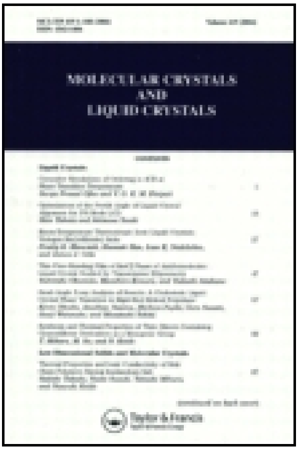

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Characterization of the Hexatic B and Crystal B phases by Optical Microscopy

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Characterization of the Hexatic B and Crystal B Phases by Optical Microscopy

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Recent investigations concerning the structure of the B phase have unearthed a variety of packing arrangements of the molecular layers for this smectic modification. Two general structures have been discovered; one in which the B phase has three-dimensional crystalline order (crystal B), and one that is characterized by short-range in-plane positional ordering of the constituent molecules, and long-range bond orientational order, both within and between the layers (hexatic B). In this present study *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) has been synthesized and its smectic phases characterized. Typically, this ester exhibits an A,B,E phase sequence, with the B phase being of the hexatic type. The synthesis, microscopic textures, and miscibility studies are reported here. The results show that while the two types of B phase appear co-miscible by conventional optical methods, in fact X-ray diffraction studies show that a transition occurs between the two phases in certain binary mixtures. Thus, the hexatic B and crystal B modifications are thermodynamically *distinct* phases.

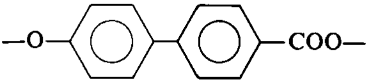
INTRODUCTION

Detailed X-ray diffraction studies of the B modification have shown that the phase can possess one of two general forms. One structural form (crystal B) was reported to have three-dimensional crystalline order,[1] a result which has since been confirmed by high-resolution X-ray diffraction studies.[2,3] This crystal B phase is subdivided into a number of categories by the positional stacking of the molecular layers one on top of another (e.g., ABABAB or ABCABC etc., in direct analogy to the packing of spheres). Furthermore, changes in the packing arrangements of the layers were shown to occur with change in temperature for this phase[4,5] (e.g. ABCABC packing changing to ABABAB packing on heating).

Recent reports, however, have indicated that some B phases do not appear to have long-range interlayer correlations.[4] Detailed X-ray studies[6,7] have shown that this second structural form (hexatic B) has only short-range positional ordering of the molecules within the layers. The layers, however, do have a local hexagonal structure and the bond orientational order of this structure is long-range.

This current investigation sought to prepare a stable material possessing particular phase types (including A and hexatic B phases) in order to be suitable for study by X-ray diffraction using the free-standing film technique.[6,7]

From a report by Leadbetter, Frost, and Mazid[4] it is apparent that from the materials selected for study, those containing a Schiff's base (—CH=N—) central linkage usually exhibit crystal B properties, whilst compounds containing an ester linkage (—CO.O—) are more liable to exhibit a hexatic type B phase. Bearing these facts in mind derivatives of the 4'-oxy-biphenyl-4-carboxylate



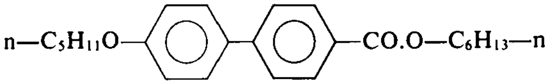
system were chosen as suitable candidates for further investigation.

A number of *n*-alkyl 4'-*n*-alkoxybiphenyl-4-carboxylates had previously been synthesized and charcterized by Goodby and Gray,[8] but none were found to exhibit the desired enantiotropic phases suitable for investigation. Therefore, members of the homologous series with shorter *n*-alkoxy terminal carbon chain lengths were synthesized because of their greater tendency to exhibit orthogonal phases in comparison to those studied previously, which often showed injections of tilted phases into their homologous series. Thus, the syntheses of a number of *n*-alkyl 4'-*n*-pentyloxybiphenyl-4-carboxylates were carried out. The phase sequence and transition temperatures associated with *n*-hexyl 4'-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) warranted further investigation of this material. In the following sections the classification of the smectic modifications and the optical textures of each phase of this material are discussed. The preparation of 65OBC and its miscibility with the standard material *N*-(4'-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8) (N,A, crystal B phases) are also reported.

RESULTS AND DISCUSSION

(1) Optical Microscopy

A purified sample of *n*-hexyl 4'-*n*-pentyloxybiphenyl-4-carboxylate was examined firstly by thermal optical microscopy. The transition temperatures and the classification of the phase types exhibited by this compound were initially obtained from textural observations. The transition temperatures determined by optical microscopy for *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) are as follows:



Iso → A → B → E → Crystal m.p.
85 67 60 57 66

Structural studies of the phases exhibited by this compound confirmed the above phase sequence, and showed that the B phase was indeed of the hexatic type.[7] The B phase appears to have extensive bond orientational order but with the in-plane molecular positional correlations only extending over a distance of 150 Å, and no positional coupling or correlations of the molecular layers.

The phases exhibited by *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate were initially classified by textural observations. Microscopic investigation of a thin preparation of 65OBC at 85° between crossed polarizers showed a smectic A phase separating from the isotropic liquid in the form of bâtonnets on cooling. On further slight cooling the bâtonnets coalesced to form a typical clear, focal-conic fan texture, compatible with that of a smectic A phase (see Plate 1). Further cooling produced a transition to another phase that was char-

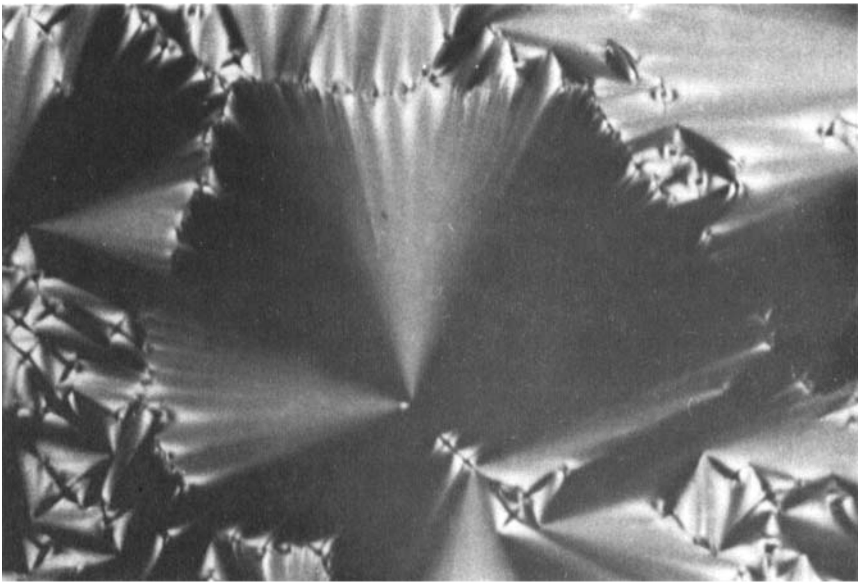


PLATE 1 The focal-conic fan texture of the smectic A phase of *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (×100).

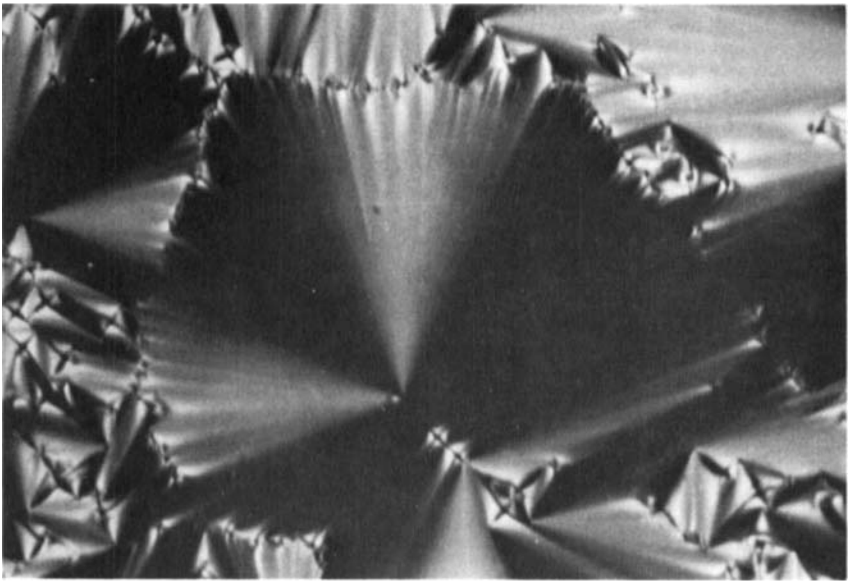


PLATE 2 The focal-conic fan texture of the hexatic B phase of *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (×100).

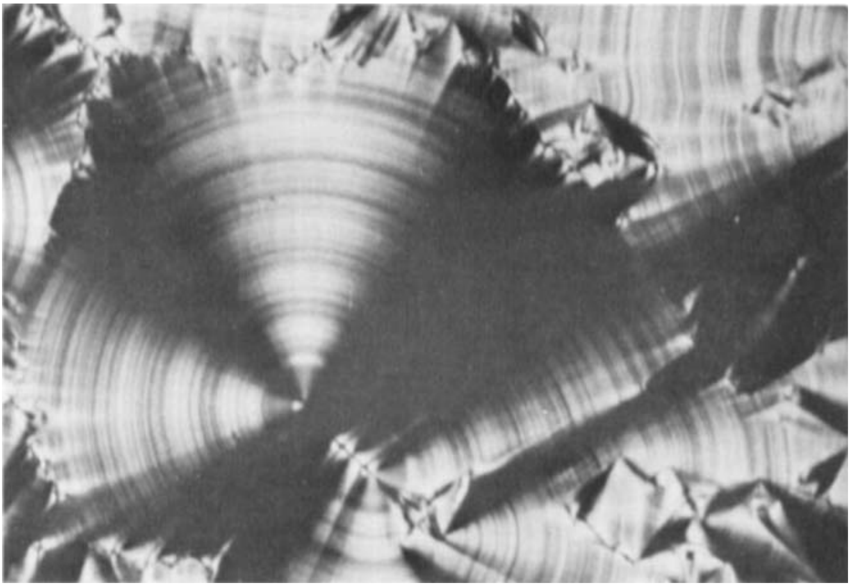


PLATE 3 The arced focal-conic fan texture of the smectic E phase of *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (×100).

acterized by its homeotropic and clear fan textures as being of the B type. The transition, however, was *not* typical of that associated with an A to crystal B transition. *No transition bars* were observed at the phase change and instead the fan backs merely cleared a little (compare Plate 2 with Plate 1). Further reduction in temperature, produced a phase that exhibited the platelet and arced focal-conic fan textures (see Plate 3) which are indicative of the phase being of the E type.

(2) Parabolic focal-conic defects

An interesting observation was made on heating the hexatic B phase of 65OBC so that a transition back to the A phase occurred. The focal-conic fan texture of the A phase was covered by small parabolic focal-conic defects (wishbones) instead of being clear (see Plate 4).

Parabolic defects can be obtained by a buckling of the layers occurring at transition. These defects occur when the molecular layers are stressed to give a buckle, and when the layer strains are large enough distortions will localize into parabolic line disclinations of the layers. This line will then form in a particular direction.[9] A similar set of buckles occurs in a plane at right angles to

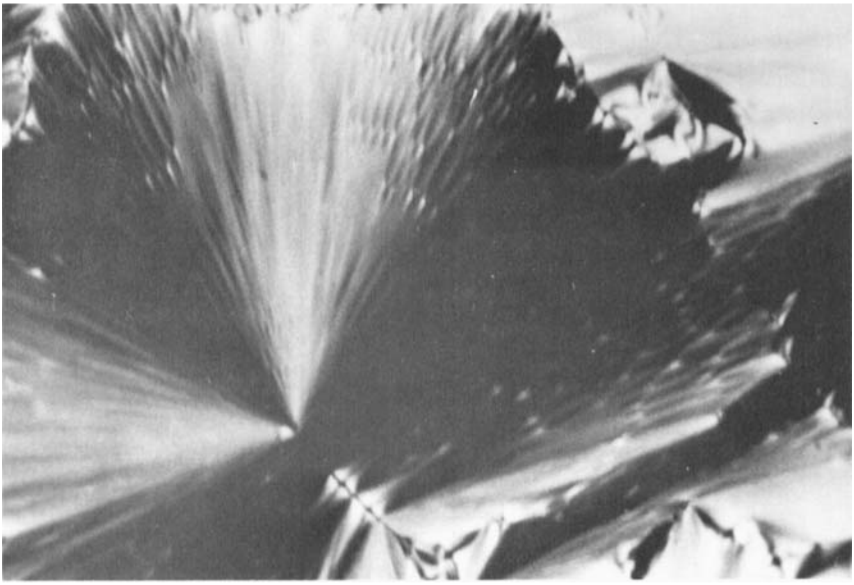


PLATE 4 The parabolic focal-conic defects of the smectic A phase of *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (×100).

the first set (see Figure 1). Thus, lines of optical discontinuity are observed at the parabolic edges of the buckles, hence the term *parabolic focal-conic defect*. Microscopic observation of this defect shows a 'wishbone' effect as the full parabolic line of optical discontinuity is observed in one plane (for one arm of the parabolic pair of focal-conics) whilst the straight edge of the other parabola is seen at right angles to its own plane.

Microscopic investigation of 65OBC shows that the A phase is obtained from the isotropic liquid *via* the formation of bâtonnets on cooling. The bâtonnets nucleate in the bulk liquid, coalesce and finally become attached to the surface of the glass supports. The fan backs are almost parallel to the surface, and therefore the layers at the surface are effectively perpendicular to it. However, the layers curve away on moving into the bulk phase. Transition to the B phase occurs with a small change in the volume as the molecules pack tighter together. Thus, the volume of the fans shrink as transition occurs. This produces movement in the radial lines of the focal-conic domains. Reversal of the transition now produces an increase in the volume of each individual fan. The layers, which are still attached to the glass, buckle to relieve the stress of expansion giving rise in the process to the formation of parabolic focal-conic defects (see Figure 1). Cooling back to the B phase reverses this second procedure annealing the defects.

An interesting demonstration of the stress related origin of the parabolic defects can be obtained in contact preparations with a nematogen. A contact

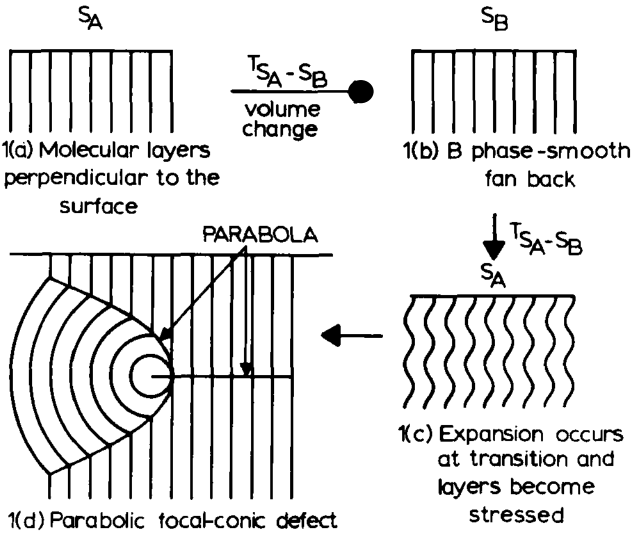


FIGURE 1 The structure of the parabolic focal-conic defect and its formation *via* a B to A transition.

preparation between *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC, A, hexatic B, and E phases) and *N*-(4′-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8, N, A and crystal B phases) can aid the formation of a nematic phase preceding the A and crystal B phases in a wide range of binary mixtures (see miscibility diagram of state for binary mixtures of these two compounds).

If the contact region between these two materials is observed, then transition from the crystal B phase to the A phase takes place normally with transition bars occurring at the point of transition. On completion of the transition the focal-conic fan texture of the A phase becomes totally covered with parabolic defects (Plate 5). Further heating produces a transition to the nematic phase, but because the area under observation is the contact region between 65OBC and 4O.8 the transition to the nematic phase progresses slowly across the field of view as the temperature is increased. As the concentration of the mixed region changes across the contact so does the transition temperature of the A to nematic phase change, i.e. this temperature increases with the increasing proportion of 65OBC in the binary mixture until a certain percentage is reached where the nematic phase disappears. Thus it is possible to move the N-A phase 'barrier' across the field of view (to any position) simply by changing the temperature. As the transition to the nematic phase occurs the general outline of the focal-conic domains is retained indicating some formation of

PLATE 5 Focal-conic fan texture of the smectic A phase of the contact region between *N*-(4′-*n*-butyloxybenzylidene)-4-*n*-octylaniline (left) and *n*-hexyl 4′-pentyloxybiphenyl-4-carboxylate (right), showing parabolic focal-conic defects (×100).

cybotactic areas and adhesion to the surface. The parabolic defects however, disappear as transition to the nematic phase occurs (see Plate 6). Transition back to the A phase leaves the fan texture looking clear and without the defects.

Thus it is possible to obtain a focal-conic texture for the A phase in which the fans on one side are still covered in parabolic defects (not having undergone transition to a nematic phase) and those for the other side have been left clear by a transition from the nematic phase (see Plate 7).

These results indicate that the formation of parabolic focal-conic defects depends on whether the molecular layers in the A phase are stressed (as at the B to A transition) or unstressed (as at the nematic to A transition).

(3) Textures at the A-B transition—transition bars

The A to B phase change has often been characterized by the textural changes that occur in the focal-conic fan texture at the point of transition. The observation of the variety of textural changes occurring at the A to B transition made in this and related studies permit us to tentatively divide the types of change observed into five categories as follows:

(i) Faint transient lines that run parallel to the molecular layers and which occur only at the point of transition, and then disappear quickly as transition

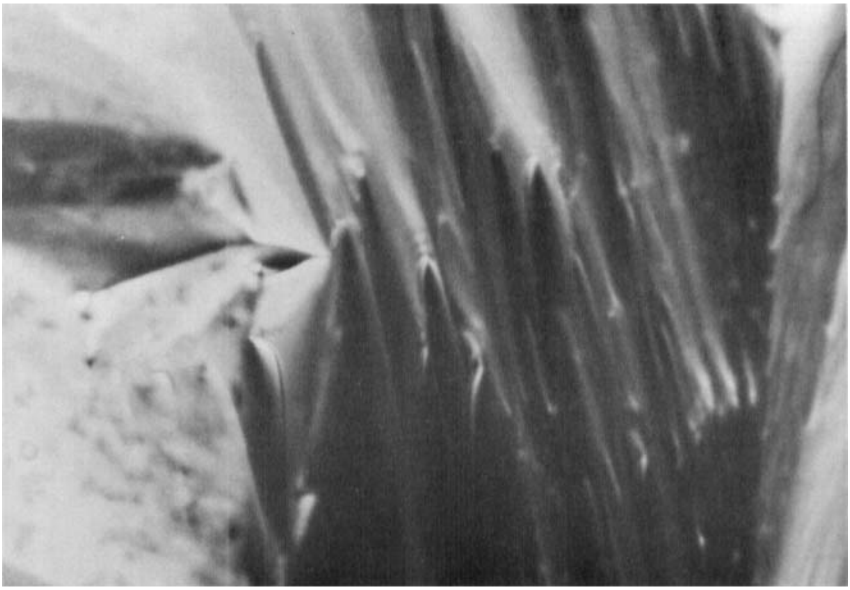


PLATE 6 The N—S_A transition 'barrier' as it crosses the contact region so destroying the parabolic focal-conic defects. The contact preparation is between *N*-(4′-*n*-butyloxybenzylidene)-4-*n*-octylaniline (left) and *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (right) (×100).

ends, thus producing a clear fan texture. This transition bar phenomenon is observed for both the A to hexatic B and A to crystal B phase changes.

(ii) Lines that cross the fans at transition and run parallel to the molecular layers. As the transition proceeds the lines widen until they meet and disappear, thus producing a clear focal-conic texture. Typically, these transition bars are observed at an A to crystal B phase transition, as shown in Plate 8 for *N*-(4′-*n*-octyloxybenzylidene)-4-*n*-butylaniline (8O.4).

(iii) Transition bars occur at the A to B phase change on the first cooling cycle from the isotropic liquid. Transition back to the A phase is not accompanied by the 'bars', but the A phase then exhibits *parabolic focal-conic defects.*

(iv) On cooling from the A phase to the B phase the fan backs become clearer and there is movement along the radial 'spines' of the focal-conic domains. Reversal of this process produces an A phase which exhibits *parabolic focal-conic defects.* Subsequent cooling anneals these defects. This type of textural change is observed for both A to crystal B and A to hexatic B phase changes. (i.e. for both 65OBC and 4O.8)

(v) No textural change is observed at the A to B transition. This observation (or lack of it) is often made for A to hexatic B phase changes.

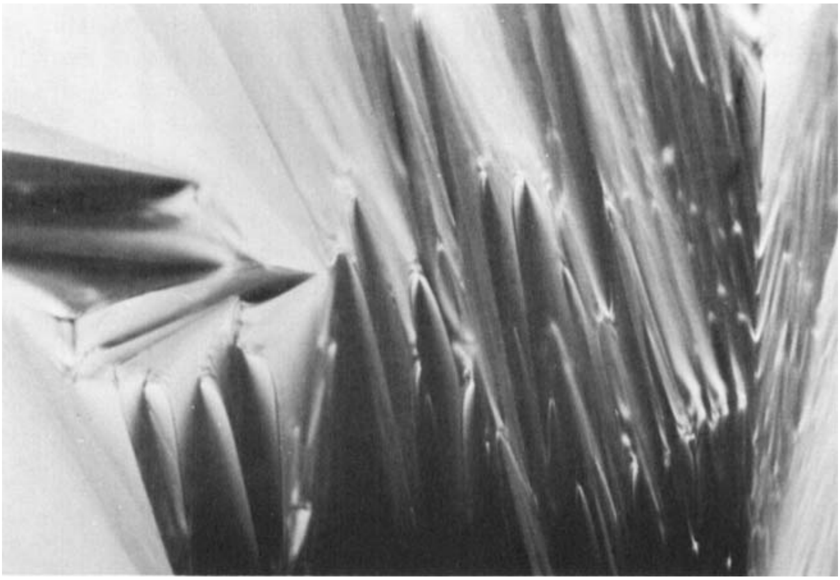


PLATE 7 The focal-conic fan texture of the smectic A phase of the contact region between *N*-(4′-*n*-butyloxybenzylidene)-4-*n*-octylaniline (left) and *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (right). The area that underwent transition to the nematic phase no longer shows the parabolic focal-conic defects (×100).

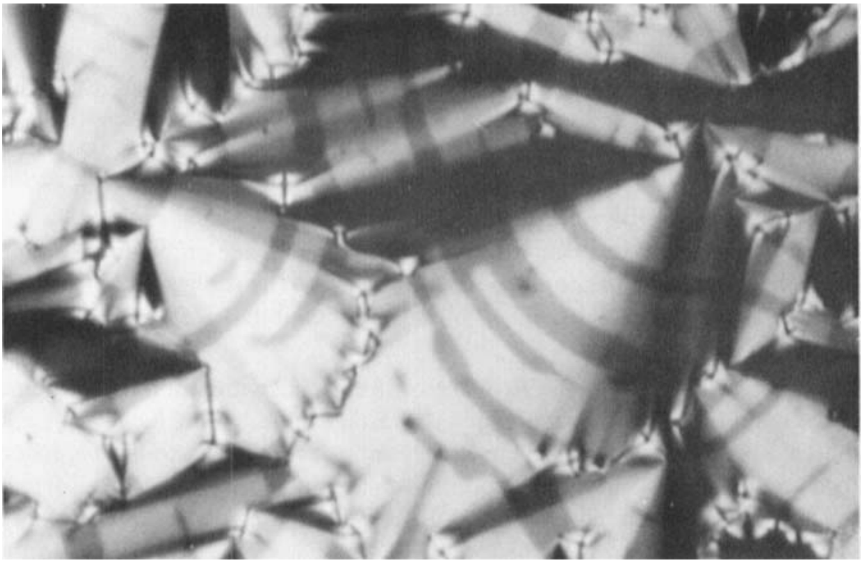


PLATE 8 Transition bars occurring at the A to crystal B transition for *N*-(4′-*n*-octyloxybenzylidene)-4-*n*-butylaniline (8O.4) (×100).

Types (ii) and (v) are two extremities of textural change which can aid the classification of the B phase into the crystal or hexatic types. Moreover, the transition bar phenomenon has sometimes been attributed to impurity effects,[10] however recent studies have indicated that they may be related to build up of long-range interlayer correlations or mixed regions of A and B phases.[11]

Further distinctions between the hexatic B and crystal B phases can be made from observation of the shapes of the focal-conic domains in the B phase. These domains are often deformed in the crystal B phase (unlike the hexatic B) and have sometimes been referred to as mosaics.

These tentative observations of fan structure and the textural changes occurring at transition can aid the identification of B phases in *some but not all* cases.

(4) Miscibility studies

Structural studies have shown that two types of B phase exist; thus the hexatic B and crystal B phases are distinct and should be immiscible as are the analogous I or F and G phases. Indeed to assume the two types of orthogonal B phase are co-miscible would be to signal the end of miscibility methods as the prime criterion for classification of phase types. Therefore, a miscibility study involving two materials that exhibit different B types was undertaken. The two materials chosen for the investigation were *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC) which exhibits a hexatic B phase[7] and *N*-(4′-*n*-butyloxybenzylidene-4-*n*-octylaniline (4O.8) which exhibits a crystal B phase.[2]

The initial study by the contact method revealed no immiscible regions within the temperature range of the B phase, nor did it show any abnormal extra changes that could have been construed as hexatic to crystal B transitions. The weighed miscibility method gave similar results to that of the contact method, no other transitions except those which would normally be expected for N-A, A-B and B-E were observed. However, small changes in the focal-conic fan texture of the B phase of binary mixtures in the region of 80–90% by wt. of 4O.8 were observed. These changes were not truly reversible and were attributed to stressing of the fans giving rise to radial lines running down their backs. The miscibility diagram of state for binary compositions of 65OBC and 4O.8 is given in Figure 2, optical studies in this case infer that the two B modifications are co-miscible.

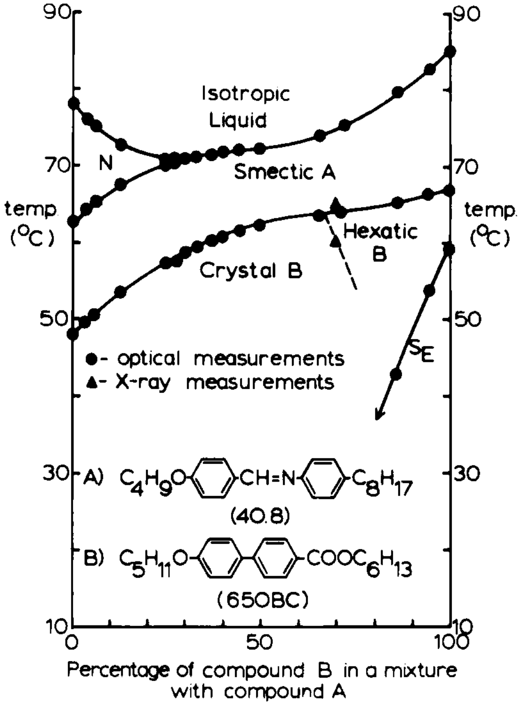


FIGURE 2 The miscibility diagram of state for binary mixtures (wt. %) of *N*-(4′-*n*-butyloxybenzylidene)-4-*n*-octylaniline (4O.8) and *n*-hexyl 4-*n*-pentyloxybiphenyl-4-carboxylate (65OBC). Portions of the solid lines contain two-phase regions. The extent of these regions is difficult to determine by optical microscopy, so they have not been indicated. The dashed line is schematic of how the hexatic B-crystal B transition line might cross the one point where the transition has been observed. Negative results for lower and higher concentrations indicate that this line must have a slope at least as steep as illustrated.

A third investigation[12] into the miscibility of the two types of B phase was made by using X-ray scattering techniques of freely suspended films. A variety of mixtures of 65OBC and 4O.8 were studied. The samples were prepared by weighing out definite amounts of each component into a glass phial and heating until a clear liquid was obtained. The solution was then mixed thoroughly by vibrating the phial vigorously. A thin film of each mixture was then prepared in the usual manner. All of the mixtures except one showed B phases with either similar structures to that of 4O.8 or 65OBC; no immiscible regions or B-B phase changes were observed on cooling from the A phase down to room temperature.

However, the binary mixture of 69.1% by wt. of 65OBC and 30.9% by wt. of 4O.8 showed a ***transition from*** the ***hexatic B*** phase ***to*** the ***crystal B*** phase on cooling. The mixture has constants of

$$\begin{array}{ccccc} A & \rightarrow & \text{Hexatic B} & \rightarrow & \text{Crystal B} \\ & 66 & & 60 & \end{array}$$

demonstrating that a 6°C temperature range of the hexatic B phase exists between the A and crystal B phases, i.e. it clearly is ***not*** a pretransitional effect.

Thus, X-ray diffraction clearly indicates that the hexatic B and crystal B phases are thermodynamically ***distinct*** phases with separate identities.

Microscopic investigations of this particular mixture showed no textural changes occurring at the temperature indicated for the phase change from X-ray techniques. Thus, either the textural changes taking place at transition are too subtle to be detected or else no change at all occurs and therefore the transition cannot be detected. If the latter is true, then obviously it is ***impossible*** to classify the two B phases apart by the simple miscibility method involving optical microscopy, i.e. we have reached the ***limitation*** (in this case) of the ***identification*** of ***phase types by observation of microscopic textures.***

(5) Classification and nomenclature

The results obtained in this study show that a phase transition can occur between the hexatic B and crystal B phases, thus both phases have separate identities and therefore should have different miscibility code-letters. The original concept of the B phase, however, was one in which the hexagonally close-packed layers were free to slide over one another (uncorrelated) even though some of the early materials investigated have now been shown to be of the crystal B type. Therefore, the ***hexatic*** phase exhibited by 65OBC should ***retain*** its original ***classification of B.***

Once having classified the hexatic phase the major dilemma is the classification of the crystal phase. The fundamental issues surrounding the definitions of "smectic" and "liquid crystal" plus the present instability in the lettering system of 'smectic phases' pose considerable problems for any classification of this phase. Recent structural studies[13] of bis-(4′-*n*-heptyloxybenzylidene)-1,4-phenylenediamine suggest that the new J and K phases were erroneously categorized. yet ironically the code-letters may be retained.[14] In this event, the classification of the *crystal phase* would be S_L, if the "phase" is to be retained within the conventional system of classifying smectic modifications. However, to reject the crystal B modification from this scheme because of its crystalline nature would also mean the rejection of the other 'crystal phases' E, G, H, (J and K). In the strictest sense, the modifications E, G, H, crystal B, (J and K) are indeed disordered solids and should always be regarded that way. However, historically they have always been shown to share some of the same characteristics of the other phases (e.g., co-miscibility etc.). Moreover, these types of crystal phase have only been observed in liquid crystal systems.

Thus, it is apparent that the present definitions of "smectic" and "liquid crystal" and the system of nomenclature do not adequately describe this complex situation. Therefore, until these problems have been solved we have chosen to call the two phases—*hexatic B* and *crystal B* (deleting all reference to smectic or liquid crystal).

Conclusions

The hexatic B and crystal B phases are thermodynamically distinct modifications and belong to separate miscibility classes. Until the general classification scheme is reviewed it is suggested that the two phases be *distinguished* by the terms *crystal B* and *hexatic B.*

Conventional methods of phase identification involving microscopic investigation of miscibility diagrams of state cannot be used to distinguish between the two B phases. Therefore, one must resort to X-ray diffraction techniques in order to give an absolute classification of the phase type under examination. Nevertheless, detailed studies of the subtle features of the microscopic textures of the B phase may be useful in the initial identification of the phase type.

EXPERIMENTAL

Preparation of materials

*Synthesis of 4-*n*-Pentyloxy-4′-bromobiphenyl* 4-Benzenesulphonyloxy-4′-bromobiphenyl (20 g, 0.05 mol) was dissolved in dioxan (24.0 ml). To this solution, a solution of sodium hydroxide (4.8 g, 0.12 mol) in distilled water (120 ml) was added. The mixture was then heated under reflux for 3 hrs.

After 3 hrs, 1-bromopentane (9 g, 0.06 mol) was added, and the mixture was heated under reflux for a further 2 hrs. The mixture was allowed to cool slowly before being poured into water (360 ml). The resulting precipitate was filtered off and crystallized from ethanol to give white plate-like crystals melting at 130–133°, lit., 132.5–133°.[15] The yield was 12 g 60%.

*Synthesis of 4-*n*-pentyloxy-4′-cyanobiphenyl* The thoroughly dry 4-*n*-pentyloxy-4′-bromobiphenyl (3.5 g, 0.011 mol) was dissolved in dry 1-methyl-2-pyrrolidinone (12 ml). To this stirred solution, cuprous cyanide (2 g, 0.22 mol) was carefully added, and the mixture was heated under reflux with vigorous stirring for 3 hrs. The mixture was cooled, and then poured into a solution of ferric chloride (4.4 g, 0.035 mol) in water (50 ml) and concentrated hydrochloric acid (1 ml). The resulting mixture was heated for 20 min. at 70° and then allowed to cool to room temperature. The mixture was then shaken with ether (2 × 200 ml); then the ethereal extract was washed with water (2 × 50 ml), and dried over anhydrous sodium sulphate. The ether solution was filtered to remove the desiccant and the ether removed by evaporation under reduced pressure. The residue was purified by column chromatography on silica-gel (60–200 mesh, 30 × 3 cm) using dichloromethane as eluant. The dichloromethane of the fractions containing the product was removed by evaporation under reduced pressure, and the residue was crystallized from light-petrol (bp 35–60°). The white crystalline product obtained had the following constants C—N, 48; N—I, 65°, lit.,[15] values C—N, 48°; N—I, 67.5°. The yield was 2 g, 48%.

*Synthesis of 4′-*n*-pentyloxybiphenyl-4-carboxylic acid* Potassium hydroxide (15 g, 0.27 mol) was dissolved in a mixture of water (10 ml) and methanol (40 ml). This solution was added to a solution of 4-*n*-pentyloxy-4′-cyanobiphenyl (4.3 g, 0.016 mol) in methanol (50 ml). The mixture was then heated under reflux until no more ammonia was evolved (usually 5 days). The reaction mixture was then poured into water and just acidified with concentrated hydrochloric acid. The mixture was stirred for a further 2 hr., and the solid collected by filtration. The resulting acid was crystallized from ethanol. The white crystalline product had the following constants C—Sc, 215°; Sc—N, 217°; N—I, 260°; lit., values,[16] C—Sc, 227.5°; Sc—N, 229.5°; N—I, 275°. The yield was 3.5 g, 76%.

*Synthesis of *n*-hexyl 4′-*n*-pentyloxybiphenyl-4-carboxylate (65OBC)* To 4′-*n*-pentyloxybiphenyl-4-carboxylic acid (1 g, 0.0035 mol) 1-hexanol (0.4 g, 0.004 mol) in toluene (50 ml), and concentrated sulphuric acid (0.05 ml) were added. The mixture was heated under reflux for 10 hr, and then allowed to cool. The solvent was removed by evaporation under reduced pressure and the residue was purified by column chromatography on silica-gel (60–200 mesh, 30 × 3 cm) using dichloromethane as eluant. The solvent of the combined fractions was removed by evaporation under reduced pressure and the residue was crystallized from *n*-hexane. The white, powdery solid was found to have the following constants C—S_B, 66°; S_B—S_A, 67°; S_A—I, 85°; S_B—S_E, 60°. The yield was 0.6 g, 46%.

Physical Measurements

Determination of transition temperatures of pure materials and binary mixtures was made using a Zeiss Universal polarizing microscope in conjunction with a Mettler FP52 hot-stage and control unit.

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