



## Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

### The Phase Behavior of bis-(4'-n-Heptyloxybenzylidene)-1,4-Phenylenediamine (HEPTOBPD), Crystal J and K Phases

P.A.C. Gane<sup>a</sup>, A. J. Leadbetter<sup>a</sup>, P. G. Wrighton<sup>a</sup>, J. W. Goodby<sup>b</sup>, G. W. Gray<sup>c</sup> & A. R. Tajbakhsh<sup>c</sup>

<sup>a</sup> Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD, England

<sup>b</sup> Department of Chemical Physics, Bell Telephone Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey, 07974, USA

<sup>c</sup> Department of Chemistry, University of Hull, Hull, HU6 7RX, England

Version of record first published: 20 Apr 2011.

To cite this article: P.A.C. Gane, A. J. Leadbetter, P. G. Wrighton, J. W. Goodby, G. W. Gray & A. R. Tajbakhsh (1983): The Phase Behavior of bis-(4'-n-Heptyloxybenzylidene)-1,4-Phenylenediamine (HEPTOBPD), Crystal J and K Phases, *Molecular Crystals and Liquid Crystals*, 100:1-2, 67-74

To link to this article: <http://dx.doi.org/10.1080/00268948308073720>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Mol. Cryst. Liq. Cryst.*, 1983, Vol. 100, pp. 67-74  
0026-8941/83/1002-0067/\$18.50/0  
© 1983 Gordon and Breach, Science Publishers, Inc.  
Printed in the United States of America

# The Phase Behavior of bis-(4'-*n*-Heptyloxybenzylidene)-1,4- Phenylenediamine (HEPTOBPD), Crystal J and K Phases

P. A. C. GANE, A. J. LEADBETTER,<sup>†</sup> P. G. WRIGHTON,

*Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD,  
England*

J. W. GOODBY

*Department of Chemical Physics, Bell Telephone Laboratories, 600 Mountain  
Avenue, Murray Hill, New Jersey 07974, USA*

and

G. W. GRAY\* and A. R. TAJBAKSHI

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

*(Received January 19, 1983)*

Detailed X-ray diffraction studies of bis-(4'-*n*-heptyloxybenzylidene)-1,4-phenylenediamine (HEPTOBPD) have led to a positive phase identification, subsequently given confirmation by texture and miscibility studies. No new smectic liquid crystal phases, but two disordered crystal phases (J and K) are found which are analogous to G and H phases except for the direction of tilt.

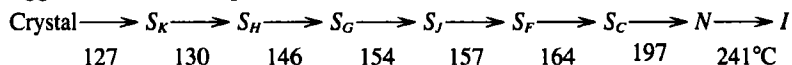
## INTRODUCTION

An examination of the richly polymorphic system HEPTOBPD by optical microscopy and differential scanning calorimetry<sup>1</sup> led to the following

---

<sup>†</sup>Now at: Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, England.

suggestion about the phase behavior:



where the nomenclature for smectic  $G$  ( $S_G$ ) and smectic  $H$  ( $S_H$ ) is that now generally accepted;<sup>2</sup>  $S_K$  and  $S_I$  were thought to be new smectic phases. It was emphasized that these were preliminary conclusions and that confirmation must await detailed structural and miscibility work. This has now been completed and in the meantime the identity of  $S_I$  as a stacked hexatic phase, and its relation to the similar  $S_F$  phase has been established,<sup>3,4</sup> plus the recognition that certain phases hitherto classified as smectics are in fact crystalline in the sense that the molecular positions exhibit long range 3-dimensional order.<sup>4,5,6</sup> At the same time, the molecules show dynamic rotational disorder<sup>7,8</sup> among a set of configurations consistent with the (average) crystal symmetry, so that the phases in question are in fact orientationally disordered crystals rather than smectics. However, the phases have simple characteristic layer structures, they do have considerable disorder and those of similar type are often totally miscible, so that the miscibility criterion properly applied remains a useful means of phase identification: it is therefore useful to keep the identification letter and refer to crystal  $B$ ,  $G$  and  $H$  phases.

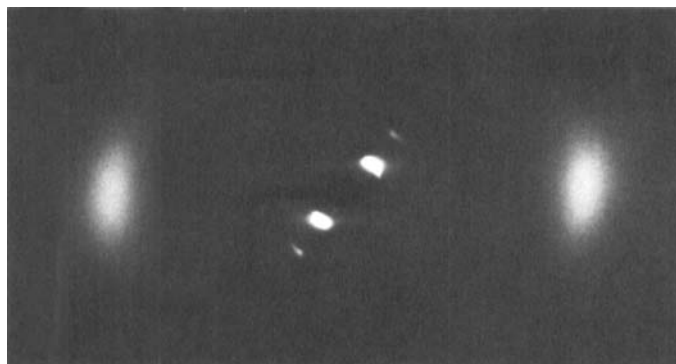
## RESULTS AND DISCUSSION

X-ray diffraction photographs have been taken on both powder and magnetically aligned samples of HEPTOBPD through the whole range from crystal to isotropic liquid ( $<120^\circ\text{C}$  to  $>200^\circ\text{C}$ ). Examples of the results are shown in Figure 1. Figure 1a shows a very good example of an aligned  $S_C$  diffraction pattern and Figure 1b shows the pattern of the phase below the  $S_C$ . This may now immediately be identified

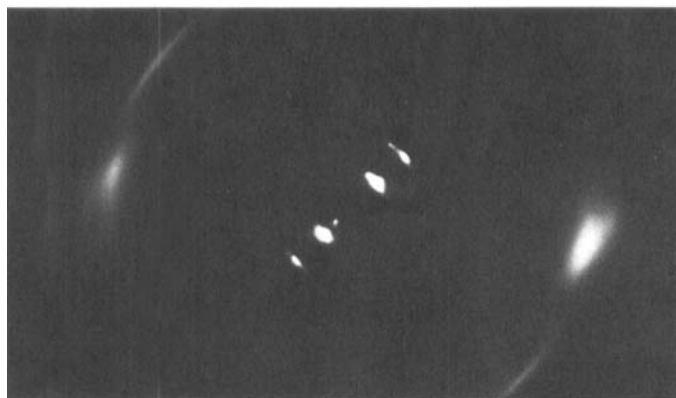
(i) as a stacked hexatic phase, because of the relatively sharp bars of scattering centred at (110), (020), etc., and extending approximately  $\pm c^*$  along the  $c^*$  direction, and

(ii) as a  $S_I$  phase, because of the geometry of the local unit cell, as readily deduced from the diffraction pattern which is that of a fibre-aligned specimen with a few major domains.

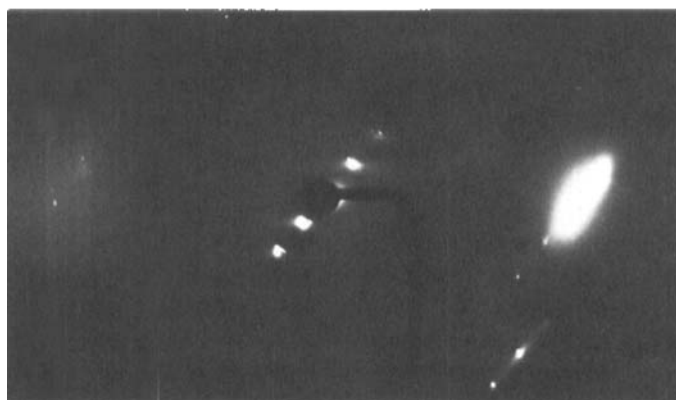
The cell is  $C$ -centred monoclinic with  $b$  (unique axis)  $> a$  [Table I(a)]. With decreasing temperature, the bars of scattering centred at the (110) etc., reciprocal lattice points condense from  $T \approx 157^\circ\text{C}$  to become sharp Bragg reflections (Figure 1c), and at the next transition ( $T \approx 154^\circ\text{C}$ ) additional diffraction spots appear at higher angles, in particular  $121$  and  $1\bar{2}1$ , showing the disappearance of the  $C$ -centring. These extra reflections were most



(a)



(b)



(c)

FIGURE 1 X-ray diffraction photographs from aligned samples of HEPTOBPD: (a)  $S_C$  phase, (b)  $S_I$  phase, (c)  $G'$  ( $= J$ ) [and  $H'$  ( $= K$ )] phase (see text).

TABLE I

(a) HEPTOBPD: Cell Parameters					
Phase	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$\beta/^\circ$	$\cos^{-1}(d/l)/^\circ$
C			36.4	133.0	44
I	6.8	8.6	35.8	132.5	44
G' (=J)	7.0	8.4	37.0	134.0	45
H' (=K)	6.9	8.4	37.0	133.5	45
(Estimated error $\pm$ )	0.1	0.1	0.5	0.5	2
(b) HEPTOBPD: Observed and Calculated Spacings for G' (=J) and H' (=K) Phases					
Phase	$d_{\text{OBS}}/\text{\AA}$	Reflection	$d_{\text{CALC}}/\text{\AA}$		
G' (=J)	26.80	001	26.62		
	13.30	002	13.31		
	5.10	$11\bar{2}$	5.10		
	4.71	$11\bar{1}$	4.74		
	4.30	110	4.32		
	3.94	111	3.91		
	4.12	$02\bar{1}$	4.16		
	4.26	020	4.21		
	4.16	021	4.16		
H' (=K)	26.85	001	26.84		
	13.41	002	13.42		
	5.09	$11\bar{2}$	5.08		
	4.72	$11\bar{1}$	4.72		
	4.30	110	4.32		
	3.93	111	3.92		
	4.22	020	4.21		
	4.15	021	4.15		
	3.39	$12\bar{1}$	3.38		
	3.18	120	3.23		
	3.08	121	3.05		
All the $d_{\text{CALC}}$ values are well within experimental error. The error for $d_{\text{OBS}}$ is 2%					

easily found on long exposure powder photographs because the major domain in the aligned specimens did not have suitable orientation. Except for the absence of the 120, 121 and  $12\bar{1}$  spots in the more ordered phase, therefore the aligned diffraction photograph, Figure 1c, is characteristic of both phases. These results were confirmed by long exposure powder diffraction photographs which confirmed the absence of reflections with  $h + k = 2n + 1$  for  $T \geq 154^\circ\text{C}$  and their presence below this temperature.

The observed reflections are given in Table Ib, together with values calculated from the lattice parameters given in Table Ia. These, together with the symmetry of the patterns from aligned specimens, confirm that both phases have monoclinic symmetry with  $b > a$  and a pseudo-hexagonal packing of the molecules which are tilted towards the apex of the hexagon

as in  $S_I$ , rather than the edge as in  $S_F$ , crystal  $G$  and crystal  $H$  phases; the distortion from hexagonal packing is greater in the lower temperature phase. These phases are thus identical to those observed in 80SI<sup>4,9</sup> and were temporarily labelled  $G'$  and  $H'$ . However, in view of the nomenclature of  $S_F$  and  $S_I$  and of the  $G$  and  $H$  phases now widely accepted, it seems logical to propose that the phases with alternative tilt direction ( $b > a$ ) analogous to the crystal  $G$  and  $H$  phases (with  $a > b$ ) should be called crystal  $J$  and  $K$ .

With further decrease of temperature, three further phases were observed in agreement with previous work and the diffraction data are given in Table II. There is in fact at least one further crystal phase for  $T < 117^\circ\text{C}$ . The diffraction patterns for these crystal phases have not been uniquely indexed, but they are clearly different from each other and from the  $H'$  ( $= K$ ) and  $G'$  ( $= J$ ) phases.

Following the X-ray results, a re-examination of texture in the polarizing microscope was made and miscibility studies with TBBA and 80SI completed. These completely confirm the existence of the  $S_I$  phase (Figures 2a and b). As shown in Figure 2a, evidence for the immiscibility of the  $G$  phase of TBBA and the  $G'$  ( $= J$ ) phase of HEPTOBPD was obtained. On

TABLE II

HEPTOBPD: Spacings <sup>†</sup> (Å) for Crystal Modifications <sup>‡</sup>		
$C_I$	$C_{II}$	$C_{III}$
27.28 S	31.84 S	23.02 M
17.17 W	15.71 S	13.30 M
13.55 S	6.35 M	11.38 M
6.39 W	4.70 W	6.50 VW
5.10 W	4.57 W	5.72 VW
4.72 W	4.35 S	4.95 W
4.30 S	4.23 S	4.66 W
3.93 S	3.95 M	4.30 S
3.28 M	3.72 S	3.98 S
3.14 M	3.63 VW	3.80 W
2.97 M	3.38 W	3.54 VW
	3.08 M	
	2.99 M	
	2.90 M	
	2.70 W	

<sup>†</sup>Measured at the temperatures:  $131^\circ\text{C}$  ( $C_I$ ),  $128^\circ\text{C}$  ( $C_{II}$ ), and  $118^\circ\text{C}$  ( $C_{III}$ ).

<sup>‡</sup>Strengths of reflections are indicated as S = strong, M = medium, W = weak, VW = very weak.

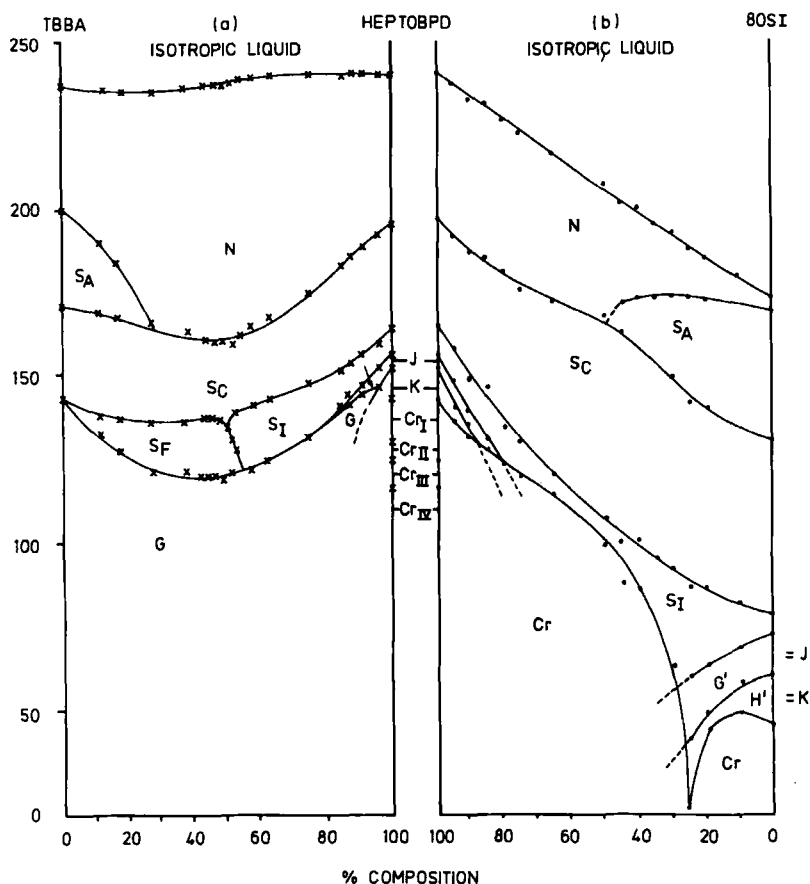
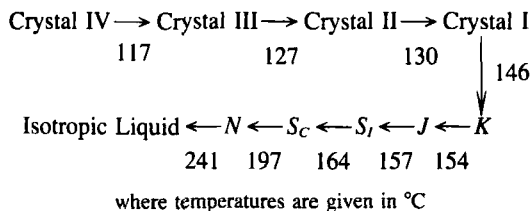


FIGURE 2 Miscibility diagrams of state for HEPTOBPD with (a) TBBA, and (b) 80SI.

the right of Figure 2a, around 80% of HEPTOBPD, two of the experimental points are consistent with  $G$  to  $J$  ( $= G'$ ) transitions. Rapid crystallization (not shown in Figure 2a) of the samples with higher HEPTOBPD concentrations made observations more difficult. However, a cooling cycle on one sample in the narrow concentration region marked with an arrow appeared to give the sequence of transitions  $S_I-G' (= J)-G-H'$  ( $= K$ )-Cr. Rather rapid cooling had to be used, and the experimental points (regarded as rather inaccurate) are not included in the figure. If this interpretation is correct, the  $J-K$  transition curve falls, as shown by that part drawn in full line, but the dashed portion of the curve ( $G-K$  transitions) is hypothetical.

As seen in Figure 2b, the fall in the  $S_I$ - $G'$  ( $S_I$ - $J$ ) and  $G'$ - $H'$  ( $J$ - $K$ ) transition lines on moving away from either side of the phase diagram, coupled with the rapid crystallization of the  $S_I$  phases of the intermediate mixtures, prevented our obtaining evidence for the separate miscibility of either (i) the  $G'$  ( $= J$ ) phases, or (ii) the  $H'$  ( $= K$ ) phases of the two compounds.

The phase behavior of HEPTOBPD is therefore now established as the following:



It is worth commenting finally on the criteria which have been previously used for phase identification especially between crystal and liquid crystal; these are:

- (i) reversibility of transition temperatures on heating and cooling as a test of whether the transition is crystal—liquid crystal or smectic—smectic etc. and which is related mainly to the magnitude of  $\Delta H$ ;
- (ii) miscibility, which can of course only be used as a positive confirmation of phase;
- (iii) texture, which even with great experience may sometimes be misleading;
- (iv) softness, which is both subjective and arbitrary.

It is thus essential for positive phase identification that direct structural investigations be carried out, although preferably as part of a study using all the above techniques.

With regard to the magnitude of  $\Delta H$ , re-examination of the DSC data of Ref. 1 shows the transition at  $\sim 146^\circ\text{C}$  has a very large  $\Delta H$  and must be a strong order-disorder type of change. This is consistent with the change found for crystal-liquid crystal (or crystal-orientationally disordered crystal) found in very many systems, but is certainly too large for a smectic-smectic change as suggested earlier.<sup>1</sup> Its reversibility on heating and cooling is, however, very unusual.

In conclusion, it should be noted that recent results on particular compounds showing crystal  $B^{10}$  and  $G^{11}$  phases have shown that there may be more than one type of structure, distinguished by different interlayer stacking and also perhaps by subtle changes of intralayer packing. The identifying letters suggested here, namely  $B$ ,  $E$ ,  $G$ ,  $H$ ,  $J$  and  $K$  should therefore be regarded as denoting only phase types and indicating merely the exis-

tence of a clear layer structure, orientational disorder and the gross features of the molecular packing and layer symmetry.

### References

1. E. M. Barrall II, J. W. Goodby and G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 319 (1979).
2. D. Demus, J. W. Goodby, G. W. Gray and H. Sackmann, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 311 (1980).
3. S. Diele, D. Demus and H. Sackmann, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 217 (1980).