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Calorimetric investigation of phase transitions in butyloxybenzylidene heptylaniline (40.7)

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Résumé. — Une étude calorimétrique des transitions de phase dans le butyloxybenzylidène heptylaniline (40.7) fait apparaître des comportements différents de ceux de son homologue (40.8). L'amplitude du pic de chaleur spécifique $C_p$ associé à la transition nématique-smectique A est bien plus faible pour (40.7) où le domaine nématique est plus important, et l'exposant critique effectif $\alpha$ est plus faible pour (40.7) que pour (40.8). En outre, on observe, sur (40.7), un faible pic de $C_p$ juste au-dessus de la transition de fusion de la phase B à la phase smectique A. Ce pic, non observé pour (40.8), permet de supposer que, dans une plage étroite, (40.7) peut se comporter comme un cristal liquide smectique B hexatique.

Abstract. — An ac calorimetric study of the phase transitions in butyloxybenzylidene heptylaniline (40.7) shows several interesting differences from the behaviour in the homolog 40.8. The magnitude of the $C_p$ peak associated with the nematic-smectic-A transition is much smaller in 40.7, as expected since the nematic range is greater, and the effective critical exponent $\alpha$ is smaller in 40.7 than in 40.8. Furthermore, there is a very small $C_p$ peak in 40.7 just above the melting transition from the B phase to the smectic-A liquid crystal phase. This peak, which is not present in 40.8, suggests that there may be a narrow range of hexatic smectic-B liquid crystal behaviour in 40.7.

Butyloxybenzylidene heptylaniline (40.7) undergoes a series of phase transitions from a plastic crystal B phase to a liquid crystal smectic-A phase (SmA) to nematic (N) to the isotropic (I) liquid. As with 40.8 the B phase exhibits 3-dimensional long-range positional order (hcp structure) [1], and the B-SmA transition is the melting transition. However, the nematic range is much greater in 40.7 than in 40.8 [2], and this is expected to influence the magnitude of the heat capacity peak at the second-order SmA-N transition [3]. The results of an ac calorimetric study of 40.7 are reported here and compared with previous measurements on 40.8 [4].

Measurements were made over the 25-95 °C range on a bulk (~ 100 mg) sample with a computer-controlled calorimeter [5] using peak-to-peak temperature oscillations of 5-10 mK. The 40.7 sample (from CPAC-Organix) was vacuum pumped to remove any residual solvent and then sealed in a silver cell. Long equilibration times (> 30 min.) were used at every point to insure thermodynamic equilibrium in one-phase regions.

Figure 1 shows the heat capacity variation asso-
associated with the B-SmA, SmA-N, and N-I transitions. The observed transition temperatures
\[ T_{BA} = 48.15 \, ^\circ C = 321.30 \, K \]
\[ T_{NA} = 55.944 \, ^\circ C = 329.094 \, K \]
\[ T_{NI} = 82.35 \, ^\circ C = 355.50 \, K , \]
were slightly lower (by \(~ 0.65 \, K\)) than those reported by Smith and Gardlund [2], and the B-SmA coexisting region was 0.7 \, K wide (47.8 to 48.5 \, ^\circ C). Although this indicates that small amounts of impurities are probably present in our 40.7 sample, such impurities do not appear to have distorted the heat capacity data. In particular, the \( C_p(NA) \) peak was sharp and there were no signs of a shift in \( T_{NA} \) during 4 days over which data were taken in the region \( T_{NA} \pm 0.5 \, K \). Note also that the N-I peaks in 40.7 and 40.8 are almost identical [6], including the width (\(~ 150 \, mK\)) of the coexistence region. Indeed, the \( C_p \) variation in 40.7 over a 20 \, K range below \( T_{NI} \) provides a strong confirmation of the choice of \( C_p \) (background) made earlier [4] for 40.8.

It was reported previously [2] that 40.7 exhibits a smectic-F phase with a F-to-B transition at 29 \, ^\circ C. Figure 2a shows in detail the \( C_p/R \) variation over the range from 25 \, ^\circ C to 37 \, ^\circ C, and it is clear that no thermal anomaly occurs in this region. The absence of any ac calorimetric evidence for an F phase is puzzling in view of the DSC transition enthalpy of 4000 \, J. \, mol^{-1} reported in reference [2]. However, our result is completely consistent with X-ray measurements [1] that show no structural transition but only restacking of hexagonal close-packed layers occurring in the B phase between 30 and 35 \, ^\circ C. Such stacking changes also occur in 40.7 without any observable thermal effects [7].

1. B-SmA transition. — Figure 2b shows the details of the \( C_p/R \) variation near the B-SmA melting transition. Although this transition is strongly first-order, pretransitional effects are observed, especially above the B-SmA coexistence region. The linear background below \( T_{BA} \) has a slope of 0.27 \, K^{-1} and represents a fit to the B phase \( C_p/R \) data over the 30-44.5 \, ^\circ C range. The noncritical background heat capacity just above \( T_{BA} \) is somewhat uncertain, but an excess heat capacity
\[ \Delta C_p = C_p(\text{obs.}) - C_p(\text{background}) \]
and anomalous behaviour in the range 48.5 to 51 \, ^\circ C are clearly present with any reasonable choice of background. The dashed line above \( T_{BA} \) has a slope of 0.1477 \, K^{-1} and corresponds to the background line shown in figure 1. The two dot-dashed lines represent an upper limit on the background and a plausible lower limit. The excess enthalpy \( \delta H = \int \Delta C_p \, dT \) due to precursor effects (but excluding any latent heat) is \(~ 18 \) \, J. \, mol^{-1} below the B-SmA transition and 55 \pm 15 \, J. \, mol^{-1} above. These can be compared with the corresponding values of 140 and 70 \, J. \, mol^{-1} for 40.8 [4, 8]. The anomalous behaviour above \( T_{BA} \) in 40.7 is comparable in magnitude but quite different in character from that observed in 40.8. The excess heat capacity in 40.8 shows a smooth decrease over a range of \(~ 3 \) \, K above the B-SmA coexistence region (see Fig. 1). In 40.7 we observed a very small but reproducible subsidiary peak at 48.80 \, ^\circ C. The data shown in figure 2b between 48.5 and 49 \, ^\circ C were obtained from two separate passes through this limited region during an initial warming run. (This subsidiary peak was also observed 28 days later on a cooling run ; its size and shape were the same but the temperature of the peak had shifted down by 150 \, mK.) X-ray measurements on bulk 40.7 gave no indication of a structural change in this region [1]. However, these particular X-ray measurements would not have revealed the presence of a hexatic smectic-B liquid crystal phase in which there is long-range bond orientational order but no long-range positional order within the smectic layers [9]. It is tempting to speculate that a hexatic phase may exist in 40.7 just above its melting point, but new experiments will be required to resolve that question.

2. SmA-N transition. — The critical heat capacity associated with the second-order smectic-A-nematic transition is shown in figure 3 and compared with the SmA-N peak in 40.8. Due to the small magnitude of

![Image](Fig. 2. — a) \( C_p \) variation in 40.7 in the range where a F-B transition was reported in reference [2] (marked by arrow); b) \( C_p \) variation near the B-SmA transition. \( C_p \) (background) curves are indicated by dashed lines, and two alternative background choices above \( T_{BA} \) are indicated by dot-dash lines.)
the 40.7 peak, the $\Delta C_p(\text{NA})$ values are sensitive to the choice of $C_p(\text{background})$, which is somewhat uncertain due to possible overlap of pretransitional B-SmA and SmA-N features around 51°C. A linear background of the form

$$C_p(\text{background}) = aT + b$$

was used over the range 48-65°C for all our fitting procedures. The $\Delta C_p/R$ values in figure 3 were obtained by using $a = 0.1477$, and this background is the one shown by the dashed line in figure 1.

Figure 3a shows that the SmA-N peak in 40.7 looks very similar in shape to that in 40.8 but has a magnitude that is smaller by a factor of roughly 3.2. Systematic differences in the wings between $\Delta C_p(40.8)$ and 3.2 $\Delta C_p(40.7)$ are sensitive to the choice of $C_p(\text{background})$ for 40.7. Use of a slightly smaller background slope $a = 0.1085$ [the upper dot-dashed line in figure 2h] produces much better agreement between $\Delta C_p(40.8)$ and 3.2 $\Delta C_p(40.7)$ in the nematic phase for 0.3 K $< \Delta T < 5$ K. Use of a larger slope $a = 0.1869$ [lower dot-dashed line in figure 2b] generates very good agreement in the smectic phase-out to $\Delta T = -5$ K. However, figure 3b shows that the shapes of the 40.7 and 40.8 peaks do not correspond in the range $-0.15 < \Delta T < +0.15$. Furthermore, the differences close to $T_{\text{NA}}$ are not sensitive to changes in $C_p(\text{background})$ since any reasonable background is essentially constant over such a narrow temperature range. Thus we expect that the critical exponent $\alpha$ for 40.7 will be smaller than that for 40.8.

Power-law fits of the $\Delta C_p(\text{NA})$ values for 40.7 were made with the form

$$\Delta C_p/R = \begin{cases} A' t^{-\alpha} + B & \text{for } T > T_{\text{NA}} \\ A' |t|^{-\alpha'} + B' & \text{for } T < T_{\text{NA}} \end{cases}$$

where $t$ is the reduced temperature $(T - T_{\text{NA}})/T_{\text{NI}}$. Unfortunately, the resulting least-squares values of $\alpha$ and $A$ are sensitive to variations in the range of $|t|$ used as well as the choice of $C_p(\text{background})$. This is due to the quite small magnitude of $\Delta C_p$ and the relatively small number of data points over the most reliable range for fitting data $(3 \times 10^{-5} < |t| < 5 \times 10^{-3})$ [5]. The best fit over these two decades in the nematic phase yielded $\alpha = 0.11$, $A = 11.25$, and $B = -5.49$ with $T_{\text{NA}} = 329.094$ K ($\chi^2 = 0.7$), but the $\alpha$ values varied from 0.08 to 0.15 depending on range and background [10]. In the smectic phase, no really satisfactory fit could be obtained with equation (3). The « best » fit yielded $\alpha' = -0.044$, $A' = -93.65$, and $B = 77.87$ with $T_{\text{NA}} = 329.094$ K ($\chi^2 = 0.6$), but $\alpha'$ values ranged from $-0.14$ to $+0.22$ depending on range and background. Close to $T_{\text{NA}}$, where the choice of background slope has less effect, a satisfactory fit could be obtained with $\alpha' = 0.15$ but there are only six data points in the decade $2.8 \times 10^{-5} < |t| < 2.8 \times 10^{-4}$.

These 40.7 results can be compared with fits to the excess heat capacity $\Delta C_p$ of 40.8. In the latter case, stable fits were obtained with the critical exponent $\alpha = 0.33$ for the nematic phase and $\alpha' = 0.18$ for the smectic phase [4, 11]. Thus it appears that a change in the nematic range (i.e., a change in the parameter $T_{\text{NA}}/T_{\text{NI}}$) causes a change in both the magnitude of the $\Delta C_p(\text{NA})$ peak and the value of the effective critical exponent $\alpha$. Preliminary measurements of the correlation lengths in 40.7 [12] indicate that the critical exponents $\xi_\parallel$ and $\xi_\perp$ are larger in 40.7 than in 40.8, which would support the apparent difference in $\alpha$ values for these two materials since $2 - \alpha = \xi_\parallel + 2 \xi_\perp$ according to hyperscaling. Furthermore, the correlation volume $\xi_\parallel^2 \xi_\perp^2$ is appreciably larger in 40.7 than in 40.8, which is qualitatively consistent with the observed difference in $\Delta C_p$ magnitudes for 40.7 and 40.8.
Figure 4 shows the trend in the variation of the excess entropy

$$\delta S_{NA} = \int \Delta C_p(NA) \, d \ln T \simeq \delta H_{NA}/T_{NA} \quad (4)$$

with the parameter $T_{NA}/T_{NI}$ for several cyanobiphenyl and nO.m systems. Included in figure 4 is a value we have determined for 4O.8 at 850 bar. Note that the effect of pressure on the width of the nematic range is much smaller for 4O.8 than for 8OCB or 8CB. This appears to be a general feature of nO.m compounds since preliminary work on 7O.7 indicates a small variation in that case also

$$[d(T_{NI} - T_{NA})/dp \approx 3 \text{ K. kbar}^{-1}].$$

Perhaps the high sensitivity of the width of the nematic range to pressure in cyanobiphenyls is connected with the role of dimerization in these materials.

As a final point, let us comment on the large difference (a factor of ~ 9) in the magnitude of $\delta S_{NA}$ for nO.m and cyanobiphenyls at any given $T_{NA}/T_{NI}$ value. The difference in $\delta S(N)$, the nematic phase contribution to $\delta S_{NA}$, can be almost completely explained in terms of two-scale-factor universality and the fact that the bare correlation lengths in cyanobiphenyls are longer than those in nO.m compounds (see reference [11] for a detailed discussion of 4O.8 and 8OCB). However, there is an asymmetry in the magnitude of $\delta S(\text{SmA})$ and $\delta S(N)$ for nO.m materials that is not seen in the biphenyls. In 4O.8 and 4O.7 the ratio $\delta S(\text{SmA})/\delta S(N)$ is ~2.4, while this ratio is ~1.0 in 8OCB and 8CB. New experiments to characterize critical behaviour in the SmA phase of both nO.m and cyanobiphenyl compounds would clearly be of interest.

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References

[6] The transition enthalpy $\delta H_{NI} = \int \Delta C_p(NI) \, dT$ due to excess heat capacity associated with the transition but excluding any latent heat is 1 625 J.mol$^{-1}$ for 4O.7 compared to 1 570 J.mol$^{-1}$ for 4O.8.
[8] In retrospect, the B phase background used in reference [4] may have had too low a slope. If so, the excess enthalpy for 4O.8 below $T_{NA}$ should be reduced to ~ 80 J.mol$^{-1}$. In any case, thermal anomalies in the B phase prior to melting are definitely smaller in 4O.7 than in 4O.8.

[10] For the «inner» decade $3.5 \times 10^{-4} < t < 3.3 \times 10^{-3}$, the best nematic fitting parameters were $a = 0.15$, $A = 5.65$, and $B = - 9.88$. For the «outer» decade $2.7 \times 10^{-5} < t < 3.5 \times 10^{-4}$, the best values were $a = 0.15$, $A = 5.12$, and $B = - 8.13$. Such a change in the amplitude $A$ at $\Delta T \simeq 0.1$ K is consistent with the behaviour shown in figure 3 but seems very artificial.

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Figure 4. — Dependence of the SmA-N transition entropy $\delta S_{NA}$ on the parameter $T_{NA}/T_{NI}$ for 4O.7, 4O.8, and several cyanobiphenyl systems (references [3-5], [13]). For high-pressure points, the value of the pressure in kbar is indicated. The lines are merely guides for the eye.