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## X-Ray Study and Microscopic Study of the Reentrant Nematic Phase

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We report results from x-ray experiments on mixtures of *N*-(*p*-hexyloxybenzylidene)-*p*-aminobenzonitrile (HBAB) in *N*-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline (CBOOA); very recent microscopic observations on mixtures of cyanohexyloxybiphenyl in cyanooctyloxybiphenyl are in agreement with these results. The evidence suggests that the reentrant nematic phase is similar to the classical nematic phase but may coexist with crystalline fluctuations.

It has been shown recently<sup>1</sup> that mixtures formed with two liquid crystals could exhibit with decreasing temperature the following sequence of phases: nematic, smectic *A*, and then again nematic. The nematic phase which occurs at low temperature is called the reentrant nematic phase (Fig. 1). The same phenomenon has also been observed with pure compounds under pressure.<sup>2</sup> By increasing the pressure from the nematic phase, we observe the smectic phase and then again a nematic phase at high pressure. The nematic phase which occurs at high pressure is also called the reentrant nematic phase. All these results have been obtained using the light microscope.

A model has been proposed<sup>3</sup> for the organization of the molecules in this reentrant nematic phase. In this model, the molecules are assumed to be associated in antiparallel pairs in the smectic-*A* phase, which then can be destabilized as shown in Fig. 2.

Here we present for the first time the results of an x-ray investigation of this unusual phase, and also very recent results of a microscopic study with a new mixture of thermotropic liquid crystals (Fig. 1). The observations obtained with the two techniques are in agreement and suggest that the reentrant nematic phase with its very close packing gives rise to the unusually slow nucleation of a crystallinelike phase some 20°C below the normal melting temperature. Further,

this crystalline phase *melts* at exactly the reentrant transition temperature to the smectic-*A* phase.

We have used an improved x-ray diffraction system equipped with a rotating anode and a bent-quartz-crystal monochromator. The patterns are registered with a stable position-sensitive x-ray detector. This apparatus has been previously described.<sup>4</sup> The exposure time for each pattern

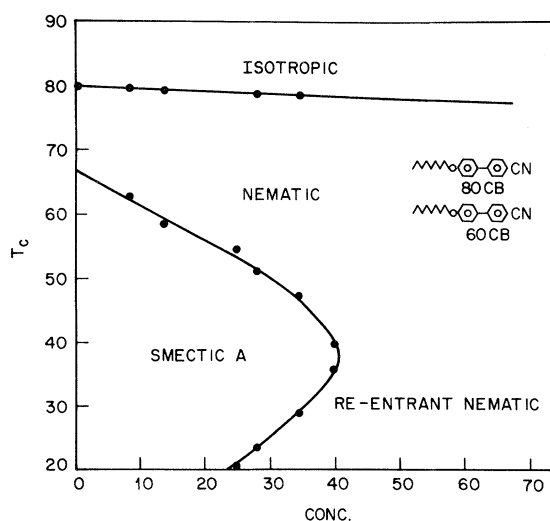


FIG. 1. Transition temperatures versus concentration for equal-weight 6OCB (cyanohexyloxybiphenyl) in 8OCB (cyanooctyloxybiphenyl).

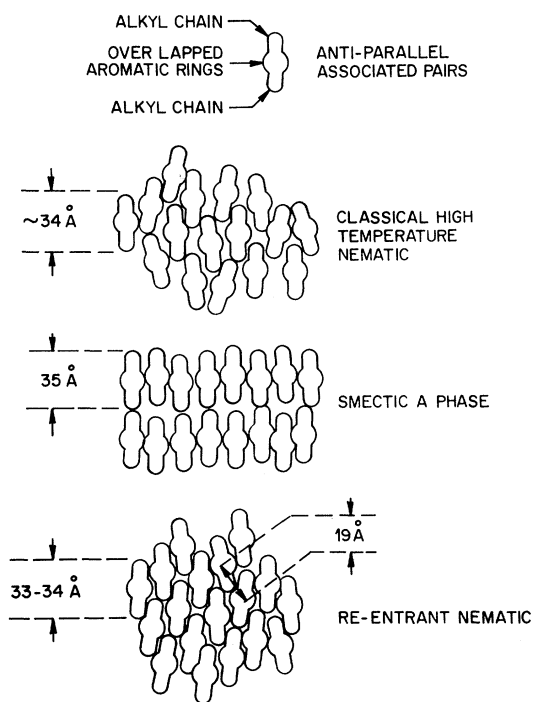


FIG. 2. Scheme showing the classical nematic, smectic-A, and reentrant nematic phases. The associated spacings are indicated on the figure.

varied from 10 to 30 minutes.

For each experiment, we have used cylindrically oriented samples. The axis of the long-range orientational order is radial at the walls. This geometry enables us to see all of reciprocal space using a linear counter and was effected using a surfactant<sup>5</sup> in a quartz capillary of 1 mm diam. The sealed capillary was put in an oven which was evacuated. In all the experiments, the x-ray beam passed through the edge of the capillary in order to avoid the regions of intense curvature in the vicinity of the disclination at the center of the capillary.<sup>6</sup>

We have used mixtures of HBAB [N-(*p*-hexyloxybenzylidene)-*p*-aminobenzonitrile] and CBOOA (N-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline).<sup>1</sup> We have performed our experiments on three samples (A, B, C), the composition of which are the following: A, 7.7% HBAB in CBOOA; B, 7.3% HBAB in CBOOA; C, 6.02% HBAB in CBOOA.

Each sample was heated to the high-temperature nematic phase to ensure a good orientation. The patterns were taken by decreasing the temperature in 1° to 2° increments. About half an hour was needed to stabilize the temperature.

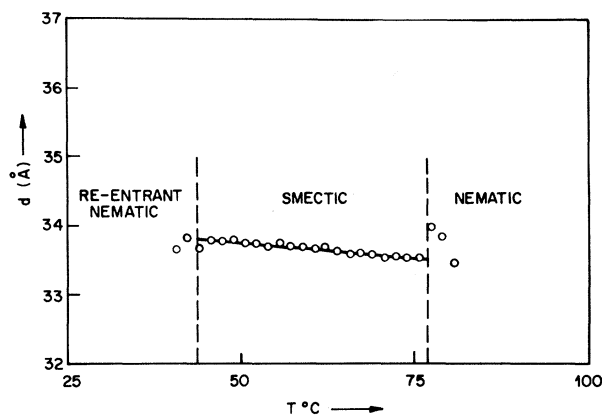


FIG. 3. Change in layer spacing of the smectic-A phase with decreasing temperature shown for 7.7% HBAB in CBOOA measured on cylindrically oriented layers. The precision of the measurements is 0.1 Å.

Here we summarize our results:

*Sample A.*—At high temperature ( $>75^{\circ}\text{C}$ ), we observe a wide peak, the spacing of which corresponds to 33.5–34 Å. This is the classical nematic pattern, showing smectic fluctuations in the nematic phase. Decreasing the temperature leads to the smectic-A phase. The variation of the layer spacing as a function of decreasing temperature is shown in Fig. 3. It varies from 33.5 to 33.8 Å, which represents about 1% variation. When we approach the low-temperature nematic phase transition, the intensity of the Bragg peak corresponding to the layer spacing decreases. We find again a nematic phase at about  $48^{\circ}\text{C}$ , which is characterized by a wide peak at 33.5 Å. The transition from smectic-A to reentrant nematic phase is reversible from the point of view of x-ray diffraction, in agreement with results obtained optically. The sample crystallizes at  $38^{\circ}\text{C}$  with a layer spacing of 45.5 Å.

*Sample B.*—The variation of the layer spacing with decreasing temperature in the smectic-A phase is the same as shown in Fig. 3 for sample A. When the reentrant nematic phase appears, we observe first a wide peak corresponding to a spacing of 32–33 Å. As the temperature decreases, another peak appears, corresponding to a spacing of 18.5–19 Å [Fig. 4(a)]. We note that as the temperature decreases, the intensity of this additional peak increases. The phenomenon is reversible; by increasing the temperature, we again find only the wide peak of 32 Å, and immediately the smectic-A phase appears. Decreasing the temperature to  $41^{\circ}\text{C}$ , the sample crystallized with a characteristic spacing of 25 Å.

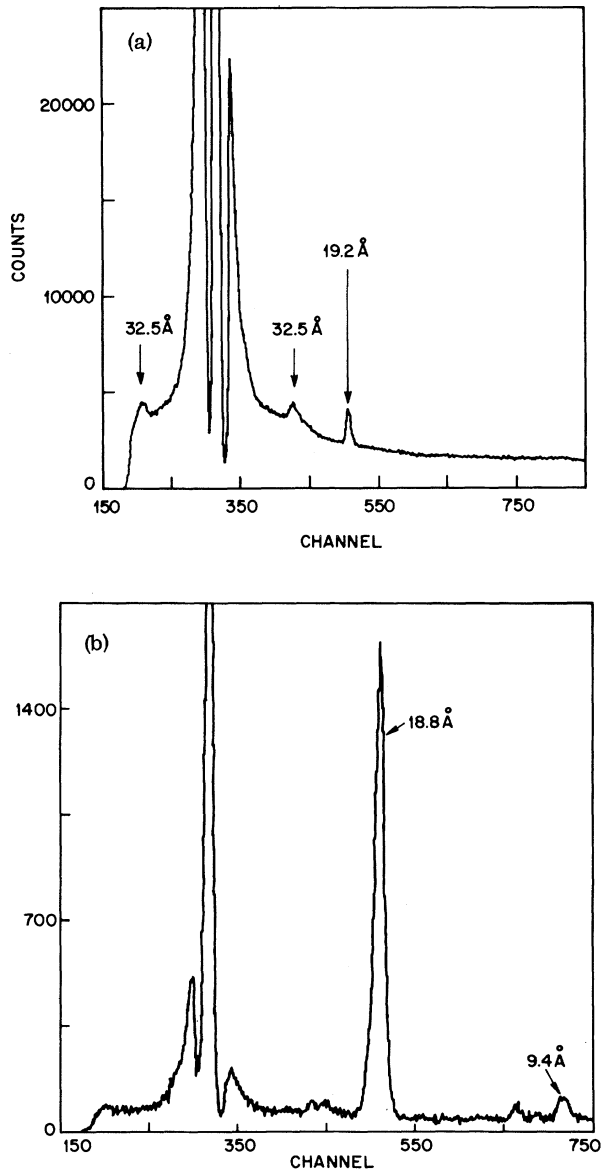


FIG. 4. (a) X-ray diffraction pattern of the reentrant nematic phase for the mixture of 7.3% HBAB in CBOOA. (b) X-ray diffraction pattern of the reentrant nematic phase for the mixture of 6.02% HBAB in CBOOA.

*Sample C.*—By decreasing the temperature from the smectic-A phase, instead of seeing the pattern of the classical nematic phase, we observed one with an intense but wider peak than in the smectic phase corresponding to a 19.2-Å spacing [Fig. 4(b)]. This pattern is stable over a 12°C range of temperature until the onset of crystallization. The layer spacing in that last crystalline phase is 25 Å.

From these observations, the reentrant nematic

phase appears quite different from the higher-temperature nematic phase. We find that for all the patterns we have registered in the nematic phase at high temperature, we have only observed the wide peak of the classical nematic phase, which corresponds to a spacing of 35 Å, while for two mixtures of different composition, we have registered patterns with two different spacings. All the observations under the microscope for the previous mixtures have shown (in a parallel-plate configuration as well as the same capillaries we have used in our x-ray diffraction pattern) the following phases in order of decreasing temperature: nematic, smectic A, reentrant nematic, and crystal; these observations are very reproducible.

For the 19-Å peak, the width at half maximum corresponds to 30 to 50 molecules. For the 33-Å peak, the width corresponds to only 10 to 20 molecules. Thus there is a significant narrowing of the larger-angle maximum. Some very recent observations on another mixture of liquid-crystal compounds (25% cyanohexyloxybiphenyl in cyano-octyloxybiphenyl) (see Fig. 1) show another phase nucleating in the reentrant nematic phase. The additional phase appears to be crystalline and can coexist a very long time (several months) with the nematic phase. Upon increasing the temperature, the two coexisting phases transform to the smectic phase *at the same temperature*. These observations are in complete agreement with the x-ray diffraction results reported above on mixture B. The extra peak at 19 Å has also been observed very recently<sup>7</sup> in the reentrant nematic phase of pure CBOOA under pressure.

We interpret the two maxima in the reentrant nematic as follows: The smaller-angle (35 Å) broad maximum corresponds to a classical nematic phase. This peak has the same breadth and corresponds to the same spacing as that found in the high-temperature nematic. The second, larger-angle maximum (19 Å) is sharper than the broad nematic peak at 35 Å. Since the consequence of disorder is only to broaden or diminish x-ray reflections of higher order, the presence of a sharper maximum at a *larger* angle indicates the coexistence of a new structural phase with longer-range order. We suggest that this new phase consists of microcrystallites in equilibrium with the nematic phase and that it is these microcrystallites which are responsible for the sharper reflections, whereas the reentrant nematic is responsible for the broad smaller-angle reflection. In both cases we believe the mole-

cules to be associated in antiparallel pairs such as shown for example in Refs. 2 or 3. The origin of the 19-Å line may be due to a more-dense superassociation of the antiparallel pairs such as shown in Fig. 2 (bottom), which has been proposed for the reentrant nematic.<sup>3</sup> Although we believe that the diffraction peak observed at 19 Å arises only from microcrystals, the fact that these microcrystals *coexist* with the nematic phase and *melt to the smectic-A phase at the same temperature as the reentrant nematic* suggests that the two structures are compatible (energetically) and may share similar structural features. Thus we tentatively propose the densely packed model for the reentrant nematic phase as well as the microcrystalline phase, attributing the difference in the two phases as being due to the difference in the range of the 19-Å ordering. In the crystalline phase it is presumably of long range (hence the sharp peaks), whereas in the reentrant nematic phase it is of very short range.

In summary, the two samples which exhibited the 19-Å line [and even a possible second order, Fig. 4(b)] crystallized to a 25-Å stable crystal, whereas the sample which did not show the 19-Å spacing crystallized with a characteristic spacing of 45 Å. Because of the broadness of the 19-Å line (Fig. 4) we suggest that it is due to large-scale associations (~50–60 molecules) of the sort shown in Fig. 2 (bottom) and which we believe slowly grow to eventually produce the large monodomain crystallites coexisting with a nematic phase observed in the room-temperature reentrant nematics of Fig. 1. The optical sign of these crystallites is positive excluding their being “skewed cybotactic groups.”<sup>8</sup> In addition,

they demonstrate their kinship to the reentrant nematic phase by *melting* to the smectic-A phase *at the same temperature* as does the reentrant nematic.

The possibility that the reentrant nematic is actually a smectic-C phase was excluded<sup>1</sup> on experimental grounds: (1) The reentrant nematic is uniaxial—not biaxial as is smectic C, and (2) the defect structure of the reentrant nematic observed in a cylindrical geometry was identical to that observed for the classical nematic<sup>6</sup>—more precisely, but also more technically, we have observed a pair of  $S = \frac{1}{2}$  defects and the escaped defects with  $S = 1$  in the reentrant nematic phase.<sup>9</sup> These are defects characteristic of a nematic phase and neither of these can occur in a smectic-C phase.

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