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THE PREVIOUSLY UNCLASSIFIED SMECTIC PHASES OF  
BIS-(4'-n-HEPTYLOXYBENZYLIDENE)-1,4-PHENYLENEDIAMINE  
(HEPTOBDP)

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**Abstract:** Re-examination of the bis-(4'-n-alkoxy-benzylidene)-1,4-phenylenediamines, particularly the heptyloxy homologue, by optical microscopy and differential scanning calorimetry has confirmed the existence of two hitherto unclassified smectic phases, which are now assigned the code letters J and K (S<sub>J</sub> and S<sub>K</sub>).

**Introduction:** Early in 1978, we re-examined some members of the well known<sup>1,2,3</sup> homologous series of bis-(4'-n-alkoxy-benzylidene)-1,4-phenylenediamines to ascertain the extent and nature of the smectic polymorphic behaviour of the system. Our attention was concentrated on the heptyloxy homologue, and it was quickly evident that at least one hitherto unclassified smectic phase existed. The work at the University of Hull involved optical microscopy, but in September 1978 we interested Professor EM Barrall II, of the IBM Corporation at San Jose, in these compounds, and he carried out DSC studies on the heptyloxy compound. These confirmed the existence of the new smectic phase (S<sub>J</sub>) which we had observed, but revealed the presence (on cooling cycles) of a second new smectic phase (S<sub>K</sub>). This second new phase was then confirmed by optical microscopy for both heating and cooling cycles.

We decided not to publish our observations until structural studies had been carried out on the new phases,

although we were aware from conversations which we had with W Spratte and GM Schneider at the Seventh International Liquid Crystal Conference at Bordeaux that they were examining the effects of pressure on the liquid crystal properties of these materials. Although the structural studies being carried out by Professor Leadbetter's group at Exeter University are still incomplete, the very recent publication by Spratte and Schneider<sup>4</sup> of their results now makes it desirable that we record the observations we have made and the conclusions we have reached so far.

*Results and Discussion:* We have recently resynthesised and characterised a number of bis-(4'-n-alkoxybenzylidene)-1,4-phenylenediamines. Arora *et al.*<sup>2</sup> had earlier shown that a number of these materials are pentapolyomorphic with regard to their smectic properties, but they did not give any definite characterisation of the phases in their publication. With the aid of optical microscopy and detailed differential scanning calorimetry, we have now shown that bis-(4'-n-heptyloxybenzylidene)-1,4-phenylenediamine is hexapolyomorphic with regard to its smectic properties, and therefore we will confine this preliminary report of our results to this material.

Our initial studies by optical microscopy confirmed the five smectic phases detected by Arora *et al.*<sup>2</sup> At a later date, however, the presence of a sixth phase was indicated by DSC and confirmed by optical microscopy. The phase sequence for the heptyloxy compound can therefore be written\* as:



Solid  $\xrightarrow{127} S_6 \xrightarrow{130} S_5 \xrightarrow{146} S_4 \xrightarrow{154} S_3 \xrightarrow{157} S_2 \xrightarrow{164} S_1 \xrightarrow{197} N \xrightarrow{241} I$

where  $S_1 = S_C$ ,  $S_2 = S_F$ ,  $S_3 = \text{unknown}$ ,  $S_4 = S_H$ ,  $S_5 = S_G$ ,  
 $S_6 = \text{unknown}$

The above transition temperatures were obtained by optical microscopy using a Mettler FP52 hotstage and control unit; all transitions, except that from  $S_6$  to the solid, were reversible within narrow temperature limits on cooling.

\* Spratte and Schneider<sup>4</sup> adopt the nomenclature system of the Halle group and use  $S_G$  for the phase which we denote<sup>5</sup> as  $S_H$ .

Optical microscopy has shown clearly that  $S_A$ ,  $S_B$ ,  $S_D$ , and  $S_E$  phases are not exhibited by this material and therefore, as it is hexapolyomorphic, then at least two of the smectic phases must be *new*.

*Optical Studies:* Our initial investigations had shown that on cooling the nematic phase of the heptyloxy compound, it gave a smectic C phase characterised by its schlieren and broken fan textures. On further cooling of this phase, a transition to a smectic F phase was detected; the smectic F phase exhibited typical schlieren and broken fan textures. Spratte and Schneider<sup>4</sup> have in fact designated this phase as smectic B, but, our observations definitely show that the molecular orientation in the layers of this phase is tilted and not orthogonal.

On cooling the smectic F phase, a smectic phase ( $S_3$ ) exhibiting either a broken fan or a mosaic texture was formed. On further cooling, this phase underwent a transition to another smectic phase ( $S_4$ ) exhibiting almost identical textures. The transition was characterised by faint zig-zag lines crossing the mosaic areas; these lines occurred only at the point of transition and existed over a  $0.1$  to  $0.3^\circ$  temperature range. We have never before observed this particular phenomenon with any of the known smectic phases, and therefore we believe that this characterises a new type of transition.

Further cooling of this phase gave a transition to a smectic G phase. The transition was characterised by the appearance of a cross-hatching of the mosaic areas. On cooling over a further  $3-4^\circ$ , these cross-hatched areas healed to give a mosaic texture in which the individual mosaic areas had smaller dimensions than those in the previous phase. The cross-hatching and the breaking up of the mosaic texture characterise the occurrence of the smectic G phase. Still further cooling produced the second new transition. The mosaic areas became slightly fluid at the point of transition, and the lines of discontinuity at their borders became rounded and lost their angular appearance. On further slight cooling, the mosaic patches set in a slightly more broken fashion than in the preceeding smectic G phase.

Miscibility studies with terephthalylidene-bis-4-n-pentylaniline (TBPA) ( $N$ ,  $S_A$ ,  $S_C$ ,  $S_F$ ,  $S_H$ , and  $S_G$  phases) confirmed that the  $S_1$  phase was  $S_C$  in type, the  $S_2$  phase was

$S_F$ , the  $S_4$  phase was  $S_H$ , and the  $S_5$  phase was  $S_G$ , because of their separate co-miscibility with the appropriate phases of the standard TBPA. These studies also showed that an  $S_A$  phase was not exhibited by the heptyloxy compound, and that the  $S_3$  and  $S_6$  phases were not miscible with any of the known phases of TBPA.

Conoscopic observations showed that all of the phases exhibited by the heptyloxy material were in fact *biaxial*, confirming that it does not exhibit either a smectic A or a smectic B phase.

*Differential Scanning Calorimetry:* On first heating, this material shows eight endothermal transitions (Figure 1, peaks 2-9) beginning with a crystalline solid-solid transition ( $C_2$ - $C_3$ ) at  $116.3^\circ$  and concluding with a nematic to isotropic liquid transition at  $234.9^\circ$ . The transition temperatures and the enthalpy values for the transitions are shown in Table 1.

On second and subsequent heatings, the solid phase is found to consist of a new form which constitutes the majority of the sample and gives a solid-solid transition at  $115.1^\circ$ . Thus on *first* heating, solid  $C_2$  gives solid  $C_3$  which melts (Figure 1, peak 3) via the  $S_6$  phase to give the  $S_G$  phase. The enthalpy peak for the change of the solid  $C_3$  to smectic 6, on heating, is incorporated in the large melting peak (Figure 1, peak 3) and is therefore not observed. However, on cooling, the transition of the  $S_G$  to the  $S_6$  phase is observed (Figure 1, peak 4') due to the supercooling preceding formation of the solid  $C_3$  from  $S_6$ . Solid  $C_3$  then forms a mixture of  $C_2$  and mainly the new solid -  $C_1$  (Figure 1, peaks 1 and 2, cooling). Reheating gives resolved peaks for the mixed  $C_1$ - $C_3$  and  $C_2$ - $C_3$  transitions.

Very detailed examinations, involving greatly amplified time base DSC scans, were made of the smectic-smectic transitions, but the results of these investigations are too complex and lengthy to discuss here. We have, however, chosen to include the enthalpy data (Table 1) in this short communication and these will be discussed in further detail in a subsequent publication.

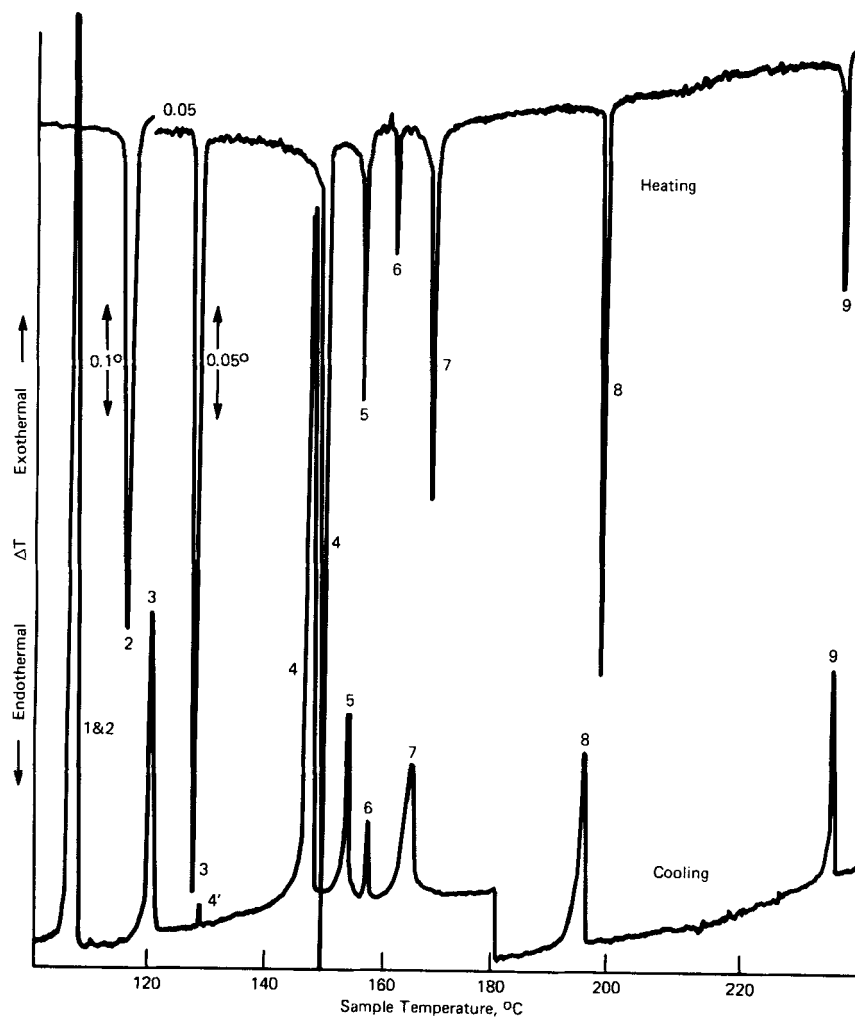


FIGURE 1  
DSC scans (heating and cooling) for HEPTOBPD

TABLE 1

Peak number*	Transition temperature (°C)		Transition	Transition heat Cal/g
	T <sub>b</sub>	T <sub>m</sub> T <sub>e</sub>		
†	111.2	115.1 116.0	C <sub>1</sub> -C <sub>3</sub>	6.68
2	116.0	116.3 117.5	C <sub>2</sub> -C <sub>3</sub>	
3	126.3	127.2 129.7	C <sub>3</sub> -SK-SG	2.78
4 <sup>†</sup>	129	130 131	SK-SG	~0.12 <sup>††</sup>
4	143.0	147.3 150.1	SG-SH	5.22
5	151.3	153.7 156.8	SH-SJ	0.993
6	160.2	160.7 162.0	SJ-SF	0.234
7	163.7	167.4 170.7	SF-SC	1.50
8	187.8	192.1 193.8	SC-N	1.68
9	228.9	234.9 236.4	N-I	1.00

\*  
†  
††

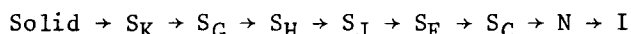
With reference to Figure 1  
Not shown in Figure 1, heating cycle  
Observed only on cooling cycles  
(see Figure 1)

T<sub>b</sub> = temperature at the beginning of the peak  
T<sub>m</sub> = temperature at the peak maximum  
T<sub>e</sub> = temperature at the end of the peak

*Note: The transition temperature, obtained by DSC agree very closely with those obtained by optical microscopy up to about 150°. Thereafter the DSC temperatures lie progressively higher, the difference being about 6° for the N-I change*

*Conclusions:* By the process of elimination of certain phase types ( $S_A$ ,  $S_B$ ,  $S_D$ ,  $S_E$ ) and the positive results of our investigations, it would appear that  $S_3$  and  $S_6$  are new smectic phases. As  $S_3$  was observed first we will give it the code letter J ( $S_J$ ), and consequently  $S_6$  should have the letter K ( $S_K$ ). We have purposely avoided the use of the code letter I, as the common use of this letter to denote 'isotropic' could cause confusion.

Using these new code letters, the full phase sequence for bis-(4'-n-heptyloxybenzylidene)-1,4-phenylenediamine is:



When we compare the present results with those obtained by Spratte and Schneider<sup>4</sup> for this compound, remembering that they use the Halle nomenclature and denote  $S_H$  as  $S_G$ , four main points emerge: (a) their  $S_B$  phase is our  $S_F$  phase, (b) their sm 3 is our  $S_J$  phase, (c) their sm 1 is our  $S_G$  phase, (d) they did not detect our  $S_K$  phase. The transition temperatures obtained by Spratte and Schneider by DTA are very close to the values we obtained by optical microscopy in the case of the lower and the two highest temperature transitions. The biggest differences occur for the intermediate  $S_F$ - $S_C$  and  $S_J$ - $S_F$  transitions in the region 157-164°C; their temperatures are higher by some 4-5°C.

Before we can be absolutely certain of the assignment of the particular phases specified to the  $S_J$  and  $S_K$  categories, a wider range of carefully selected miscibility experiments must be of course be carried out. A description of the results we obtain and a full characterisation of the new phases will be published in due course.

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#### References:

- <sup>1</sup> GW Gray, JB Hartley, A Ibbotson, and B Jones, *J Chem Soc*, 4359 (1955).
- <sup>2</sup> SL Arora, TR Taylor, JL Fergason, and A Saupe, *J Amer Chem Soc*, 91, 5382 (1969).



326 E. M. BARRALL II, J. W. GOODBY and G. W. GRAY

- <sup>3</sup> D Demus and R Rurainski, *Mol Cryst Liq Cryst*, 16, 171 (1972).
- <sup>4</sup> W Spratte and GM Schneider, *Mol Cryst Liq Cryst*, 51, 101 (1979).
- <sup>5</sup> JW Goodby and GW Gray, *J Physique*, in press.