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## Calorimetric study of phase transitions in the liquid crystal butyloxybenzylidene octylaniline (4O.8)

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**Résumé.** — La capacité calorifique du butyloxybenzylidène octylaniline a été mesurée entre 0° et 95 °C. Des effets prétransitionnels significatifs sont observés non seulement près de la transition du premier ordre entre le cristal rigide normal et la phase cristalline plastique B mais encore près de la transition de fusion du premier ordre entre la phase B et la phase cristal liquide smectique A. Les données au voisinage de la transition du second ordre smectique A-nématique déterminent un exposant critique  $\alpha$  très supérieur à zéro, en accord avec des résultats récents obtenus sur d'autres matériaux.

**Abstract.** — The heat capacity of butyloxybenzylidene octylaniline has been measured from 0° to 95 °C. Significant pretransitional effects are observed near both the first-order transition from the normal rigid crystal to the B phase plastic crystal and the first-order melting transition from the B phase to the smectic-A liquid crystal phase. Data near the second-order smectic-A to nematic transition require a critical exponent  $\alpha$  considerably greater than zero, in agreement with recent results on other materials.

Butyloxybenzylidene octylaniline (4O.8) undergoes a series of cooperative phase transitions from the normal crystal (K) to a « smectic-B » phase (B) to a smectic-A phase (SmA) to nematic (N) and finally to the isotropic (I) liquid. There has been recent interest in this material because of structural studies of the B phase and the B-SmA transition [1-4]. It is now established that 4O.8 does not exhibit a *liquid crystal* smectic B phase since the observed B phase has 3-dimensional long-range positional order and is best described as a very soft plastic crystal with

a hcp structure [3, 4]. Thus the K-B transition is an order-disorder transition from a rigid to a plastic crystal phase with very low shear stiffness (due to weak interlayer coupling), and the B-SmA transition is the true melting transition.

A high-resolution calorimetric investigation of 4O.8 has been carried out over the 0°-95 °C range in order to characterize the thermal behaviour at all four transitions (see Fig. 1). The 4O.8 sample (from CPAC-Organics) was vacuum-pumped to remove any residual solvent and was then stored

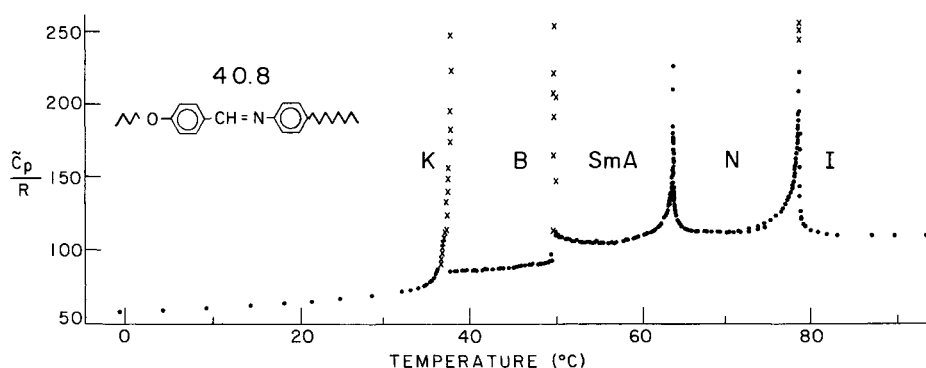


Fig. 1. — Molar heat capacity of 4O.8. For data points denoted by  $\times$  the phase shift of the  $T_{ac}$  signal was clearly anomalous, indicating the coexistence of two phases.

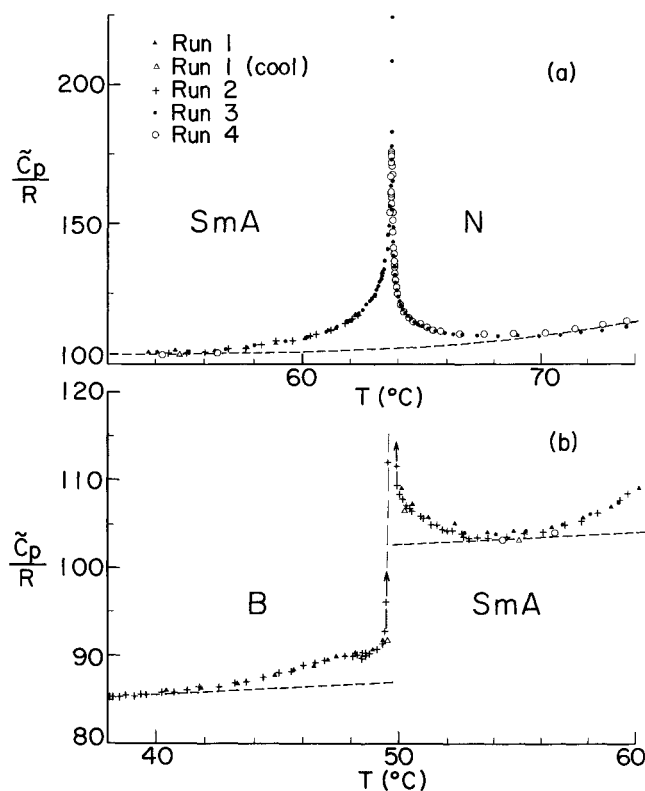


Fig. 2. — Detail of  $\tilde{C}_p$  variation near (a) SmA-N and (b) B-SmA transitions. The dashed background curve above  $T_{BA}$  is a smooth extrapolation of the  $C_p(NI)$  peak. Between 50 and 55 °C this corresponds to a linear background, and a line with the same slope was used as the background in the B phase.

under vacuum in the dark *prior* to use. The measurements were made on bulk ( $\sim 100$  mg) samples with a computer-controlled ac calorimeter [5] using temperature oscillations with 5-10 mK peak-to-peak amplitude. Thermodynamic equilibrium in one-phase regions is insured by long equilibration times ( $> 30$  min.) at every point.

The  $C_p$  variations near the N-I and SmA-N transitions correspond well with those observed in other systems [5, 6]. Interesting new features are seen near both the K-B and B-SmA transitions, as shown in figures 2 and 3. There is considerable excess heat capacity  $\Delta C_p = C_p(\text{obs.}) - C_p(\text{background})$  below  $T_{KB}$  presumably associated with a premelting of hydrocarbon tails and orientational disorder involving rotations about the chain axis [7-10]. Anomalous  $C_p$  values in the B phase below  $T_{BA}$  strongly suggest that defects play a role in melting B crystals [11]; and the excess heat capacity just above  $T_{BA}$  indicates an anomalous increase in short-range order within the SmA layers *prior* to freezing to form the B crystal.

Although the ac method cannot measure latent heats, an indication of two-phase regions can be obtained by monitoring the phase  $\phi$  of the  $T_{ac}$  signal, since  $\phi$  changes dramatically when two coexisting phases are present. This is presumably due to the inability of a two-phase system to stay in equilibrium with the imposed temperature oscillation. Figure 3

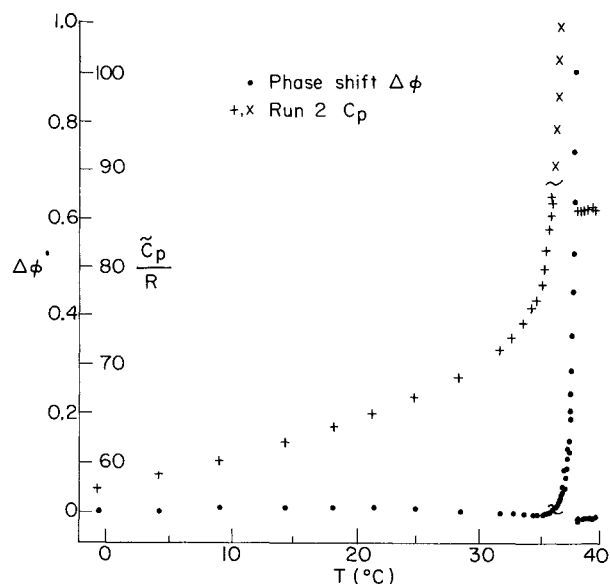


Fig. 3. — Variation of  $\tilde{C}_p$  and the phase shift  $\Delta\phi$  (in rad.) in the normal crystalline phase and just above the K-B transition.  $C_p$  (background) in the K phase was taken to be a straight line through the data points below 15 °C.

shows that the coexistence region is  $\sim 1.7$  K wide near the K-B transition, but it is also clear that there is a large pretransitional  $C_p$  anomaly extending far below this region. At the B-SmA transition,  $\phi$  shifts very abruptly on both sides of a 330-mK-wide range that corresponds well with the coexistence region established by X-ray studies on 40.8 samples from the same source [4]. No anomalous shifts in  $\phi$  were detectable near the SmA-N transition.

The transition temperatures

$$T_{KB} (38.0 \text{ }^\circ\text{C} = 311.2 \text{ K}),$$

$$T_{BA} (49.76 \text{ }^\circ\text{C} = 322.91 \text{ K})$$

and

$$T_{AN} (63.773 \text{ }^\circ\text{C} = 336.923 \text{ K})$$

were stable over a very long period (77 days) covering three warming runs, and these values are in good agreement with literature values [1, 12]. Our  $T_{NI}$  value (78.48 °C = 351.63 K) may be somewhat low due to difficulties with run 4 [13]. The values of the excess enthalpy  $\delta H \equiv \int \Delta C_p dT$  due to precursor effects *but excluding latent heats* are  $\sim 500, 210, 770, 1570 \text{ J}\cdot\text{mol}^{-1}$  for K-B, B-SmA, SmA-N, and N-I transitions, respectively. These values can be compared with the total enthalpy changes reported from DSC measurements : 4872, 1993, 350, 1406  $\text{J}\cdot\text{mol}^{-1}$  for these respective transitions [12, 14]. In the DSC work, all the transitions were identified as first order and the enthalpy was called the latent heat. It is important to note that DSC cannot distinguish latent heats from a very steep but continuous variation of enthalpy  $H$ , and this method is also beset with difficulties associated with the rapid

scanning rate and choice of background. On the basis of all available information, we estimate the true latent heats  $\Delta H$  to be  $\sim 4800$ ,  $\sim 1800$ ,  $0.5$ ,  $50$ - $300 \text{ J.mol}^{-1}$  for K-B, B-SmA, SmA-N, and N-I transitions, respectively.

**K-B TRANSITION.** — Many molecular crystals undergo transitions *prior* to melting that are associated with at least a partial loss of orientational order. These changes in orientational order often involve larger entropy changes than melting itself. In particular, some long-chain hydrocarbons transform into an hcp structure *prior* to melting [10]. This transition involves the randomization of chain configurations which allow the molecule to rotate more easily about its long axis. We suggest that a similar effect occurs in 4O.8, with orientational disorder occurring about the long axis of the molecule in the B phase [7]. Such disorder removes much of the anisotropic intermolecular interactions and thus stabilizes the hcp phase. The onset of this « 1-D » orientational disorder could easily account for the observed excess heat capacity, which is similar to that observed in many pure hydrocarbons [9, 15]. The K-B transition is thus a first-order solid-solid transition with appreciable pretransitional effects in the normal (rigid) crystal phase K.

**B-SmA TRANSITION.** — Although this transition is strongly first-order, pretransitional thermal effects are clearly present. On the basis of the  $C_p$  (background) curves shown in figure 2b, the excess enthalpy above the transition is  $70 \text{ J.mol}^{-1}$ , and that below the transition is  $140 \text{ J.mol}^{-1}$ . It should be noted that the X-ray data [4] show no indication of pretransitional changes in long-range positional correlations. Furthermore, *pretransitional behaviour* reported in the birefringence [16] appears to us to represent changes within a 300 mK coexistence region and does not correspond to the anomalous one-phase behaviour we observe. There are, however, a number of recent observations [17-19] that do correlate with our thermal effects; and we believe that these effects are intrinsic properties of 4O.8 rather than impurity-induced artifacts. (The impurity level in our sample must be quite low in view of the high transition temperatures, sharp SmA-N transition, and relatively narrow B-SmA coexistence range.)

The excess  $\Delta C_p$  in the B phase is naturally sensitive to the choice of  $C_p$  (background), but mechanical measurements [17] indicate that the shear modulus of 4O.8 is anomalous in the B phase and support the view that subtle pretransitional effects can occur

over quite a wide temperature range. Even if a greater curvature were assumed for  $C_p$  (background), a reproducible anomaly in the variation of  $C_p$  over 2-3 K just below  $T_{BA}$  would still remain. We associate this thermal anomaly with changes in the defect structure of the B plastic crystal *prior* to melting. Indeed, X-ray experiments [4] show a small decrease in mosaic spread on warming over this same temperature range, while acoustic experiments [18] reveal unusual longitudinal velocity and attenuation behaviour. The acoustic results strongly resemble dislocation damping effects associated with changes in the density and length of dislocation loops [20]. (Disclination lines are perhaps more likely than dislocations in a material with as low a shear stiffness as B phase 4O.8.)

The excess  $C_p$  just above  $T_{BA}$  strongly suggests the growth of short-range order within the SmA layers on cooling toward the B-SmA transition. Because heat capacity is sensitive to fluctuations in the local environment, not much local ordering would be necessary to give rise to the small thermal effect we observe ( $\delta H = 4\%$  of  $\Delta H_{BA}$  latent heat). One might speculate that on cooling the SmA phase, the system is approaching a transition to a true SmB liquid crystal phase (e.g., stacked hexatic phase) but that when the in-layer order is sufficiently developed the inter-layer interactions are strong enough to drive the system into the hcp B phase. Recently, acoustic [18] and nmr [19] experiments have detected anomalous behaviour in the range  $T_{BA}$  to

$$T^* \simeq T_{BA} + 2.$$

This agrees well with the  $\Delta C_p$  data, but the suggestion [18] of a new phase transition at  $T^*$  is not supported by our results.

**SmA-N TRANSITION.** — It has been predicted that an essentially second-order SmA-N transition should be analogous to the superfluid transition in helium [21]. However, the variation of  $\Delta C_p(\text{AN})$  shown in figure 2a requires an effective critical exponent  $\alpha$  in the range 0.2-0.3 [6], in good agreement with recent detailed studies of 8OCB [5] and 8CB [22]. Thus the present results strengthen the conclusion that critical SmA-N specific heats are not well described by the XY model (for which  $\alpha \simeq -0.02$ ).

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- $$\Delta \tilde{C}_p/R = At^{-\alpha} + B,$$
- where  $t = |T - T_{\text{AN}}|/T_{\text{AN}}$  lies in the range
- $$5 \times 10^{-5} < t < 5.5 \times 10^{-3},$$
- yield the critical exponents  $\alpha = 0.33$  and  $\alpha' = 0.18$ , respectively. If scaling is imposed, a simple power law gives  $\alpha = \alpha' = 0.26$  but the fit is rather poor. Improved fits with similar  $\alpha$  values can be obtained by adding corrections-to-scaling terms.
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