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## Liquid Crystals

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## Calorimetric study of the incommensurate smectic-A phase in DB<sub>7</sub>OCN + 8OCB

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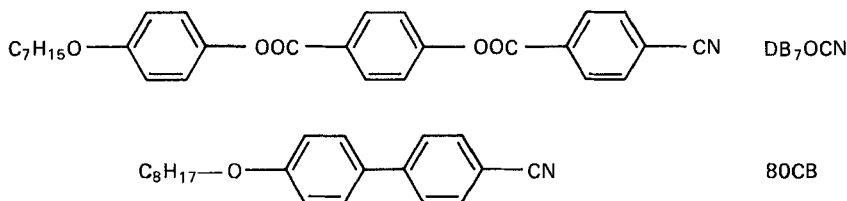
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Mixtures of heptyloxyphenylcyanobenzoyloxybenzoate (DB<sub>7</sub>OCN) and octyloxycyanobiphenyl (8OCB) exhibit partial bilayer smectic-A ( $S_{A_d}$ ) and bilayer smectic-A ( $S_{A_2}$ ) phases when the mole fraction of 8OCB is less than 0.24. For mixtures containing larger amounts of 8OCB, an incommensurate smectic-A ( $S_{A_{ic}}$ ) phase is observed between  $S_{A_d}$  and  $S_{A_2}$ . The heat capacity variation  $C_p(T)$ , determined with an ac calorimetric technique, is qualitatively different for samples going directly from  $S_{A_d}$  to  $S_{A_2}$  and those exhibiting the  $S_{A_d}$ - $S_{A_{ic}}$ - $S_{A_2}$  sequence. The direct  $S_{A_d}$ - $S_{A_2}$  results indicate a continuous supercritical evolution of the  $S_{A_2}$  phase. The results in the  $S_{A_{ic}}$  range support the presence of a new phase, as indicated by X-ray studies, rather than a broad region of coexisting bulk  $S_{A_d}$  and  $S_{A_2}$  phases.

### 1. Introduction

Liquid crystal molecules with long (three-ring) aromatic cores and strongly polar end groups exhibit a rich variety of polymorphic smectic-A phases [1]. The simplest examples are smectic-A<sub>1</sub> ( $S_{A_1}$ ) with  $d = L$ , smectic-A<sub>d</sub> ( $S_{A_d}$ ) with  $d = L'$  where  $L < L' < 2L$ , and smectic-A<sub>2</sub> ( $S_{A_2}$ ) with  $d = 2L$ , where  $d$  is the layer spacing and  $L$  is the effective molecular length. The phenomenological theory of frustrated smectics developed by Prost allows also for the possibility of incommensurate phases with two collinear incommensurate mass density modulations [2-3]. The first experimental observation of an incommensurate smectic-A ( $S_{A_{ic}}$ ) phase was in mixtures of heptyloxyphenylcyanobenzoyloxybenzoate, DB<sub>7</sub>OCN, and octyloxycyanobiphenyl, 8OCB [4]:



In this case, the  $S_{A_{ic}}$  phase occurs between partial bilayer  $S_{A_d}$  and bilayer  $S_{A_2}$  phases. X-ray data show the simultaneous presence of quasi-Bragg peaks at  $q_0 = 2\pi/2L$  and

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$q'_0 = 2\pi/L' \simeq 2\pi/1.7L$  as well as the harmonic at  $2q_0$ . A detailed analysis of the temperature dependence of  $q_0$  and  $q'_0$  shows that  $S_{A_{ic}}$  is a distinct phase and not merely a range of two-phase coexistence [4, 5].

Other systems exhibiting  $S_{A_{ic}}$  phases have recently been reported [6], but the  $DB_7OCN + 8OCB$  mixture is the one that is best characterized at this time. The phase diagram has been determined over the entire composition range from  $X = 0$  to 100, where  $X$  is the mole percent 8OCB in the mixture [7]. Microscopic examination of optical textures, static dielectric measurements on aligned samples, and differential scanning calorimetry (D.S.C.) runs have been carried out in addition to the detailed X-ray measurements [4, 5]. These techniques have been applied to the investigation of the direct  $S_{A_d} \rightarrow S_{A_2}$  transformation, which occurs for  $X \leq 24$ , and the  $S_{A_d} \rightarrow S_{A_{ic}} \rightarrow S_{A_2}$  sequence that is observed for  $X > 24$ .

The D.S.C. measurements on  $DB_7OCN + 8OCB$  showed a very rapid decrease in signal strength (apparent integrated enthalpy) as the 8OCB concentration increased [5]. A large and sharp  $S_{A_d} \rightarrow S_{A_2}$  D.S.C. peak was seen in pure  $DB_7OCN$ , whereas the D.S.C. peak for  $X = 20$  was very indistinct even at a slow (for D.S.C.) scan rate of  $-0.5$  K/min. No D.S.C. peaks were observable in the  $S_{A_d} \rightarrow S_{A_{ic}} \rightarrow S_{A_2}$  region for samples with  $X = 31$  and  $X = 35.2$ . The present calorimetric study, utilizing an ac calorimetric technique, was undertaken to provide a better characterization of the thermal behaviour associated with the  $S_{A_{ic}}$  phase. The ac technique allows slow scan rates and provides high sensitivity and high resolution.

## 2. Experimental results

The significant part of the  $DB_7OCN + 8OCB$  phase diagram is shown in figure 1. AC calorimetric measurements were carried out on pure  $DB_7OCN$  and on eight binary mixtures with  $X \leq 37$ , where  $X$  is the mole percent 8OCB. The compositions, melting points, and liquid-crystal transition temperatures inferred from the heat capacity data are listed in the table for all the investigated samples. As indicated in figure 1, there is good agreement between the transition temperatures determined calorimetrically and those determined microscopically. It should be noted that much of the  $S_{A_{ic}}$  range shown in figure 1 is metastable with respect to the crystalline ( $K$ ) phase. For  $X = 37$ , the crystal melts into the  $S_{A_d}$  phase; for  $X = 28.5$ , the crystal melts into the  $S_{A_{ic}}$  phase; and for  $X = 27.0$ , the crystal melts into the  $S_{A_2}$  phase just below the  $S_{A_2} \rightarrow S_{A_{ic}}$  transition temperature.

Transition temperatures (K) and integrated enthalpy  $\delta H$  ( $J g^{-1}$ ) for  $DB_7OCN + 8OCB$  mixtures;  $X$  represents the mole per cent of 8OCB.

| $X$  | Melting point | $T_{A_d A_2}$ | $T_{A_d A_{ic}}$ | $T_{A_{ic} A_2}$ | $\delta H$ |
|------|---------------|---------------|------------------|------------------|------------|
| 0    | 408           | 446.5         |                  |                  | 5.45       |
| 2.3  | 405           | 444.7         |                  |                  | 5.40       |
| 12.5 | 401.7         | 429.3         |                  |                  | 4.98       |
| 16.5 | 400.2         | 422.7         |                  |                  | 4.88       |
| 17.3 | 400           | 421.4         |                  |                  | 4.78       |
| 24.2 | 397.6         | 407.1         |                  |                  | 4.56       |
| 27.0 | 396.8         |               | 403.6            | 397.5            | 4.36       |
| 28.5 | 396.7         |               | 400.5            | ~ 394            | ~ 3.8      |
| 37   | 395           |               | 388              | —                | —          |

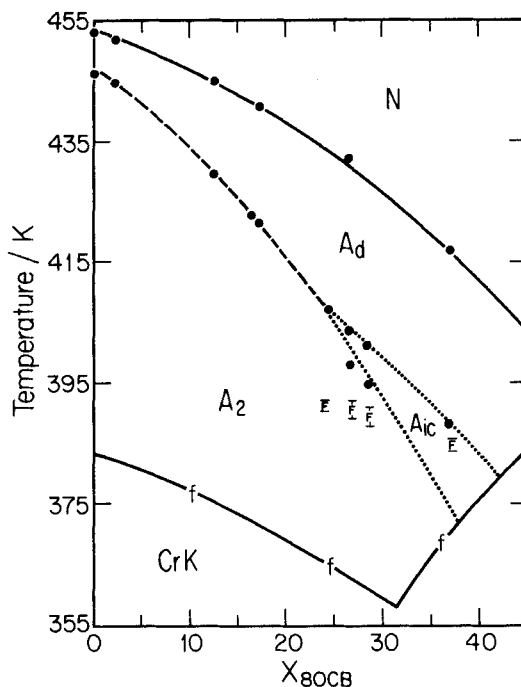


Figure 1. Partial phase diagram for DB<sub>7</sub>OCN + 8OCB binary mixtures with  $X$  denoting the mole per cent of 8OCB. The lines represent microscopic observations reported in [4]. The filled circles indicate transition features determined calorimetrically. The solid N- $S_{A_d}$  line is a second-order transition line. The dashed  $S_{A_d}$ - $S_{A_2}$  line represents the locus of finite maxima in  $C_p$  and the thermal expansion when a direct supercritical transformation from  $S_{A_d}$  to  $S_{A_2}$  occurs. The dotted lines represent  $S_{A_d}$ - $S_{A_{ic}}$  and  $S_{A_{ic}}$ - $S_{A_2}$  transitions of unusual character. The lines labelled  $f$  are the locus of freezing points observed in [4]; the error bars labelled  $F$  indicate where freezing occurred in the present experiments.

Pure 8OCB was obtained commercially from the British Drug House. Samples of DB<sub>7</sub>OCN were obtained from two sources—the Raman Research Institute and AT&T Bell Laboratories. Both samples were purified by high-pressure liquid chromatography and extensive recrystallization prior to preparation of the mixtures.

A detailed description of our ac calorimetric technique has been given previously [8]. It should be noted here that  $\sim 60$  mg of each liquid-crystal mixture was sealed in a small silver cell to prevent contact between the sample and air or water vapour. Even with sealed cells, care must be taken to minimize the effects of thermal decomposition. The temperature was never raised as high as  $T_{N_{A_d}}$  until all measurements in the smectic phases were complete. This is important since the rate of decomposition is more rapid at high temperatures and much more rapid in the nematic phase. The principal evidence of decomposition is a slow decrease in the transition temperatures on repeated scans. In the best cases ( $X = 12.5, 16.5, 24.2, 27.0$ ), the smectic-smectic transition temperatures drifted down at a rate of  $0.1\text{--}1.5$  mK h<sup>-1</sup>. In the worst cases, this drift rate was in the range  $15\text{--}30$  mK h<sup>-1</sup>. The heat capacity data presented here were obtained on the first cooling run (scan rate  $\sim 0.5$  K h<sup>-1</sup>). The results were confirmed by a subsequent heating (and often a second cooling run), which gave the same heat capacity variations except that the peaks were shifted slightly to lower temperatures.

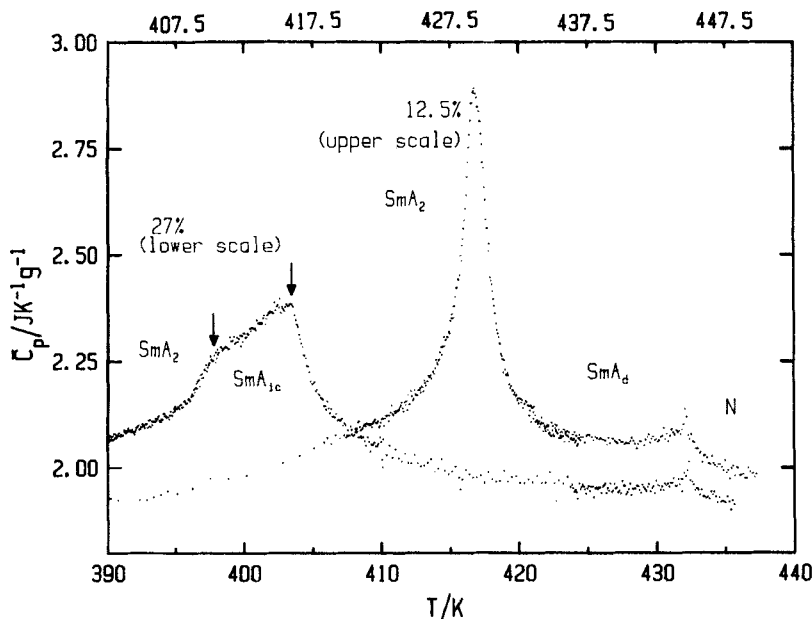


Figure 2. Variation of the specific heat capacity for two DB<sub>7</sub>OCN + 8OCB mixtures—one containing 12.5 mole per cent 8OCB and one containing 27 mole per cent 8OCB. The arrows indicate the choices of  $T_{A_d A_{1c}}$  and  $T_{A_{1c} A_2}$  for the sample with  $X = 12.5$ .

The specific heat capacity  $\bar{C}_p$  was obtained from

$$\bar{C}_p = [C_p(\text{obs}) - C_p(\text{empty})]/m, \quad (1)$$

where  $C_p(\text{obs})$  is the observed heat capacity of the filled sample cell containing  $m$  grams of liquid crystal mixture and  $C_p(\text{empty})$  is the heat capacity of the empty cell. The  $\bar{C}_p(T)$  variation for pure DB<sub>7</sub>OCN has been reported previously [9], and a detailed description of DB<sub>7</sub>OCN will not be repeated here. An overview of the  $\bar{C}_p$  variation for two DB<sub>7</sub>OCB + 8OCB mixtures is shown in figure 2. The  $X = 12.5$  sample is typical of a mixture which undergoes a direct transformation from  $S_{A_d}$  to  $S_{A_2}$ , while the  $X = 27.0$  sample exhibits an appreciable  $S_{A_{1c}}$  range. In addition to the large smectic-smectic peaks, small  $\bar{C}_p(N A_d)$  peaks are also shown in figure 2. The  $N-S_{A_d}$  transition was also studied in pure DB<sub>7</sub>OCN [9] and mixtures with  $X = 2.3$ , 17.3, and 37. These samples all exhibited  $\bar{C}_p(N A_d)$  peaks (not shown) that are identical in size and shape to those shown in figure 2.

Although the  $S_{A_d}-S_{A_{1c}}-S_{A_2}$   $\bar{C}_p$  peak for the  $X = 27.0$  sample looks truncated in a manner that might suggest a wide coexistence range for a strongly first-order transition, our data do not support this interpretation. In all well-established cases of two-phase coexistence in liquid crystals (such as  $N-I$ ,  $CrB-S_A$ , or first-order  $N-S_A$ ), the phase shift  $\phi$  for the oscillating  $T_{ac}(\omega)$  signal relative to the heat input signal shows a characteristic large and abrupt change when the system enters a two-phase coexistence region [10]. Indeed, large  $\phi$  changes were observed in the present samples when the crystal  $K$  phase melted. However, no anomalous  $\phi$  behavior was observed in the  $S_{A_{1c}}$  region for this 27.0 per cent sample (or for the 28.5 and 37 per cent samples). Furthermore, the  $\bar{C}_p$  peak was reproducible on warming and cooling runs, and the  $\bar{C}_p$  values definitely correspond to the static specific heat in the  $S_{A_{1c}}$  phase. The latter

point has been confirmed by  $C_p$  measurements at 401 K for several frequencies in the range  $0.5\omega_0$  to  $2\omega_0$ , where  $\omega_0 = 0.196$  is the standard operating frequency [8, 11]. Finally, there can be no significant latent heat effects in the  $S_{A_{ic}}$  phase since no D.S.C. peak is observed on going through this phase [5].

A comparison of the  $C_p$  peaks associated with  $S_{A_d}-S_{A_2}$  or  $S_{A_d}-S_{A_{ic}}-S_{A_2}$  transitions is given in figures 3 and 4. In both cases, the temperature scale shown is that appropriate for the  $X = 12.5$  sample and the temperature scales for other samples have been shifted (see figure legends). The excess specific heat  $\Delta\bar{C}_p$  is  $\bar{C}_p - \bar{C}_p$  (background), where  $\bar{C}_p$  (background) is taken to be a constant over the 30 K interval

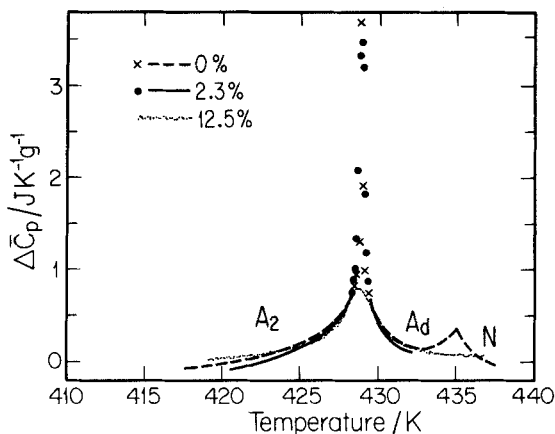


Figure 3. Superposition of  $\Delta\bar{C}_p$  peaks associated with the  $S_{A_d}-S_{A_2}$  transformation in DB<sub>7</sub>OCN + 80CB mixtures containing small amounts of 8OCB. The temperature scale shown is that for the 12.5 mole per cent 8OCB sample. The temperature scales of the pure DB<sub>7</sub>OCN and the mixture with 2.3 mole per cent 8OCB have been shifted down by 17.2 K and 15.4 K, respectively.

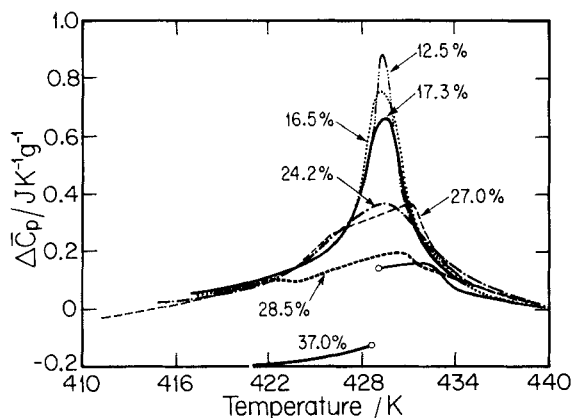


Figure 4. Superposition of  $\Delta\bar{C}_p$  peaks associated with smectic-A polymorphism. The temperature scale shown is that for the 12.5 mole per cent 8OCB sample. Note that the  $\Delta\bar{C}_p$  curve for the 12.5 mole per cent mixture is identical to that shown in figure 3. The temperature scales for other samples have been shifted up by 6.6 K (16.5 per cent), 8.0 K (27.3 per cent), 22.2 K (24.2 per cent), 27.8 K (27.0 per cent), 30.7 (28.5 per cent), and 45.4 K (37 per cent).

spanning the  $S_{A_d}$  to  $S_{A_2}$  transformation.  $\bar{C}_p$  (background) was taken to be  $2.00 \text{ J K}^{-1} \text{ g}^{-1}$  for the  $X = 12.5$  sample, and values ranging from  $1.96$  to  $2.14 \text{ J K}^{-1} \text{ g}^{-1}$  were chosen for the other samples in order to achieve the best superposition of  $\Delta\bar{C}_p$  curves. There was no systematic pattern to these  $\bar{C}_p$  (background) values; they reflect the fact that the absolute accuracy of  $\bar{C}_p$  values is 5–10 per cent for this ac calorimetric technique.

It should be noted that for samples with  $X \geq 24.2$  freezing was observed in a temperature range (indicated by  $F$  in figure 1) considerably above that observed microscopically for a thin sample between two glass slides. This is not merely a result of the slow cooling rates used in our calorimetric scans since equally slow microscope scans still gave much lower temperatures in agreement with the line labelled  $f$  in figure 1. The one sample ( $X = 37$ ) that froze while in the  $S_{A_{ic}}$  phase exhibited behavior on freezing quite different from that for the three samples in which  $S_{A_2}$  froze. In the latter cases,  $\bar{C}_p$  increased discontinuously by roughly  $1 \text{ J K}^{-1} \text{ g}^{-1}$  when the sample froze on cooling, and subsequent reheating revealed a sharp crystal  $K$  melting transition. As shown in figure 4,  $\bar{C}_p$  for the  $X = 37$  sample decreased abruptly by  $\sim 0.25 \text{ J K}^{-1} \text{ g}^{-1}$  and no sharp melting feature was seen on reheating. It seems likely that a metastable plastic crystal form different from crystal  $K$  is formed when  $S_{A_{ic}}$  freezes.

### 3. Discussion

One possibility to be considered is that the  $S_{A_{ic}}$  phase in this binary system is merely a coexistence region of two distinct  $S_{A_d}$  and  $S_{A_2}$  phases. From this point of view, the  $S_{A_d}$ – $S_{A_2}$  transition should be *strongly* first order with a very wide coexistence range when  $X > 24$ . However, detailed X-ray measurements [4, 5] carried out on a series of mixtures have ruled out this possibility. More recently, a first-order  $S_{A_d}$ – $S_{A_2}$  transition has been observed [12] which is characterized by a jump in the layer spacing and by a two-phase region in which the wavevectors  $q_0$  and  $q'_0$  (corresponding to the  $S_{A_2}$  and  $S_{A_d}$  regions) coexist. It was also observed that in this two-phase region, temperature dependences of  $q_0$  and  $q'_0$  are nothing but continuations of the corresponding trends in the  $S_{A_2}$  and  $S_{A_d}$  phases. This is in marked contrast to the behaviour in the  $S_{A_{ic}}$  phase [4, 5], wherein the variations of  $q_0$  and  $q'_0$  are *opposite* to those in the  $S_{A_2}$  and  $S_{A_d}$  phases, indicating thereby a coupling, albeit weak, between the two incommensurate wavevectors. Thus the possibility of the  $S_{A_{ic}}$  phase being a two-phase region has definitely been ruled out by X-ray studies. The present calorimetric data also support this view.

First, let us consider the direct transformation from  $S_{A_d}$  to  $S_{A_2}$  that is observed for  $X \leq 24$ . The  $\bar{C}_p$  data for all such samples support the conclusion that a continuous supercritical transformation occurs. It is predicted theoretically [13] on the basis of symmetry that a  $S_{A_d}$ – $S_{A_2}$  transition is in general first order. A line of such first-order transitions terminates at an isolated critical point, beyond which there is no transition in a formal sense but only a locus of finite maxima in the thermodynamic response functions. The situation is directly analogous to the gas–liquid phase change encountered in pure fluids as the pressure is increased beyond  $p_c$ , but the  $S_{A_d}$ – $S_{A_2}$  critical point is more complex than the Ising critical point exhibited by fluids [13]. We believe that pure  $\text{DB}_7\text{OCN}$  and all mixtures with  $X < 24$  are supercritical. This is best established calorimetrically for the samples with  $X = 12.5$  and  $16.5$ , where the  $\bar{C}_p$  peak is stable (very slow drift with no change in width) and clearly rounded (points of inflection separated by  $1.6 \text{ K}$  for  $X = 12.5$  and  $2.8 \text{ K}$  for  $X = 16.5$ ). A supercritical transformation for such samples is also strongly supported by X-ray measurements of the

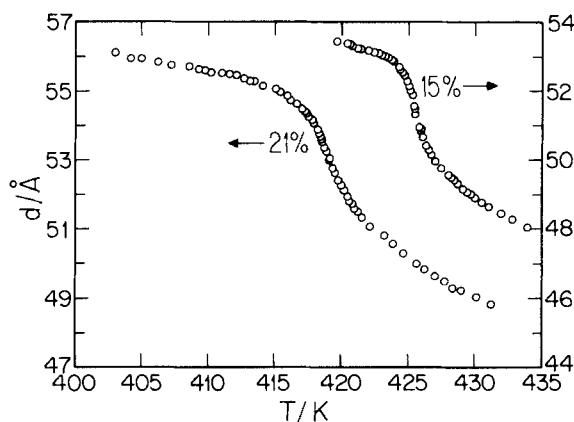


Figure 5. Evolution of the smectic layer thickness  $d$  as DB<sub>7</sub>OCN + 8OCB mixtures transform directly from  $S_{A_d}$  into  $S_{A_2}$  when  $X < 24$ .

smectic layer spacing  $d$  as a function of temperature. Pure DB<sub>7</sub>OCN exhibits a very rapid but continuous  $d(T)$  variation with no observable jump in  $d$  at the  $S_{A_d}$ - $S_{A_2}$  'transition' [14]. Samples with  $X = 15$  and  $X = 21$  show a continuous and more gradual evolution in  $d$  as  $S_{A_d}$  transforms into  $S_{A_2}$  [15], as shown in figure 5. The conclusion that the  $S_{A_d}$ - $S_{A_2}$  critical point must lie very close to the N- $S_{A_d}$ - $S_{A_2}$  'triple point' (actually a N- $S_{A_d}$  critical end point [9]) is also supported by heat capacity [16] and X-ray [17] studies of DB<sub>6</sub>CN.

As the 8OCB concentration is increased, the  $S_{A_d}$ - $S_{A_2}$   $\Delta C_p$  peak height decreases markedly but there is essentially no change in the size or shape of the wings until  $X = 24$ . For the  $X = 24$  sample, the  $\Delta C_p$  peak becomes clearly asymmetric and slightly broader. A substantial change in the  $\Delta C_p$  behaviour is observed for  $X = 27.0$  and  $X = 28.5$ . These curves are characterized by two 'kinks', regions of very rapid change in  $d\bar{C}_p/dT$ . We have identified the positions of these kinks as the  $S_{A_d}$ - $S_{A_{ic}}$  and  $S_{A_{ic}}$ - $S_{A_2}$  transformation regions, and the resulting temperatures are in quite good agreement with microscope and X-ray values. Recall also that no hysteresis in  $\bar{C}_p$  or anomalous change in the phase shift  $\phi$  of the  $T_{ac}(\omega)$  signal was observed on scanning through the  $S_{A_{ic}}$  region. Thus we conclude that  $S_{A_{ic}}$  is a distinct new phase and not a two-phase coexistence region, which agrees with the X-ray data. Note also that if first-order  $S_{A_d}$ - $S_{A_2}$  coexistence did occur for  $X > 24$ , a critical point would have to exist near  $X \approx 24$ , but our data show no indication of a critical singularity in  $C_p$ . The thermodynamic character of the  $S_{A_d}$ - $S_{A_{ic}}$  and  $S_{A_{ic}}$ - $S_{A_2}$  transitions is not clear. There is no evidence of first order character in either the X-ray or calorimetric data, and no conventional second-order features are observed either. The abrupt change in  $d\bar{C}_p/dT$  at the  $S_{A_d}$ - $S_{A_{ic}}$  transition corresponds to a similar abrupt change in  $dq'_0/dT$  reported in [4] and [5]. Formally, such features could be described as arising from an Ehrenfest third-order transition.

The variation of the integrated enthalpy

$$\delta H = \int \Delta \bar{C}_p dT \quad (2)$$

is shown in figure 6 together with the areas of the D.S.C. peaks reported in [5]. We see that the disappearance of the D.S.C. peak for  $X > 24$  is an artifact associated with



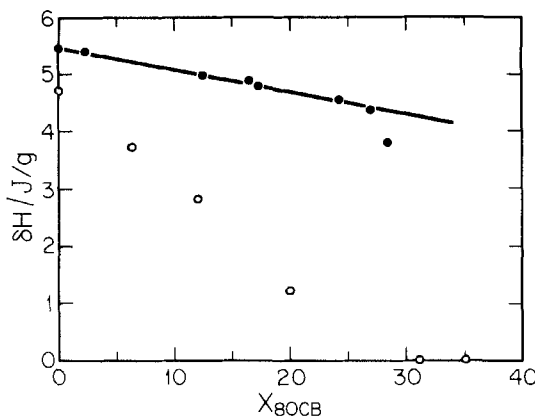


Figure 6. Integrated enthalpy  $\delta H = \int \Delta \bar{C}_p dT$  versus mole per cent 8OCB obtained from ac calorimetry (●) and a D.S.C. investigation (○). No D.S.C. peak was observable for either of two samples with  $X > 30$  mole per cent.  $\delta H(\text{ac})$  is nonzero for  $X = 37$  mole per cent, but a quantitative value is difficult to obtain in view of uncertainties in the choice of  $\bar{C}_p$  (background).

the difficulty of observing broad  $C_p$  peaks with the D.S.C. technique. Indeed, the  $\delta H$  values obtained from our ac heat capacity data change only gradually with  $X$ .

Although some of the runs on DB<sub>7</sub>OCN + 8OCB mixtures were complicated by time-dependent variations in the  $\bar{C}_p$  peak, several key samples ( $X = 12.5, 16.5, 24.2$  and  $27.0$ ) were quite stable. In particular, the drift rate was zero for the  $X = 24.2$  sample and only  $1 \text{ mK h}^{-1}$  for the  $X = 27.0$  sample. In both these cases, the  $\bar{C}_p$  peak was unchanged in size and shape over a series of two cooling and two heating scans. Thus the difference between  $\Delta \bar{C}_p$  for these samples and those for  $X < 24$  is a real and reproducible effect.

Another indication that any impurities that may accumulate during the heat capacity measurements in the  $S_{A_{ic}}$  region should have very little effect on  $\Delta \bar{C}_p$  is the sharp N- $S_{A_d}$  peak. Measurements through the second-order N- $S_{A_d}$  transition were always made after all runs in the  $S_{A_{ic}}$  range had been completed. The  $\bar{C}_p(\text{N}-A_d)$  peaks are sharp (see figure 2) and the calorimetric transition temperatures agree well with those determined microscopically, indicating a low level of impurities when the sample is first heated up to  $T_{NA_d}$ . Unfortunately, the  $\bar{C}_p(\text{N}-A_d)$  peaks are too small for critical exponent analysis, but they are qualitatively similar to the heat capacity peak observed at the  $S_A$ -reentrant N transition in octyloxybenzoyloxycyanostilbene (T8) [18].

In summary, experimental [4-6] and theoretical [3, 19] investigations of  $S_{A_{ic}}$  liquid crystals indicate complex behaviour that is not yet well understood or fully explored. However, the existence of such incommensurate structures is now well established. It would be desirable to study the  $S_{A_{ic}}$  phase and the  $S_{A_d}$ - $S_{A_{ic}}$  and  $S_{A_{ic}}$ - $S_{A_2}$  transitions in a system where first-order  $S_{A_d}$ - $S_{A_2}$  behaviour persists up to the composition where the  $S_{A_{ic}}$  phase first appears.

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