for example.

But stronger evidence that P^* is not I^* is provided by

the large temperature dependence of the layer spacing (Fig. 3) which is not observed in crystal phases, nor for that matter in any of the more ordered smectic phases like I^*, G'^*, $\widehat{G}$, $\widehat{H}'$,[5,6] F^*[7] and I, F, G, H.[8] In other compounds we observed discontinuous jumps at C^*-B transitions,[7,9] very different from the continuous change in layering throughout P^*. This large temperature dependence of layer spacing suggests that this novel intermediate phase, whose existence is also verified by DSC, be called P^*, another liquid-crystal phase.

Additional support for the liquid crystallinity of P^* and X is provided by the broadness of their wide angle scattering in x-ray diffraction (Fig. 4). Figures 5(a) and 5(b) provide a scale to judge the relative degree of in-plane order in the phases of MORA12 shown in Fig. 4. The horizontal axis is identical in Figs. 4 and 5 and the vertical axes are normalized relative to the maximum scattered intensity. One to three hours of collection time per spectrum are shown in Figs. 4 and 5. In Fig. 5(a), we show the crystal B phase of 4O.8 (butyloxybenzylidene-octylaniline)[10] and in Fig. 5(b), we show the hexatic B phase of 65OBC (n-hexyl 4-pentyloxybiphenyl-4-carboxylate).[10,11] By comparison, the P^* and X phases of MORA12 show a large degree of in-plane fluidity (Fig. 4). In contrast, the characteristic of a crystal phase as opposed to a liquid-crystal phase is the additional structure which emerges from the "wings" of the scattering when the Debye-Waller factor is sufficiently reduced.[12] Support for hexagonal in-plane order in the P^* phase is shown in Fig. 4 where a single broad peak (slightly sharper at 4.46 Å) is seen. 4.46 Å corresponds to an in-plane hexagonal lattice constant of 5.1 Å, about the same as 65OBC [Fig. 5(b)] in the hexatic phase. Crystallization peaks emerge if the sample is left in the X phase for longer than 30 min.
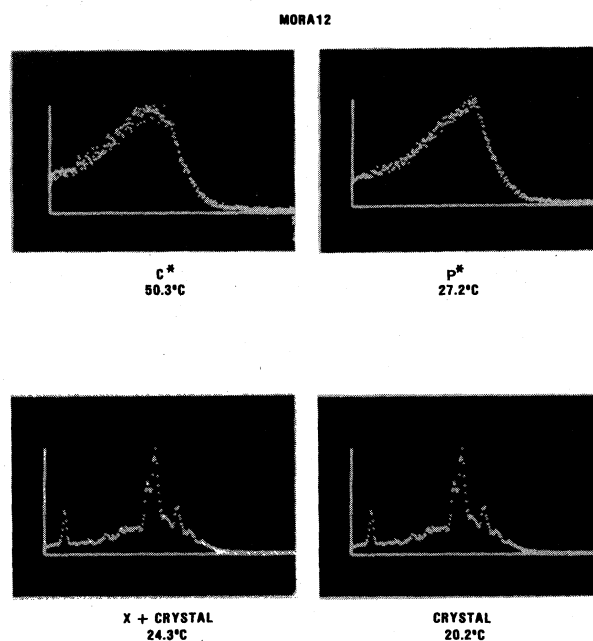
MORA12

c*
50.3°C

p*
27.2°C

X + CRYSTAL
24.3°C

CRYSTAL
20.2°C

FIG. 4. In-plane scattering intensity for the phases of MORA12. The vertical axis is intensity and the horizontal axis $\sim$(7 Å)$^{-1}$ on the left and (4 Å)$^{-1}$ on the right in all cases.

40.8

49.3°C   28.2°C

23.8°C CRYSTAL
(a)
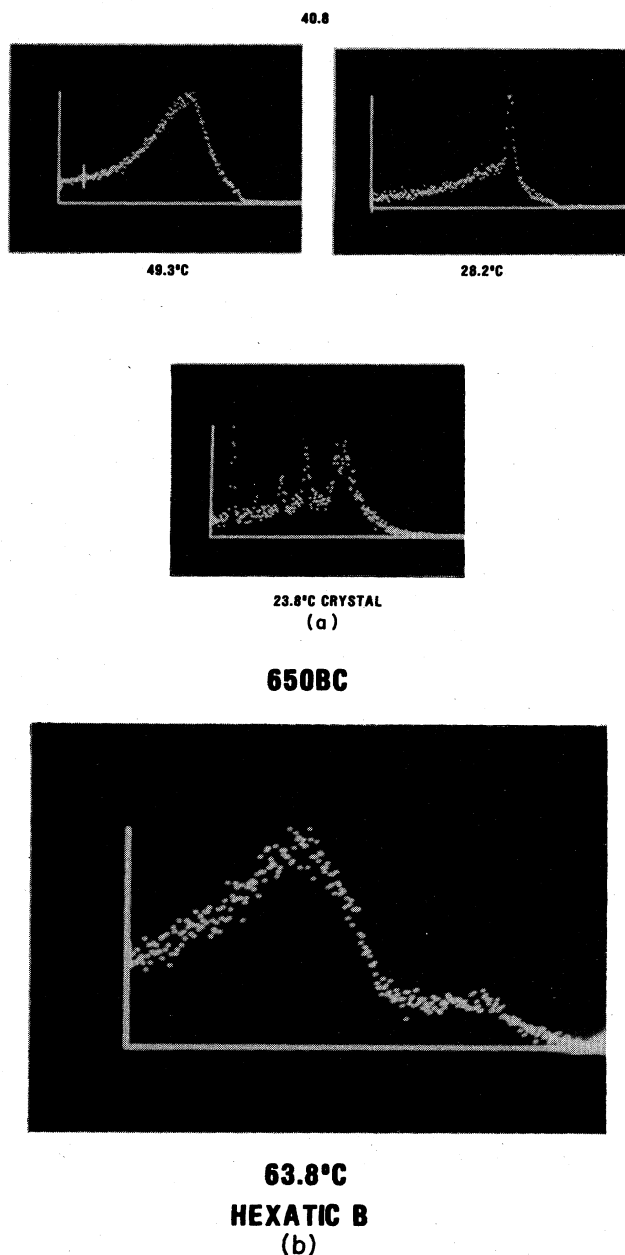
650BC

63.8°C
HEXATIC B
(b)

FIG. 5. To compare the P^* and X phase of MORA12 to known liquid-crystal phases, the in-plane scattering of the phases of (a) 4O.8 (A and crystal B, top) and (b) 65OBC taken under identical circumstances as shown in Fig. 4. The horizontal axes here are identical to those of Fig. 4.

Such peaks are not seen after 15 min at 24.3 °C when the X spectrum is only slightly sharper than the one obtained in the P^* phase with a small shift towards longer lengths.

These structural transformations affect the electro-optic response of MORA12. The C^* and P^* phases switch in the "soliton-switch mode"[13] at low fields (less than 1 V/μm) and are not bistable. At high voltages the switching time *increases* (Fig. 6) due to electrohydrodynamic instabilities induced by the applied field. Once the field is turned off, however, the sample returns to its twisted con-
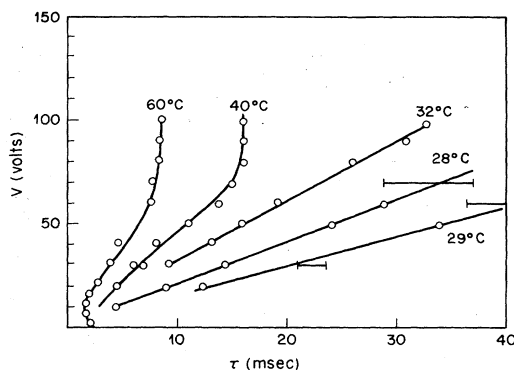

FIG. 6. Time to change the optical contrast of MORA12 vs applied voltage. The sample is 12 μm thick.

figuration. Figure 6 was obtained by monitoring the change in contrast with a photodiode upon reversal of an applied electric field.

The X phase switches bistably but the mechanism is different from that of the X phase of compounds like 8SI* $((+)[4$-$(2'$-methylbutyl)phenyl $4'$-n-ochyl-bipheny-4-carboxylate]) (Ref. 4) and HOBACPC $((-)$ [hexyloxybenzylidene-p'-amino-2-chloropropyl cinnamate]).[6] These compounds switch by wall motion parallel to the layers. In contrast, an overall loss of contrast occurs in MORA12 after a field is applied then the new uniform state emerges slowly from the perturbed intermediate state.

In some cases, the C^*—hexatic-B transition is strongly first order[9] and the molecular tilt is brutally suppressed at the transition. A 3Å jump in layer spacing is observed at the C^*—hexatic-B transition. Here, the P^*-C^* transition is only weakly first order and the loss of tilt is a gradual process observable over a range of 10 °C due to the onset of hexagonal in-plane ordering (as opposed to rectangular as at a C^*-I^* transition) at the C^*-P^* transition, even though there is no stable orthogonal phase below P^*.

It is physically reasonable that molecular tilt is incompatible with hexagonal or square[14] in-plane order because there is no easy axis in the plane for these two lattices, thus a tilt direction cannot be defined. Distorting the hexagonal lattice introduces strain anisotropy in the layers. For example, let us consider an initially untilted configuration with the molecules arranged on a 2D hexagonal net. Compress the lattice in one in-plane direction but not the other. The system can relieve this in-plane stress by tilting in the direction of the applied stress. This is equivalent to "escaping into the third dimension" by shearing the layers. In this way, a hexagonal arrangement is recovered in a plane inclined at the tilt angle to the smectic layers when the positions of molecules in neighboring layers are correlated: a single hexagon spans three layers (or four, depending upon the tilt direction) in this case. In the plane of the smectic layers, however, the packing is rectangular. Thus, we infer the rectangular in-plane packing of X from the fact that it is tilted and the hexagonal in-plane packing of P^* from the fact that tilt is being suppressed.

The general width of the scattering in the 5 Å vicinity shown in Fig. 4 does not support the notion of positional correlations over many layers. In fact, both P^* and X (Fig. 4) appear to have even less in-plane fluidity than hexatic B [Fig. 5(b)].

The unique microscopic feature of the MORA series,[1] the lateral hydroxyl group, may be responsible for the instability of orthogonal phases in general in these compounds. Usually[1] this group is shown interacting with the Schiff base nitrogen of the same molecule. But in a condensed phase, this interaction can take place just as readily between neighboring molecules; the hydroxyl group of molecule A being closer to the nitrogen of its neighbor, molecule B, say, rather than its own nitrogen. This possibility implies a shift of 1.5—2 Å between aromatic sections of molecules A and B over a lateral distance of 4—5 Å (see Fig. 7), which effectively precludes dimer formation. Thus, the hydroxyl of molecule B is forced to interact with the nitrogen of molecule C, and so forth. This model predicts layers with a tilt angle $\theta \cong \sin^{-1}(1.5/4.5) = 19.5°$ which is close to the value observed in X at 20 °C. Since the dodecyl chain is longer than the chiral chain, removing the constraint that like chains lie on the same side (as depicted in the figure) will not neutralize the overall tilted pattern as it could if the alkyl chain is much shorter than the chiral chain. MORA4 does not have an A phase but it does have a cholesteric phase above the C^* phase,[1] for example.

In an electric field, the weak nearest-neighbor bonds are broken then reformed in the new state with other neighbors, accounting for the perturbed appearance during switching in X. Once the bonds are reformed, and the field removed, the director orientation is locked in so that X is bistable. The fact that the heats of transition between X and C^* in MORA12 is about one-third that between X and C^* in other compounds, reflects the fact that the in-plane structure of X in MORA12 is not as well developed as it is in other compounds.[4,6]
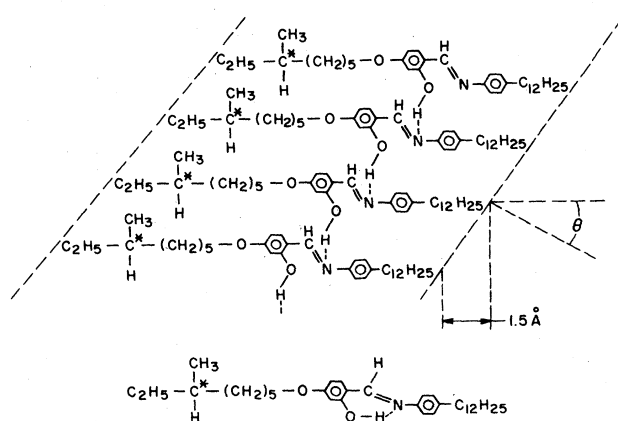

FIG. 7. Schematic representation of the microscopic picture suggested by Fig. 3, the molecular structure and the electro-optic response of MORA12 in the X phase.

In conclusion, we have observed a novel intermediate phase (P^*) between two tilted smectic liquid-crystal phases, C^* and X in MORA12. P^* is characterized by a strong dependence of its layer spacing on temperature which we have argued is due to the development of hexagonal in-plane ordering in the P^* phase. This is in contrast to other tilted phases like I^* usually observed below the C^* phase where the in-plane order is rectangular. P^* mediates the transition between a phase with a helicoidal structure, (C^*), and one without, (X), by a continuous suppression of tilt. The heat of transition separating X and C^* in MORA12 is about $\frac{1}{3}$ the value between X and C^* in other compounds.[4,6] A microscopic model was also presented to account for the general instability of orthogonal phases in the MORA series.

We thank B. Otterholm for supplying us with MORA12.

---

[1] A. Hallsby, M. Nilsson, and B. Otterholm, Mol. Cryst. Liq. Cryst. Lett. **82**, 61 (1982).

[2] For a recent review see for example: P. A. C. Gane, A. J. Leadbetter, and P. G. Wrighton, Mol. Cryst. Liq. Cryst. **66**, 247 (1981).

[3] K. Skarp, K. Flatischler, K. Kondo, Y. Sato, K. Miyasato, H. Takezoe, A. Fukuda, and E. Kuze, Jpn. J. Appl. Phys. **22**, 566 (1983).

[4] H. R. Brand and P. E. Cladis, J. Phys. Lett. **45**, 217 (1984); Mol. Cryst. Liq. Cryst. **114**, 207 (1984).

[5] A. M. Levelut, C. Germain, P. Keller, and L. Liebert, J. Phys. (Paris) **44**, 623 (1983).

[6] P. E. Cladis, H. R. Brand, P. Keller, and P. L. Finn (unpublished).

[7] P. E. Cladis and H. R. Brand (unpublished).

[8] S. Diele, H. Hartung, P. Ebeling, D. Vetters, H. Krüger, and D. Demus, in *Advances in Liquid Crystal Research and Applications,* edited by L. Bata (Pergamon, Oxford, 1980).

[9] P. Keller, P. E. Cladis, P. L. Finn, and H. R. Brand (unpublished).

[10] D. E. Moncton and R. Pindak, Phys. Rev. Lett. **43**, 701 (1979); R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, *ibid.* **46**, 27 (1981).

[11] A. J. Leadbetter, J. C. Frost, and M. A. Mazid, J. Phys. (Paris) Lett. **40**, 325 (1979).

[12] J. Doucet, A. M. Levelut, and M. Lambert, Phys. Rev. Lett. **32**, 301 (1974); Mol. Cryst. Liq. Cryst. **24**, 317 (1973).

[13] P. E. Cladis, H. R. Brand, and P. L. Finn, Phys. Rev. A **28**, 512 (1983).

[14] D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).
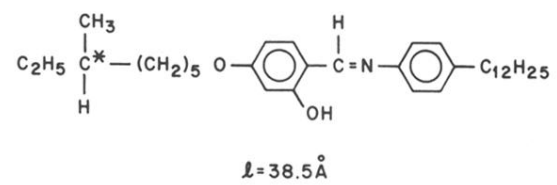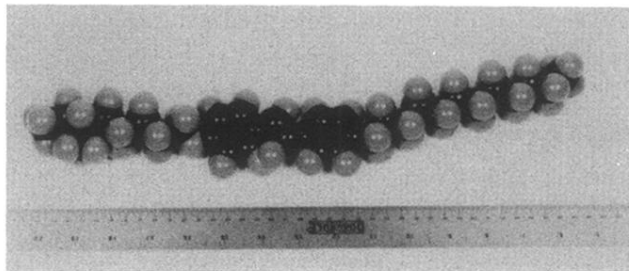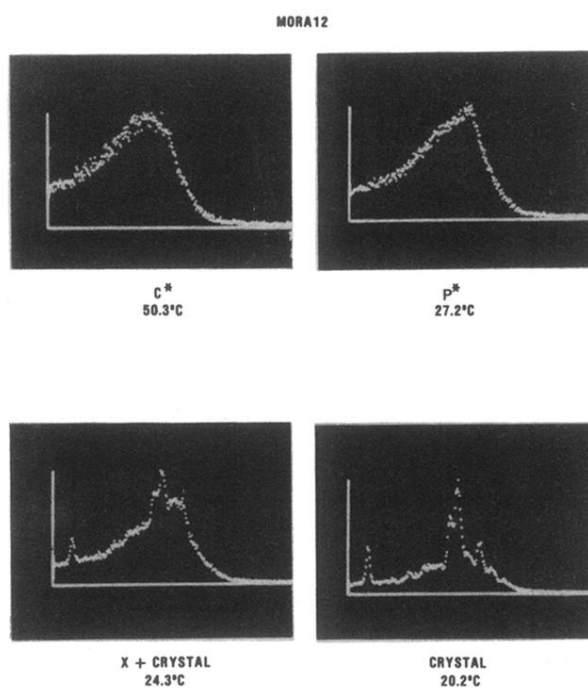
FIG. 1. The molecular structure of MORA12.

FIG. 4. In-plane scattering intensity for the phases of MORA12. The vertical axis is intensity and the horizontal axis $\sim (7\ \mathring{A})^{-1}$ on the left and $(4\ \mathring{A})^{-1}$ on the right in all cases.
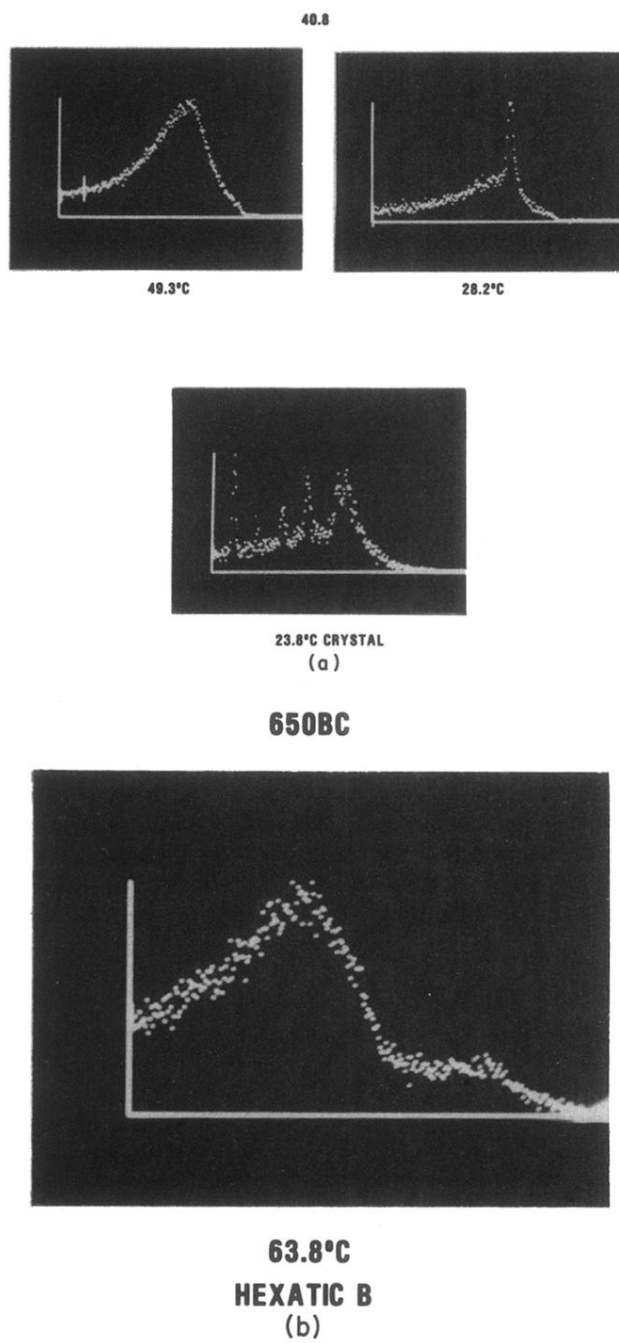
FIG. 5. To compare the P^* and X phase of MORA12 to known liquid-crystal phases, the in-plane scattering of the phases of (a) 40.8 (A and crystal B, top) and (b) 65OBC taken under identical circumstances as shown in Fig. 4. The horizontal axes here are identical to those of Fig. 4.