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TILTED SMECTIC B PHASE OR SMECTIC H PHASE? (*)

J. W. GOODBY and G. W. GRAY

Department of Chemistry, University of Hull, Hull, HU6 7RX, England

Résumé. — Dans les dernières années, une controverse a surgi à propos des phases smectiques B normales et des phases smectiques B inclinées ; celles-ci ont été déclarées miscibles, alors que les phases analogues smectiques A et C ne le sont pas, et ceci a toujours été un problème pour l'identification des phases. Récemment, toutefois, nous avons montré que deux composés présentant séparément des phases smectiques B inclinées peuvent donner naissance à une phase smectique B normale dans un mélange contenant approximativement 50% de chaque composant. Nous avons alors étudié plusieurs mélanges binaires en faisant varier la composition d'une phase B à l'autre. Par exemple, dans le cas des mélanges de TBBA et du 4 carboxylate de n-hexyl 4'-n dodecyloxybiphenyl, deux composés présentant des phases smectiques B inclinées, nous avons trouvé que les mélanges contenant approximativement 50% de chaque corps, montrent une phase B normale qui se transforme en une phase B inclinée par refroidissement. Nous avons aussi étudié plusieurs mélanges binaires dans lesquels un composé possédait une phase B normale et l'autre une phase B inclinée. Ces études de miscibilité ont montré dans chaque cas qu'il existait un intervalle étroit de composition dans lequel les deux phases B n'étaient pas miscibles. Nous avons enfin synthétisé un corps pur qui présente un changement de phase B normale à une phase B inclinée. Ce type de changement de phase a aussi été observé par d'autres auteurs dans le cas de bases de Schiff telles que N-4-n heptyloxy-benzylidène-4-n-pentyl-aniline. Ainsi, nous sommes amenés à designer la phase B inclinée comme étant une phase smectique H.

Abstract. — In recent years, the controversial situation has arisen that orthogonal B and tilted B phases have been claimed to be miscible, while the analogous A and C phases are immiscible, and this has been a constant problem in phase assignment and identification. Recently, however, we have shown that two compounds that separately exhibit tilted B phases can show an orthogonal B phase in binary mixtures containing approximately 50% of each component. Further to this, we investigated the mode of the progression with changing composition from one B modification to the other in various binary mixtures. For example, in a miscibility study involving TBBA and n-hexyl 4'-n-dodecyloxy-biphenyl-4-carboxylate, both of which exhibit tilted B phases, we found that mixtures containing approximately 50% of each component exhibited an orthogonal B phase which then gave a transition to a tilted B phase on cooling. We also investigated various binary mixtures of which one component exhibited an orthogonal B phase and the other a tilted B phase. These miscibility studies invariably showed very small percentage composition ranges in which the two B phases appeared to be immiscible. Finally, we synthesised a pure ester that we believe exhibits an orthogonal B phase to a tilted B phase change. This type of phase change has also been observed by other workers in Schiff's bases such as N-4-n-heptyloxybenzylidene-4-n-pentylaniline. Thus, the evidence clearly directs us to reassign the tilted B phase as the smectic H phase.

1. Introduction. — The smectic C phase is assumed to be the tilted analogue of the smectic A phase, as both phases have unstructured layers. The two phases have, however, been quite clearly shown to be immiscible. With the B phase, a similar structural analogy arises, and it would appear that the tilted B phase (B(t)) is the tilted analogue of the orthogonal B phase (B(o)), as both have a hexagonally close packed distribution of molecules. However, the similarity would appear to end there, as it has been claimed by many workers that these two phases are miscible, unlike the A and C phases. By a few workers, notably de Vries the assignment of both phases to the B type on the basis of the miscibility evidence is not accepted, and these workers prefer the tilted B phase to be called the smectic H phase, thus making it distinct from the orthogonal B phase. The confusion over the phase assignment of these two phases has recently been clarified by de Jeu and de Poorter [2] and by Doucet and Lambert [3] who have shown from X-ray studies that certain Schiff's bases, first prepared by Smith and Gardlund [4], exhibit smectic B (B(t)) to smectic H (B(h)) transitions.

Thus, the detection of an orthogonal smectic B
to a tilted smectic B ($S_B$) phase transition in some materials is clear evidence that the two phases should not be miscible. However, there have been no factual reports that the two B phases have been shown to be immiscible in actual miscibility experiments.

In recent miscibility experiments [5] involving TBBA and various n-alkyl 4'-n-hexadecyloxybiphenyl-4-carboxylates we have found peculiar phase behaviour and sequences of phases for certain of the binary mixtures. In a study involving TBBA ($N$, $S_A$, $S_C$, $S_H$ ($S_{BC}$), $S_G$, and $S_V$ phases) and n-heptyl 4'-n-hexadecyloxybiphenyl-4-carboxylate ($S_A$ and $S_H$ ($S_{BC}$) phases), we found that the binary mixture containing 50% by weight of each component exhibited a $S_A$ to orthogonal B phase transition. Therefore, it would appear that certain binary mixtures of two smectic H ($S_{BC}$) materials can in fact exhibit orthogonal B phases.

This unusual behaviour led us to examine closely further binary systems involving smectic H materials.

The results of these conclusive studies are now presented.

2. Results and discussion. — This section is best treated in the four parts described below:

2.1 Binary mixtures that exhibit $S_B$ to $S_H$ phase changes. — As a result of the study [5] described previously, a miscibility study of n-hexyl 4'-n-dodecyloxybiphenyl-4-carboxylate with the standard material TBBA was carried out. The n-hexyl ester was known to exhibit a $S_A$ phase and was also suspected of exhibiting additional $S_C$ and $S_H$ phases. Evidence for these two phases was therefore sought by a co-miscibility experiment with TBBA, which exhibits well defined $S_C$ and $S_H$ phases. The miscibility diagram of state for binary mixtures of these two materials is shown in figure 1.

As in the preceding study, the binary mixture containing 50% by weight of each component exhibits an orthogonal B phase ($S_{BA}$ or $S_{B'}$) although both components exhibit only $S_H$ phases ($S_{BC}$ or $S_{B'}$). On cooling, this B phase then gives rise to a $S_H$ phase, thus confirming the existence of $S_B$ to $S_H$ transition.

It can be seen from the miscibility diagram of state that the $S_C$ phase is not continuous across the composition range, as required for the co-miscibility of the two $S_C$ phases to be proved. This is probably due to the fact that the $S_A$ to $S_C$ transition temperature line falls below the $S_A$ to $S_B$ transition line, and therefore an injection of orthogonal B properties occurs in this region. The orthogonal B phases then form tilted $S_B$ phases at lower temperatures, thus giving the impression that the n-hexyl ester may not have a $S_C$ phase. The n-hexyl ester was in fact shown to exhibit a smectic C phase by another miscibility study which is discussed in section 2.

Thus, the most striking feature of this miscibility diagram of state is that it shows the occurrence of a $S_B$ to $S_H$ transition, but if the two phases were truly miscible, this would not be possible. The standard material exhibits $N$, $S_A$, $S_C$, $S_H$, $S_G$, and $S_V$ phases, whilst the test ester was shown to exhibit $S_A$, $S_C$, and $S_H$ phases by other miscibility studies. In the mixtures of around 50% of each component, the orthogonal B phase underlies the $S_A$ phase, and the transition was clearly characterised by transition bars. On cooling this $S_B$ phase, a broken fan texture was then formed. Now this broken fan texture was not of the $S_G$ type and furthermore, the $S_G$ to $S_H$ transition temperature curve was shown to fall away sharply on moving away from pure TBBA. Thus, as an orthogonal B phase underlies the A phase in the 50% range of mixtures, the phase underlying the B phase cannot be $S_A$ or $S_C$, as both are of higher thermal stability than the B phase. The tilted phase is not a G phase, and therefore not a $S_P$ phase either. Moreover, it cannot be an E phase, as the texture exhibited is decidedly not of the E type (and the E phase is not exhibited by either component). Thus, by a process of elimination, the phase must be $H$ in type.

The microscopic evidence for the phase sequence of the 1:1 mixture of TBBA and n-hexyl 4'-n-dodecyloxybiphenyl-4-carboxylate is illustrated by Plates 1-4.

On cooling from the isotropic liquid, the mixture formed a smectic phase which exhibited both focal-
conic fan (Plate 1) and homeotropic textures; this phase separated from the isotropic liquid in the form of bâtonnets. Since the highest temperature smectic phase of both TBBA and the test ester is the $S_A$ phase, this phase must therefore be of the $S_A$ type. On cooling this phase, the backs of the clear fans in the focal-conic texture became crossed with a large number of arcs (Plate 2). The homeotropic areas, however, remained unchanged, and the arcs persisted only through a cooling range of $20^\circ$ C before disappearing. They are therefore transition bars. The resulting phase exhibited the clear fan and homeotropic textures. Thus, the characteristics of the phase transition and the resulting microscopic textures confirmed that the phase was of the orthogonal B type (Plate 3).

On further cooling of this phase, a transition to a tilted phase occurred. The fan texture of this phase was considerably broken, and the backs of the fans adopted a mottled pattern (Plate 4). Moreover, the homeotropic areas of the preceding phase gave rise to a faint mosaic texture, thus indicating that the phase was $S_H$ in type.

2.2 IMMISCIBILITY IN BINARY MIXTURES OF $S_H$ AND $S_B$ MATERIALS. — In the previous section, it was shown that a $S_B$ to $S_H$ transition can occur in binary mixtures, and this suggests that the two phases must be immiscible. Thus, it was important actually to show that the two phases were immiscible in a miscibility experiment. This was done in a miscibility study involving the 4-n-octyloxyphenyl ester of 4'-n-octyloxybiphenyl-4-carboxylic acid ($S_A$, $S_C$, and $S_B$ phases) and TBBA ($N$, $S_A$, $S_C$, $S_B$, $S_O$, and $S_V$ phases) (Fig. 2).

The mixture of 80 % by weight of TBBA and 20 % of the ester showed total phase immiscibility (not shown in figure 2) when observed microscopically. The two components of the mixture were heated together on a microscope slide until the isotropic liquid was formed; this was then well mixed before a coverslip was placed on top. When observed microscopically, the smectic C phase of the mixture appeared continuous throughout the preparation. However, on cooling, this phase gave a most peculiar transition to what can only be described as a mixture of two phases.

When the $S_C$ phase was in its schlieren texture, the resulting phase obtained on cooling was partially homeotropic and partially a mosaic (Plate 5). The
homeotropic areas were shown to have a uniaxial interference figure by conoscopic observation, and the edges of the mosaic texture were wispy and ill-defined.

If the S<sub>C</sub> phase was in the broken fan texture, then on cooling, the resulting phase showed areas of absolutely clear fans and areas of broken fans (Plate 6). The areas of broken fans and clear fans were not simply found in one particular region, but were uniformly distributed throughout the preparation. Moreover, there was not a sudden change from broken to clear fans, but a progression from one type to the other.

It was found that a similar situation occurred with all mixtures within ± 3 % of the original mixture composition. Thus, it would appear that the two phases are indeed immiscible, but that immiscibility occurs only over a narrow composition range of the binary mixtures. Therefore, it would be easy to miss this narrow region of immiscibility when actually performing miscibility experiments.

A number of other similar miscibility studies gave closely related results. It was found from most of the studies undertaken that the percentage composition ranges from which binary mixtures of S<sub>H</sub> and S<sub>B</sub> phases were immiscible were quite small, i.e., of the order of 4 to 8 %.

Two further examples of miscibility diagrams of state that show immiscible regions of the two phases are given in figure 3 and figure 4.

Figure 3 shows the miscibility diagram of state for mixtures of n-hexyl 4'-n-dodecyloxybiphenyl-4-carboxylate (S<sub>A</sub>, S<sub>C</sub>, and S<sub>H</sub> phases) and the 4-n-pentyloxyphenyl ester of 4'-n-octoxybiphenyl-4-carboxylic acid (N, S<sub>A</sub>, S<sub>C</sub>, and S<sub>H</sub> phases). This shows only a very small percentage composition range (~ 2 %) over which the phases were found to be immiscible.

Figure 4 shows the miscibility diagram of state for mixtures of TBBA (N, S<sub>A</sub>, S<sub>C</sub>, S<sub>H</sub>, S<sub>G</sub>, and S<sub>V</sub> phases) and the 4-n-octyloxyphenyl ester of 4'-n-octyloxybiphenyl-4-carboxylic acid. In this case, the region of immiscibility is much larger. On cooling the S<sub>C</sub> phase of a mixture of 60 % by weight of TBBA and 40 % by weight of the ester, it was found that the schlieren texture of the S<sub>C</sub> phase gave rise to the mosaic texture of the S<sub>H</sub> phase. On cooling a further 0.2 °C, the mosaic texture then gave rise to a mixture of two textures, namely the mosaic and homeotropic textures. Thus, the fact that the transition temperatures for each phase are slightly different in this mixture is further
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A. C8H17-OCO- COO- C8H17
B. C12H25-OCO-C8H17

1. Evidence of the immiscibility of the two phases. If the phases were truly miscible, only one precise transition would occur at a definite temperature.

2. A $S_B$ to $S_H$ transition exhibited by a pure compound. — During the study of the immiscibility of the B and H phases, as mentioned earlier, we prepared the 4-n-octyloxyphenyl ester of 4'-n-octyloxybiphenyl-4-carboxylic acid. This ester is thought to exhibit $S_A$, $S_B$, and $S_H$ phases, although this has not yet been conclusively proved. However, the transition temperatures for this ester can be listed as follows:

\[
\begin{align*}
&\text{n-C}_8\text{H}_{17} \quad \text{COO} \quad \text{COO} \quad \text{C}_8\text{H}_{17}
&\text{C} \quad \text{102°C} \quad \text{S}_A \quad \text{153°C} \\
&\text{I} \quad \text{153°C} \quad \text{(S}_A \quad \text{98°C} \quad \text{S}_B \quad \text{67°C} \quad \text{S}_H \quad \text{66°C} \quad \text{C}
\end{align*}
\]

( ) Monotropic transitions.

The final phase exhibited by the ester on cooling is extremely shortlived and appears to induce rapid recrystallisation. This makes the liquid crystalline behaviour of this material very hard to study, and differential thermal analysis using heating and cooling rates of 5 °C min. did not give enough resolution to separate the enthalpy peaks for the $S_b$ to $S_H$ phase transition and the crystallisation of the $S_B$ phase.

Miscibility studies involving this ester will always prove to be extremely difficult. With a standard $S_B$ material we will simply obtain a normal $S_B$-miscibility diagram: with a standard $S_H$ material (Fig. 4), if the region of immiscibility is not detected, the conclusion could be reached that the $S_B$ phase of the test ester is miscible with the $S_H$ phase of the standard material. However, even when the immiscible region is detected, the fall-off in the $S_B$ to $S_H$ transition line of the test ester, together with crystallisation of the mixtures, makes it impossible to prove that the two $S_H$ phases are continuously miscible. Even with a standard material that exhibits $S_B$ and $S_H$ phases, the miscibility study need not yield definitive evidence, as it has been shown that two $S_H$ phases can produce a $S_B$ phase in the region of the 50% mixture. This can result in a large depression of the $S_H$-$S_B$ transition line, making verification of a continuous $S_H$ region difficult, particularly if crystallisation tends to occur readily. However, we did attempt such a miscibility study using N-4-n-heptyloxybenzylidenecarboxylic acid (B).

Therefore, evidence for the ester exhibiting a $S_H$ phase comes totally from microscopy. On cooling the isotropic liquid, the ester gave a smectic phase which exhibited two types of texture, i.e., the clear fan texture (Plate 7) and the homeotropic texture. This phase
Percentage of compound B in a 100 mixture with compound A

FIG. 5. — Diagram of state for mixtures (wt. %) of N-4-n-heptyloxybenzylidene-4-n-pentylaniline (A) and the 4-n-octylphenyl ester of 4'-n-octylbiphenyl-4-carboxylic acid (B).

separated from the isotropic liquid in the form of bâtonnets.

On further cooling, there was a transition to a second smectic phase, and the transition was characterised by transition bars (Plate 8). The resulting phase again exhibited the clear fan texture (Plate 9), in which the backs of the fans appeared less lined than in the preceding texture. This phase also exhibited homeotropic areas which were shown to be uniaxial by conoscopic observation. Thus, this transition is typical of a $S_A$ to $S_B$ transition.

On further cooling, there was a transition to a second smectic phase, and the transition was characterised by transition bars (Plate 8). The resulting phase again exhibited the clear fan texture (Plate 9), in which the backs of the fans appeared less lined than in the preceding texture. This phase also exhibited homeotropic areas which were shown to be uniaxial by conoscopic observation. Thus, this transition is typical of a $S_A$ to $S_B$ transition.

On further cooling of this $S_B$ phase, just before recrystallisation occurred (and also very distinct from it), the clear fans began to break and give the appearance of the mottled fans of a $S_C$ phase. However, a $S_C$ phase cannot underlie a $S_B$ phase, and this phase must be either a $S_H$ or $S_G$ phase. The phase exhibited...
mainly the broken fan texture (Plate 10) and the homeotropic areas from the preceding phase became faintly birefringent (mosaic). Thus, the phase was found to have the textures usually attributed to the S_H phase.

If this final phase is S_H in type, this ester provides a further example of a S_B/S_H material and confirms that the S_B to S_H transitions observed previously in binary mixtures do exist.

2.4 Confirmation of S_B to S_H Transitions in Other Materials. Recently [2, 3], it has been shown that certain Schiff's bases exhibit S_B to S_H transitions. For example

\[ n\text{-C}_7\text{H}_{15}\text{O} \underset{\text{C}_2\text{H}_5}{\text{CH}}=\underset{\text{C}_3\text{H}_{11}}{\text{N}} \text{(70.5)} \]

\[ n\text{-C}_2\text{H}_{11}\text{O} \underset{\text{C}_7\text{H}_{15}}{\text{CH}}=\underset{\text{C}_3\text{H}_{11}}{\text{N}} \text{(50.7)} \]

\[ n\text{-C}_7\text{H}_{15}\text{O} \underset{\text{C}_2\text{H}_5}{\text{CH}}=\underset{\text{C}_7\text{H}_{15}}{\text{N}} \text{(70.7)} \]

all exhibit N, S_A, S_C, S_B, and S_H phases. There was at one time considerable confusion in literature reports of the microscopic textures and phase sequences of these materials, and the existence of the S_B to S_H transition was only recently proven by X-ray techniques [2, 3]. However, our examination of these three materials has shown that the S_H phases formed from the S_B phases have typical microscopic textures, namely the broken-fan and mosaic textures. These are shown together in Plate 11. The mosaic platelets are extremely small, giving the impression of a speckled texture.

![Plate 11](image)

**Plate 11.** The broken fan and mosaic textures of the S_H phase of N-4-n-heptyloxybenzylidene-4-n-pentylaniline (70.5) (x 200).

3. Conclusions. — 1) The main conclusion is that the two B phases are immiscible, and that the S_Bc phase should be separately designated as the S_H phase.

2) The region of immiscibility in the diagram of state is exceptionally small in binary mixtures and can easily be missed experimentally. As shown by figure 2, where we have not indicated the immiscible region, it is obvious that if only transition temperatures are measured, and the region of immiscibility is missed, the conclusion will be reached that S_B and S_H phases are of the same type. The immiscibility does not therefore affect the general outcome from a miscibility study if we are simply concerned to prove that an unknown phase is S_B or S_H.

There can be problems in identifying the smectic phases if a new material exhibits both B and H phases.

3) It is clear that two S_H phases can give rise to a S_B phase in mixtures over certain composition ranges, and, as for pure materials that exhibit both B and H phases, the B phase is always the more thermally stable of the two. This places the thermal stability of the H phase below that of the B phase, in accordance with the order for the analogous unstructured S_C and S_A phases.

4. Materials. — The preparation and purity of the materials used in this study have been described elsewhere [5], with the exception of the 4-n-octylphenyl ester of 4'-n-octylbiphenyl-4-carboxylic acid. This ester was made by a standard procedure and purified by column chromatography (silica gel), using a 1:1 mixture of chloroform and light petroleum (b.p. 40-60°) as eluant. The structure of the product (single spot by t.l.c.) was checked by mass spectrometry and infra-red spectroscopy.

5. Physical Measurements. — Observations of microscopic textures and measurements of transition temperatures for both the pure esters and their mixtures were carried out using a Nikon polarising microscope in conjunction with a Mettler FP52 heating stage and control unit.

*Note added in proof.* — It should be emphasised that there is no disagreement between the results given in this paper and those reported by H Sackmann in his paper on The Stand of the System of Smectic Liquid Crystals by Miscibility Measurements which also appears in these proceedings. Both investigations show that the tilted, hexagonally ordered smectic phase which succeeds the S_C phase of TBBA on cooling is immiscible with orthogonal, hexagonally ordered smectic phases, i.e., with the S_B phase. In both pieces of work, this tilted, hexagonally ordered phase of TBBA has been shown by miscibility methods to be of the same type as the phase which succeeds the S_F phase of the pyrimidine on cooling. The apparent differences are entirely ones of nomenclature.

In this paper, we call the tilted, hexagonally ordered phases of TBBA and the pyrimidine S_BH, whereas Sackmann calls them S_G. Consequently, a reversed nomenclature has arisen for the next smectic phase which succeeds the tilted, hexagonally ordered smectic
phase of TBBA on cooling. We call this \( S_G \), whereas Sackmann calls it \( S_H \).

In summary, our nomenclature gives the following phase sequences:

TBBA: \( I, N, S_A, S_C, S_{11}, S_{22}, S_{33} \)

Pyrimidine: \( I, S_A, S_C, S_F, S_H \)

Sackmann’s nomenclature gives:

TBBA: \( I, N, S_A, S_C, S_G, S_H \)

Pyrimidine: \( I, S_A, S_C, S_F, S_G \)

There is however no disagreement concerning the natures of these phases for which we have simply used different code letters.

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