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P. Das[a]; K. Ema[ab]; C. W. Garland[a]
[a] Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, U. S. A. [b] Department of Physics, Tokyo Institute of Technology, Tokyo, Japan

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Calorimetric study of the smectic A–smectic C transition in TBBA

by P. DAS, K. EMA‡ and C. W. GARLAND
Department of Chemistry and Center for Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

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An a.c. calorimetric technique has been used to measure the heat capacity variation associated with the smectic A–smectic C transition in terephthal-bis-(4*n*)-butylaniline (TBBA). Contrary to expectations based on the recent observation of petransitional acoustic effects in the smectic-A phase, the heat capacity shows no evidence of critical fluctuations and can be well described by a Landau mean-field model.

The smectic A (S_A)–smectic C (S_C) liquid crystal transition has been extensively investigated in numerous compounds with a variety of experimental techniques [1–6]. It has been predicted theoretically [7] that this transition should belong to the 3D-XY universality class, assuming that one can neglect the effects of anisotropy and the Landau–Peierls instability of the smectic layers. However, mean-field behaviour has been observed in almost all experimental studies, of which the investigation of butyloxybenzylidene heptylaniline (4O.7) provides the most detailed example [4]. In 4O.7 the absence of critical XY behaviour can be understood in terms of the Ginzburg criterion since the bare correlation lengths characterizing tilt fluctuations are so large that the asymptotic critical region is unobservably small (reduced crossover temperature $t_x \leqslant 10^{-5}$) [2, 4]. There are still unresolved questions about the character of the S_A–S_C transition in only one material, azoxy-4,4′-di-undecyl-α-methylcinnamate (AMC-11) [4–6]. In all other materials studied to date, the S_A–S_C transition is well described by an extended mean-field model with an unusually large sixth-order term in the Landau free-energy expansion [5].

In the present work we are concerned with terephthal-bis-(4*n*)-butylaniline (TBBA or TB4A). This compound is a nonpolar liquid crystal with an aromatic core containing three benzene rings. It exhibits the following sequence of phase transitions:

$$X\text{tal} \longrightarrow S_G \xrightarrow{417\,\text{K}} S_C \xrightarrow{445\,\text{K}} S_A \xrightarrow{473\,\text{K}} N \xrightarrow{505\,\text{K}} I$$

A recent ultrasonic investigation of the S_A–S_C transition in the TBBA has revealed significant anisotropic pretransitional effects in the acoustic velocity and attenuation above T_{AC} [8]. These ultrasonic data can be very well represented by the Andereck–Swift fluctuation theory [9]. Furthermore, X-ray measurements of the tilt angle ϕ in the S_C phase of several TBnA homologues show that ϕ evolves continuously via a second-order transition for $n = 3$ and 4 but undergoes a discontinuous first-order jump at the S_A–S_C transition for $n = 5$–8 [10]. This indicates that a tricritical S_A–S_C point should occur in a TB4A + TB5A mixture and suggests that TB4A itself might exhibit near tricritical behaviour. If fluctuations are significant in TBBA and it is

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† Present address: Department of Physics, Tokyo Institute of Technology, Oh-Okayama, Meguro, Tokyo 152, Japan.

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near a tricritical point, one would expect a large heat capacity peak with comparable amplitudes above and below the transition temperature [11].

A high-resolution a.c. calorimetric study of TBBA has been undertaken to look for evidence of pretransitional thermal fluctuations in the S_A phase near the S_A–S_C transition. To the best of our knowledge, this represents the first detailed calorimetric study of the S_A–S_C transition in a mesogen with a three-aromatic-ring core. A description of our microcomputer-controlled a.c. calorimetric method is given elsewhere [5, 12]. It will suffice here to note that a very low frequency temperature oscillation is used ($\omega = 0{\cdot}196$, corresponding to a 32 s period) and that the TBBA is hermetically sealed in a silver sample cell using a cold-welded tin seal [13].

The aromatic core of TBBA contains Schiff-base linkages (–CH=N–), which are quite susceptible to oxidation and hydrolysis. Thus TBBA will deteriorate rapidly if it is in contact with air at high temperatures, and a high degree of sample purity and isolation from the atmosphere is crucial in order to prevent sample deterioration [14]. Commercially available high-quality TBBA was recrystallized several times from ethanol and acetone until the N–S_A transition temperature as measured with a polarizing microscope was 473 K. This recrystallized material was always handled in a dry argon atmosphere. After loading the sample, we pumped on the open silver cell at $\sim 10^{-3}$ torr for 30 minutes before the cell was sealed. It has been shown that even with extensive precautions about the handling of TBBA, slow deterioration occurs in the nematic phase but not in the S_A phase [14]. Therefore, we have avoided heating the sample above ~ 453 K except very briefly during the filling procedure.

The filled and sealed cell weighed 610 mg, of which 36·2 mg was due to TBBA. The specific heat capacity of TBBA in J K^{-1} g^{-1} units was obtained from

$$C_p = \frac{C_p(\text{obs}) - C_p(\text{empty})}{m}, \tag{1}$$

where C_p(obs) is the observed heat capacity of the filled cell, C_p(empty) is that of the empty cell, and m is the TBBA mass in grams. The empty-cell heat capacity was measured over the 420–455 K range and is well represented in J K^{-1} units by

$$C_p(\text{empty}) = 0{\cdot}1668 + 5{\cdot}68 \times 10^{-5}(T - 435) + 8{\cdot}17 \times 10^{-6}(T - 435)^2. \tag{2}$$

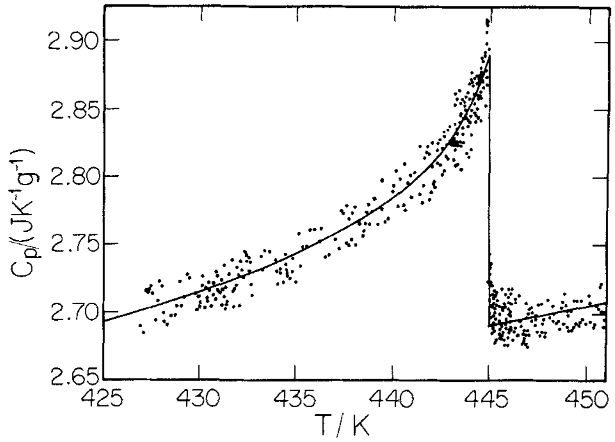
This TBBA sample exhibited a strongly first-order S_C–S_G transition at 417·35 K and a second-order S_A–S_C transition at 444·94 K. Measurements in the vicinity of T_{AC} were carried out both on warming and on cooling (the slowest scan rate being 70 mK h^{-1} over the region $T_{AC} \pm 2$ K), and no hysteresis was observed in the C_p values. The sample exhibited exceptional stability: no measurable drift in T_{AC} was observed over a period of 12 days at temperatures above 425 K.

The figure shows the C_p variation in the vicinity of the S_A–S_C transition on a warming run. It is immediately obvious that there is no excess (fluctuation) heat capacity in the S_A phase above T_{AC}. Indeed, our C_p data are well represented by a Landau model in which the free energy expansion has the form

$$G = G_0 + at\,\phi^2 + b\phi^4 + c\phi^6, \tag{3}$$

where ϕ is the S_C tilt-angle order parameter and $t \equiv (T - T_{AC})/T_{AC}$ is the reduced temperature. It has been shown [3, 5] that equation (3) leads to

$$\tilde{C}_p/R = \begin{cases} \tilde{C}^0_p/R, & \text{for } T > T_{AC}, \\ \tilde{C}^0_p/R + A\dfrac{T}{T_{AC}}\left(\dfrac{T_m - T_{AC}}{T_m - T}\right)^{1/2}, & \text{for } T < T_{AC}, \end{cases} \tag{4}$$



Specific heat capacity of TBBA near the S_A–S_C transition. The line represents a Landau fit to these data using equations (5*a*) and (5*b*).

where $\tilde{C}_p/R$ is the dimensionless ratio of the molar heat capacity to the gas constant R, $A \equiv a^2/2bRT_{AC}$, $T_m \equiv T_{AC} + (b^2T_{AC}/3ac)$, and $\tilde{C}_p^0$ is the background molar heat capacity arising from G_0. The quantity T_m is the metastability limit where the heat capacity of the ordered phase would diverge on warming if the sample had not undergone a second-order transition at a lower temperature T_{AC}. For such a second-order transition, a, b, and c are all positive and $\tilde{C}_p/R$ undergoes a discontinuous change of magnitude A at T_{AC}. For the specific heat capacity, equation (4) can be rewritten as

$$C_p = C_p^0 = B + E(T - T_{AC}), \qquad \text{for } T > T_{AC}, \qquad (5a)$$

$$= B + E(T - T_{AC}) + \bar{A}\frac{T}{T_{AC}}\left(\frac{T_m - T_{AC}}{T_m - T}\right)^{1/2}, \text{ for } T < T_{AC}, \qquad (5b)$$

where the regular background term C_p^0 is represented by a linear temperature dependence as usual and the coefficient $\bar{A} = AR/M$, where $M = 396{\cdot}6\,\mathrm{g}$ is the molecular mass of TBBA.

A non-linear least-squares fit to the data shown in the figure was carried out with equations (5), and the resulting Landau curve is in excellent agreement with our experimental data. The least-squares parameters are $T_{AC} = 444{\cdot}94\,\mathrm{K}$, $T_m = 447{\cdot}00\,\mathrm{K}$, $\bar{A} = 0{\cdot}201\,\mathrm{J\,K^{-1}\,g^{-1}}$, $B = 2{\cdot}690\,\mathrm{J\,K^{-1}\,g^{-1}}$, and $E = 0{\cdot}0029\,\mathrm{J\,K^{-2}\,g^{-1}}$. In order to compare this Landau fit with those for other compounds exhibiting S_A–S_C transitions, it is convenient to calculate A and the quantity $t_0 \equiv 3(T_m - T_{AC})/T_{AC} = b^2/ac$, which characterizes the shape of the excess heat capacity $\Delta\tilde{C}_p/R = (\tilde{C}_p - \tilde{C}_p^0)/R$. The excess $\Delta\tilde{C}_p/R$ in the S_C phase drops from A at T_{AC} to $\frac{1}{2}A$ at $t = -t_0$. As shown in the table, the magnitude A of the TBBA heat capacity peak is comparable to that of other compounds. However, the value of t_0 is rather large when compared with previously determined values. This means that the second-order S_A–S_C transition in TBBA is not very close to a Landau tricritical point (at which $b = 0$ and thus $t_0 = 0$).

In summary, TBBA exhibits mean-field behaviour at the S_A–S_C transition that is qualitatively the same as that observed in all other systems. No evidence of critical energy fluctuations has been observed in the S_A phase. This implies that anomalous

Heat capacity jump A and characteristic reduced temperature t_0 associated with the S_A–S_C transition.

Material	Ref.	A	$10^3\,t_0$
$\bar{8}$S5	[2]	5	6·5
2M4P9OBC	[3]	16	5·5
DOBAMBC	[3]	15	3·2
4O.7	[5]	7·7	1·3
7O.6	[5]	30·8	1·6
7O.4	[5]	47·8	0·8
TBBA	—	9·6	13·9

pretransitional acoustic effects observed above T_{AC} must be interpreted in terms of a more general theory than the Andereck–Swift fluctuation model.

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