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Liquid Crystalline Compounds Exhibiting Two Smectic B Modifications

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Four liquid crystalline compounds, i.e., three terephthal-bis-4-*n*-alkylanilines (TBAA; alkyl = pentyl, hexyl, and heptyl) and *N*-(4-*n*-heptyloxybenzylidene)-4-*n*-hexylaniline (HBHA) were synthesized and the phase transitions were studied by means of optical microscope, differential scanning calorimeter and miscibility relationships. It is indicated that all the compounds exhibit a smectic B–smectic B phase transition of which the transition heat is very small. Furthermore, a brief description is given of a smectic phase of TBAA which occurs only monotropically.

INTRODUCTION

Sackmann and Demus have indicated on the basis of miscibility relations, microscopic textures and X-ray diffraction patterns that smectic phases can be further subdivided into at least seven modifications which are denoted by the letter *A* through *G*.[1] De Vries has studied in detail smectic liquid crystals by means of X-ray diffraction and suggested in addition to seven smectic modifications the presence of another smectic phase (H) having a three dimensional order.[2,3] However, Sackmann *et al.* do not classify smectic H as a separate phase, but regard it as a variety of smectic B on the basis of miscibility. According to their classification, there are two subgroups of smectic B: one with molecules normal and the other with molecules tilted to the layer.[1,4] Furthermore, de Vries has recently suggested the classification that the smectic B can be divided into three subgroups, B_1, B_2, and B_3.[5] In order to shed light on the difference between the subgroups of the smectic B, it is of much interest to determine if there is a compound which exhibits two or three smectic B modifications. In this report we wish to suggest that the smectic B–B phase transition can indeed exist in some liquid crystals.

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EXPERIMENTAL

Smectogenic liquid crystal compounds used in this study are as follows: terephthal-bis-4-*n*-pentylaniline (TBAA(5)), terephthal-bis-4-*n*-hexylaniline (TBAA(6)), terephthal-bis-4-*n*-heptylaniline (TBAA(7)), and *N*-(4-*n*-heptyloxybenzylidene)-4-*n*-hexylaniline (HBHA). All the compounds were synthesized in our laboratory from appropriate aldehyde and 4-*n*-alkylaniline by refluxing in ethanol solution, and recrystallized twice from ethanol and benzene.[6,7] They were thoroughly dried under vacuum in order to remove the solvent and moisture.

Transition heat was determined by differential scanning calorimetry (DSC). A Rigaku differential scanning calorimeter used in this study was calibrated in terms of temperature and energy by use of potassium nitrate, indium, benzoic acid, and tin. All samples were contained in closed aluminum sample pans. Each sample was heated and cooled several times at 5°C/min under a flow of nitrogen gas to prevent decomposition of the sample.

The liquid crystal textures were observed with an ordinary polarizing microscope. The samples were placed between carefully cleaned glass slides as thin as possible since the liquid crystal texture is quite dependent on the thickness of samples and the cleanness of substrates.[1,8]

RESULTS AND DISCUSSION

Figure 1 illustrates the DSC thermograms of TBAA(5). It should be noted that a monotropic phase transition occurs at about 61°C and that the enthalpy change at the phase transition temperatures of 140 and 179°C is very small, as shown in Table I. The phase transition temperatures expected from the change of the texture are in good accord with those obtained by DSC thermograms. The phase transitions of TBAA(5) obtained by both the DSC studies and the texture changes are as follows:

$$\begin{tikzcd}
\mathrm{K} \arrow[r, "68^\circ\mathrm{C}"] & \mathrm{S(IV)} \arrow[r, leftrightarrow, "140^\circ\mathrm{C}"] \arrow[d, leftrightarrow, "61^\circ\mathrm{C}"] & \mathrm{S(III)} \arrow[r, leftrightarrow, "149^\circ\mathrm{C}"] & \mathrm{S(II)} \arrow[r, leftrightarrow, "179^\circ\mathrm{C}"] & \mathrm{S(I)} \arrow[d, leftrightarrow, "212^\circ\mathrm{C}"] & \\
 & \mathrm{S(V)} \arrow[ul] & & & \mathrm{N} \arrow[r, leftrightarrow, "233^\circ\mathrm{C}"] & \mathrm{I}
\end{tikzcd}$$

Smectic I phase exhibits easily a homeotropic alignment by a cover slip displacement. On cooling from the smectic I with the homeotropic texture smectic II phase gives a schlieren texture characteristic of smectic C phase, as shown in Figure 2(a). For the purpose of classifing a smectic phase into one of

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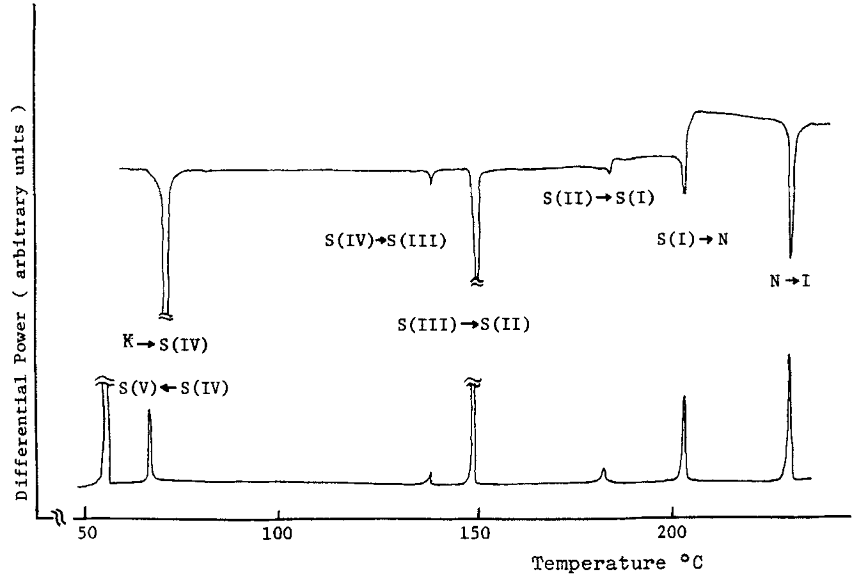

FIGURE 1 DSC thermogram for TBAA(5) on heating at 5°C/min (upper curve) and on cooling (lower curve).

TABLE I

Transition temperatures and transition heats (cal/mole) of compounds studied. The phase S(V) occurs only on cooling.

K	S(V)	S(IV)	S(III)	S(II)	S(I)	N	I
TBAA(5)	(61°C) (220)	68°C 3500	140°C 15	149°C 860	179°C 10	212°C 180	233°C 260
TBAA(6)	(60°C) (100)	66°C 3800	143°C 5	153°C 1000	187°C 10	208°C 340	215°C 380
TBAA(7)		57°C 3700	144°C 5	157°C 1100	192°C 25	209°C 400	212°C 430
HBHA		40°C 9400	58°C 50	66°C 700	70°C 60		80°C 1200

$$\begin{tikzcd}
\text{TBBA} & K \arrow[r, "113^\circ\text{C}"] & S(B) \arrow[r, leftrightarrow, "144^\circ\text{C}"] \arrow[d, leftrightarrow, "87^\circ\text{C}"] & S(C) \arrow[r, leftrightarrow, "172^\circ\text{C}"] & S(A) \arrow[r, leftrightarrow, "200^\circ\text{C}"] & N \arrow[r, leftrightarrow, "236^\circ\text{C}"] & I \\
& S(V) \arrow[u, "63^\circ\text{C}"] \arrow[r, "74^\circ\text{C}"'] & S(IV)
\end{tikzcd}$$

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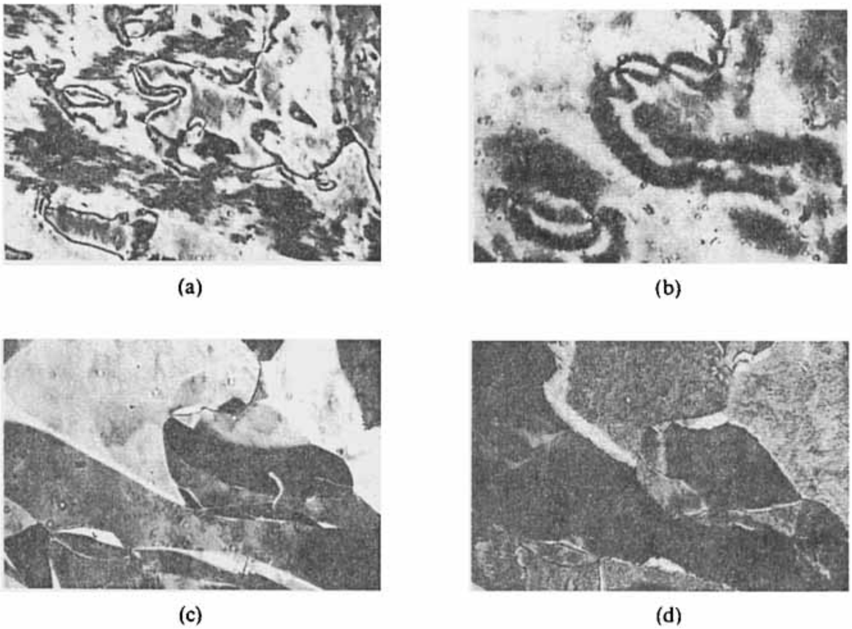

FIGURE 2 Photomicrographs of TBAA(5) between crossed polarizers, magnification ca. 120X: (a) smectic C, (b) smectic III, (c) smectic IV, (d) smectic V.

the smectic modifications, it is necessary to study the miscibility relations in a binary system. Liquid crystalline properties of terephthal-bis-4-*n*-butylaniline (TBBA), a homologue of TBAA, have been extensively investigated by different experimental methods,[6,9–13] and the phase transitions are well established as shown in Table I. Especially, the smectic B phase of TBBA has been studied by several authors, and it has been accepted that in the smectic B state the molecules are tilted with respect to the layer and form a local three-dimensional hexagonal structure which extends over several smectic layers.[11]

Figure 3(A) indicates the relations of the miscibility between TBBA and TBAA(5) measured by us. From this diagram it is concluded that the smectic I and II should be identified as the smectic A and C, respectively. It is well-known that the transition energy associated with the smectic A–C phase transition is quite small.[9,14,15] A very weak peak at 179°C in the DSC thermogram shown in Figure 1 and the appearance of the smectic textures previously metioned are consistent with the above conclusion.

At the phase transition of the smectic II (smectic C) to smectic III the microscopic texture changes clearly and abruptly as shown in Figure 2. The smectic III phase exhibits a characteristic schlieren texture which can be

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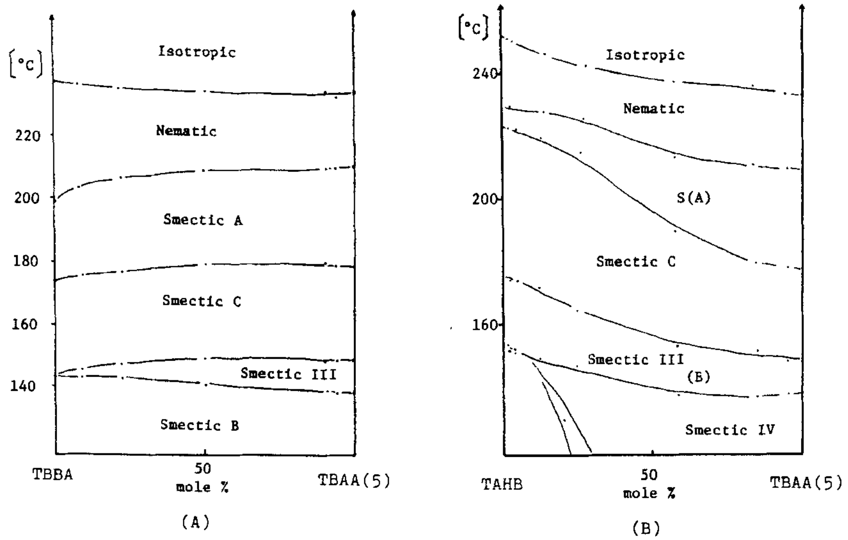

FIGURE 3 Phase diagrams, (A): for TBBA and TBAA(5), (B): for TAHB and TBAA(5).

easily distinguished from that observed in the smectic C state.[1,16] Saupe and Nehring[17,18] have indicated from theoretical considerations that the occurrence of schlieren texture can be expected in thin plane layers of tilted smectic liquid crystals, if the layers are parallel to the substrates. In practice, Demus *et al.*[16,19] have observed in the smectic B phase of octadecyloxyazoxybenzene the smectic schlieren texture which is quite similar to that observed in the smectic III phase of TBAA(5). The fact that the smectic III of TBAA(5), as mentioned above, exhibits the smectic schlieren texture and does not give homeotropic alignment at all, suggests that in this smectic phase the molecules are quite likely to have a tilted layer structure and optically biaxial properties.[16–19]

It is known that there are at least three other smectic phases i.e., smectic B, F and G which occur at a lower temperature than the smectic C state.[1,20] Recently, Billard has reported that *N*-(4-*n*-heptyloxybenzylidene)-4-*n*-heptylaniline (HOHA) and *N*-(4-*n*-heptyloxybenzylidene)-4-*n*-pentylaniline (HOPA) exhibit both the smectic F and G besides the smectic C and A.[21] The smectic III phase of TBAA(5) is not miscible with any smectic phase of HOHA, as illustrated in Figure 4. This shows that the smectic III phase can not be classified as smectic F or G. Furthermore, as is apparent in Figure 3(A), it should be noted that the smectic III phase of TBAA(5) exhibiting the schlieren texture forms a series of an uninterrupted mixed liquid crystal in a binary system of TBAA(5) and TBBA. This fact suggests that the smectic III

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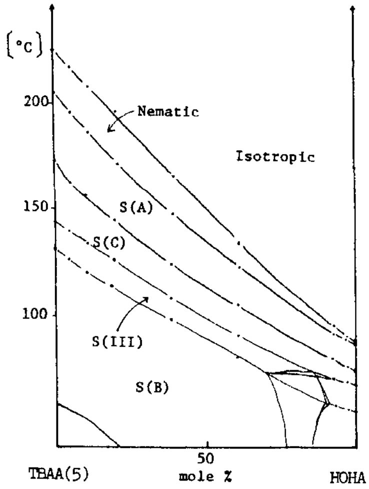

FIGURE 4 Phase diagram for TBAA(5) and HOHA.

phase is closely related to the smectic B. Terephthal-bis-4-amino-*n*-hexyloxybenzene (TAHB) has been reported to exhibit the smectic B state besides the smectic C and A.[22,23] Figure 3(B) indicates the miscibility relations between TAHB and TBAA(5). It is evident from Figure 3(B) that the smectic III phase of TBAA(5) is miscible with the smectic B of TAHB. Therefore, the smectic III phase should be identified as one of the smectic B modifications (hereafter this smectic B is referred to as B_S). In addition, it should be stressed that the phase transition heat between the smectic II (smectic C) and III (smectic B_S) of TBAA(5) is quite large compared with other mesomorphic transitions, as is apparent in Table I. This is without difficulty understood by taking account of the difference of a molecular packing in layers between the smectic C and smectic B. It is well recognized in the smectic B state that there is high degree of order in the layer and that the molecules adopt a hexagonal arrangement in the layer. On the other hand, the molecules in the smectic C state are disordered within the layer but tilted. Such a striking difference of molecular packing between the smectic B and C is expected to accompany a large enthalpy change at the phase transition. The large transition energy stated above is consistent with other measurements for smectic C–B phase transition.[9,24]

On cooling from the smectic III (smectic B_S) to smectic IV the schlieren texture of the smectic B_S distinctly changes to a mosaic texture, as shown in Figure 2(c). As demonstrated in Figure 3(A), the smectic IV phase of TBAA(5) is shown to be identical with the smectic B phase of TBBA from miscibility criterion (referred to as B_M). Therefore, it follows that in the case of TBAA(5)

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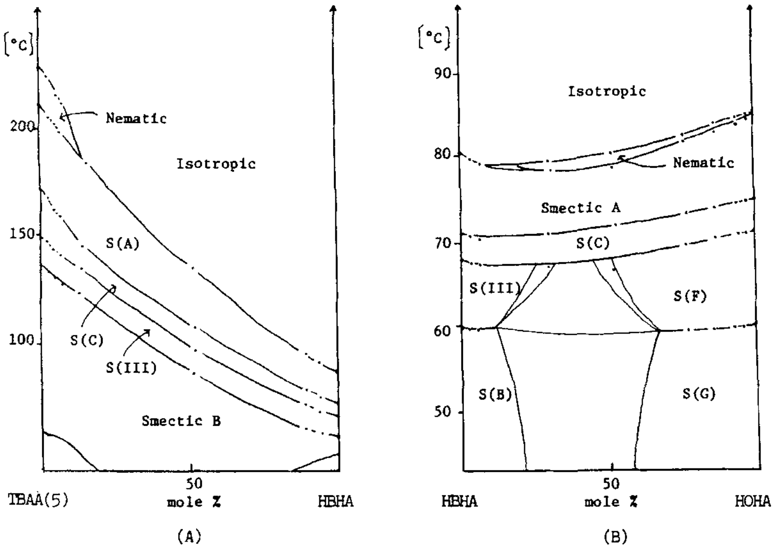

FIGURE 5 Phase diagrams, (A): for TBAA(5) and HBHA, (B): for HBHA and HOHA.

both the smectic III and IV phases should be classified as the smectic B. However, it seems that the smectic B_S phase has no identical layer structure with the smectic B_M, because the small but definite enthalpy change, as described previously, exists at the phase transition between the smectic III(B_S) and smectic IV(B_M).

TBAA(6) shows identical liquid crystal transitions with TBAA(5), apart from the temperature of phase transition, as shown in Table 1. TBAA(7) gives also similar mesomorphic transitions to TBAA(5) except that a monotropically occurring smectic V phase is not observed for TBAA(7). In addition, HBHA gives quite similar smectic textures and phase transitions to TBAA(5) although HBHA exhibits no nematic state. Figure 5(B) indicates that both the smectic III and IV of HBHA are not miscible with smectic phases of HOHA. In addition, from the miscibility relation between TBAA(5) and HBHA shown in Figure 5(A), it follows that HBHA exhibits four smectic phases, i.e., smectic A, C, B_S, and B_M.†

It should be borne in mind that the transition heat at the smectic B_S–B_M transition is very small in all the compounds studied, as shown in Table I. Such a small transition heat between smectic phases has been so far measured only for C–A transition. This small enthalpy change suggests that the smectic

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† Smith and Gardlund (Ref. 15) have reported that HBHA exhibits only three smectic phases. They did not observe the smectic phase transition corresponding to the smectic B_S–B_M transition because of a very small transition energy.

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B_S–B_M transition is of a weak first order. Furthermore, it is reasonably inferred that there is no essential difference between the smectic B_S and B_M in the molecular arrangement within the smectic layer. A possible explanation of the difference between the smectic B_S and B_M may lie in the extent over which a regular hexagonal array of molecules is preserved in the smectic B state. However, other studies, e.g., X-ray diffraction would be necessary to determine the exact layer structure of the smectic B_S and B_M.

TBAA(5) and TBAA(6) exhibit a monotropic smectic V phase whose texture is characterized by cracks occurring within the mosaic domains, as shown in Figure 2(d). This texture is similar to that of smectic IV phase of TBBA. Doucet et al. have recently suggested from their X-ray diffraction study that the smectic IV phase of TBBA is a smectic E_C phase with molecules tilted to the smectic layer.[25] However, the optical textures of the smectic V of TBAA(5) as well as the smectic IV of TBBA are considerably different from those observed for the smectic E_C of *n*-alkyl-4-*p*-phenylbenzylideneaminocinnamates which have been studied by Gray and Harrison.[26] On the other hand, Richter and Demus have indicated that the smectic IV of TBBA is a smectic G.[27] Therefore, the exact nature of this smectic phase lying at lower temperature than the smectic B_M still remains ambiguous.

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