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Ac-Calorimetry Studies at the Hexatic-B Smectic-A and Crystal-B Hexatic-B Phase-Transitions in 2 Compounds With Hydrogen-Bonding

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Two compounds of the 1-(4′-alkoxyphenylamino-3-[5″-(2″-menthylpirydil)]-propen-1-one-3 (PIRn) series that exhibit the hexatic-B (Hex-B) to smectic-A (Sm-A) and the crystal-B (Cry-B) to Hex-B phase transitions were studied by high resolution ac calorimetry. The Hex-B–Sm-A phase transition was found to be of first order and continuous for PIR7 and PIR9, respectively. The tricritical point was located at the concentration for which $T_{\text{Cry-}B\text{–Hex-}B}/T_{\text{Hex-}B\text{–Sm-}A}=0.980\pm0.004$, i.e., a hexatic range of 7 K. At both sides of the tricritical point, nonclassical and non-three-dimensional-XY specific heat exponents α were observed. The Cry-B–Hex-B phase transition was of first order and was associated with a small or immeasurable C_p anomaly.

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The liquid to hexatic phase transition in liquid crystals is associated with the development of long range bond orientational order (BOO) [1,2]. The symmetry of the order parameter places this transition in the three-dimensional (3D) -XY universality class, which is recognizable by a heat capacity critical exponent of $\alpha=-0.007$ [3]. Among liquid crystals with the simplest (orthogonal) ordered phases, the in-plane melting process has been almost exclusively studied in compounds belonging to the n-alkyl-4′-n-alkoxybiphenyl-4-carboxylate (nmOBC) series. Heat capacity experiments in these materials [4,5] have shown that the hexatic-B to smectic-A (Hex-B–Sm-A) phase transition is continuous with an unexpectedly large critical exponent $\alpha=0.5$, which obviously is not consistent with theoretical predictions. The discrepancy between theory and experiment suggests that the BOO is not the only symmetry breaking field at this phase transition [5]. Thus fluctuations of herringbone order (HBO) were proposed to be responsible for the discrepancy in systems exhibiting a smectic-E (Sm-E) phase below the Hex-B phase [5,6]. Indeed, the presence of weak HBO in the Hex-B phase of nmOBC compounds was confirmed by x-ray scattering experiments [7].

In order to test the influence of HBO on the hexatic phase, it is necessary to compare previous results with those for systems lacking HBO, i.e., for systems where the Sm-E phase is replaced by a crystal-B (Cry-B) phase. Unfortunately, in the only compound that has been previously tested possessing a Cry-B–Hex-B–Sm-A phase sequence, 4-propionyl-4′-n-heptanoyloxyazo-benzene, the Hex-B–Sm-A phase transition was found to be strongly first order, making the determination of the critical exponent α impossible [8].

Recently, new compounds with the Cry-B–Hex-B–Sm-A phase sequence have been synthesized [9]. For the ac-calorimetry studies reported here, two compounds of the 1-(4′-alkoxyphenylamino)-3[5″-(2″-menthylpirydil)]-propen-1-one-3 (PIRn) series, where n is the number of carbons in the alkoxy chain, were chosen: PIR7 and PIR9, with 7 and 9 carbons in the terminal alkoxy chains, respectively. They were characterized by differential scanning calorimetry (DSC) studies and the absence of HBO was confirmed by x-ray measurements [10].

The ac-calorimetry measurements were carried out at a heating frequency of 110 mHz on 5 mg bulk samples that were placed on a 1 cm diameter, 0.1 mm thick sapphire disk provided with a thermobead temperature sensor and a heater. The imposed temperature oscillations were maintained below 2 mK (peak to peak), while the average temperature was controlled to better than 100 μK. Lock-in amplification and computer data averaging for 15 min at every temperature were used to achieve a relative heat capacity precision of 0.1%. The temperature dependence of both the heat capacity and the phase shift between the applied heat and resulting temperature oscillations was simultaneously recorded in consecutive cooling and heating runs over a 20 K range bracketing the transitions. In the ac technique, the phase shift is usually simultaneously determined as it provides empirical information on the order of the phase transition. Further details about this experimental technique are given elsewhere [11].

The specific heat as a function of temperature for the PIR7 compound is plotted in Fig. 1. Comparing cooling and heating results, there is a 0.34 K hysteresis in the transition temperature as well as slight differences in the shape of the Hex-B–Sm-A C_p anomaly that are particularly pronounced on the low temperature branch. At the transition, the phase shift (also shown in Fig. 1) exhibits a narrow peak, which is characteristic of a two-phase coexistence region, usually present at first-order transitions [12,13]. In contrast to the PIR7 results, specific heat and phase shift measurements for PIR9 presented in Fig. 2 show that heating and cooling runs overlap exactly with no hysteresis in the transition temperature or any phase

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shift anomalies. These results suggest that the Hex-B-Sm-A transition is weakly first order for PIR7, while it is continuous for PIR9. Thus a tricritical point exists on the Hex-B-Sm-A phase transition line separating first order from continuous transitions, in agreement with the 2D-melting theory [2]. The appearance of a tricritical point in systems having a Cry-B-Hex-B-Sm-A phase sequence can be attributed to the coupling between BOO and positional order. As the terminal chain length increases in the PIRn series, the hexatic range increases while the positional order fluctuations decreases, driving the Hex-B-Sm-A phase transition continuously. In the PIRn series, the tricritical point is located for a system having a 7 K wide hexatic phase between PIR7 ($T_{BB}/T_{BA}=0.984$) and PIR9 ($T_{BB}/T_{BA}=0.976$). This position is rather different from that in the other systematically studied series (nmOBC) for which the hexatic range is less than 0.8 K ($T_{BB}/T_{BA}>0.999$) [5].

The width of the critical anomalies associated with the Hex-B-Sm-A phase transition in compounds of the PIRn series, about 2.5 K full width at half maximum (FWHM) for PIR7, is much larger than in the nmOBC series (typically 0.4 K FWHM). This indicates that the fluctuations are strong and persist over a wide temperature range for the PIRn series.

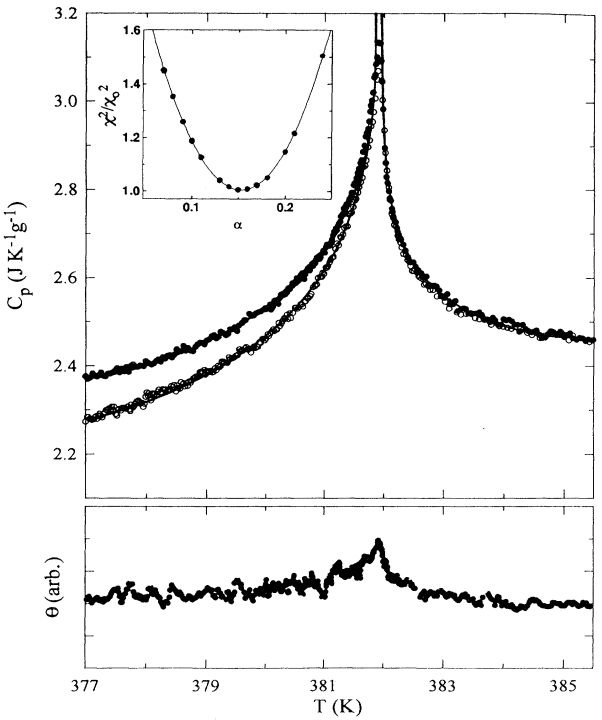

FIG. 1. (a) Specific heat near the Hex-B-Sm-A phase transition for PIR7 heating and cooling runs. The peak position in the cooling run was shifted up by 0.34 K. There is a pronounced difference in the low temperature branches between heating (upper curve) and cooling (lower curve). For clarity, only every other data point is shown. The solid lines are results of fits to Eq. (1) with parameters as given in Table I. Inset: χ^2/χ_0^2 vs α, where χ_0^2 is the value for the best fit. (b) Phase shift near the Hex-B-Sm-A phase transition for the heating run.

To quantitatively characterize the critical behavior of the specific heat, data for PIR7 and PIR9 were fitted according to the simple power law expression [14]

$$C_p = A_{\pm}|t|^{-\alpha} + B_{\pm} + Dt \ . \tag{1}$$

The first term describes the singular part of the specific heat, whereas $B_{\pm}+Dt$ is a noncritical background; $t=(T-T_c)/T_c$ is the reduced temperature. The $\pm$ subscripts refer to below ($-$) and above ($+$) T_C. In these fits, the instrumental $1/\sigma_i^2$ weighting to each data point was included, with the standard deviation σ_i taken as $0.02C_p$. The transition temperature and the slope of the background were fixed at the same values for both sides of the phase transition. The fits were only sensitive to temperature-range shrinking very close to T_C. The temperature region of the instrumentally induced peak rounding, as estimated from a log-log plot of the divergent part of C_p as a function of reduced temperature, was less than 0.2 K ($t_{\min}\approx 3\times 10^{-4}$). The results of the data analysis are summarized in Table I. The uncertainty in α is a consequence of the rather flat χ^2 surface for fits using Eq. (1) [the χ^2-α intersection is shown in the inset of Fig. 1(a)]. The resulting critical exponents, $\alpha=0.15\pm0.08$ for PIR7 and 0.18 ± 0.08 for PIR9, although lower than those found for nmOBC, are still far from the 3D-XY value. Attempts to improve the fitting results were made by including the correction-to-scaling terms [14]; these

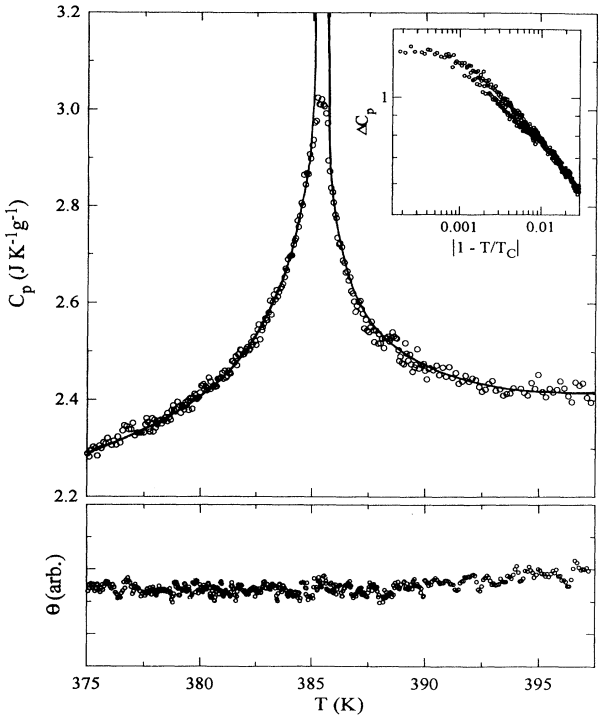

FIG. 2. (a) Specific heat near the Hex-B-Sm-A phase transition for PIR9 data from heating and cooling runs overlapped identically. For clarity, only every other data point is shown. Inset: log-log plot of the critical part of C_p vs t. (b) Phase shift near the Hex-B-Sm-A phase transition for the heating run.

TABLE I. Parameters obtained from fitting the specific heat data for PIR9 and PIR7 according to Eq. (1).

	A_+/A_-	T_C (K)	α	D ($JK^{-1}g^{-1}$)	B_+ ($JK^{-1}g^{-1}$)	B_- ($JK^{-1}g^{-1}$)	χ^2
				PIR7			
heating	0.69	382.00	0.15±0.08	0.016	1.78	1.60	1.51
cooling	0.72	381.66	0.15±0.08	0.022	1.72	1.54	1.62
				PIR9[a]			
	0.94	385.38	0.18±0.08	0.008	1.7[c]	1.7[c]	1.29
	0.78	385.44	0.5[b]	0.008	2.21	2.26	2.81
	0.99	385.43	−0.007[b]	0.009	24.0	24.2	5.10

[a]Cooling and heating data exactly overlapped.
[b]Fixed value.
[c]B_+ and B_- fixed at the same value.

did not change the resulting exponent significantly. Fitting the data with an exponent fixed at the 3D-XY value of -0.007 or to the mean-field value $\alpha=0.5$ resulted in considerably higher χ^2 values and unacceptable fits.

From x-ray diffraction studies, the significance of the order parameter fluctuations can be directly probed by investigating the scaling relation [2] $C_{6n}=C_6^{n+\lambda n(n-1)}$ between harmonics, C_{6n} describing the $6n$-fold symmetry of the order in these systems. If fluctuations are negligible as in the mean-field case, $\lambda=0$. If fluctuations dominate the critical behavior, then λ essentially increases, e.g., $\lambda=0.3-0.008n$ in the 3D-XY case. X-ray studies for PIR7 showed that the system crosses over from mean-field behavior deep in the hexatic phase to a fluctuation dominated region near the phase transition, as indicated by an increasing value of λ [14]. This behavior might explain why a purely mean-field exponent is not adequate to describe the C_p anomaly despite the first-order nature of the transition. Hence the 0.15 specific heat exponent determined here might be interpreted as an "average" crossover exponent. A similar behavior was observed for PIR9.

In addition to the Hex-B–Sm-A transition, we also studied the Cry-B–Hex-B transition. In PIR9, no C_p anomaly was detected, while PIR7 exhibited a very small anomaly. These results are shown in Fig. 3. The Cry-B–Hex-B transition enthalpy estimated from the ac-calorimetry measurements, $\Delta H_{ac}\cong 0.08\ J\,g^{-1}$, are comparable to those observed by DSC, $\Delta H_{DSC}\cong 0.13\ J\,g^{-1}$. Since the DSC does not differentiate between the latent heat and the changes in C_p near the transition, the latent heat for the Cry-B–Hex-B transition is certainly less than $0.1\ J\,g^{-1}$. Despite the small latent heat, the difference in the shape of the C_p anomaly between heating and cooling and the small but noticeable anomaly in the phase shift indicate that this transition is first order. This is consistent with x-ray scattering results which, at the Cry-B–Hex-B transition, observed the in-plane positional correlation length to range from 200 to more than 5000 Å [10]. This suggests that the growth of long range positional order is only weakly correlated with the transition enthalpy.

To summarize, results for systems without HBO are still not fully consistent with theoretical predictions. Although the existence of a tricritical point on the Hex-B–Sm-A transition line is in agreement with theory, the critical specific heat exponent is not. Our experiments are likely to have measured crossover exponents which are intermediate between mean-field and fluctuation dominated processes. The critical exponents α and β [15] found for PIR7 allow us to estimate (via the Rushbrooke equality [16]) the susceptibility exponent $\gamma=1.45\pm0.14$. While not very precise, it seems to be consistent with the predictions of the 3D-XY model. However, to elucidate if fluctuations are indeed described by a 3D-XY model, measurements for systems far from the tricritical point (i.e., longer terminal chain compounds) are needed. Also, it would be helpful to study a variety of hexatic materials as results obtained for nmOBC and PIRn are not sufficient to arrive at general conclusions regarding the

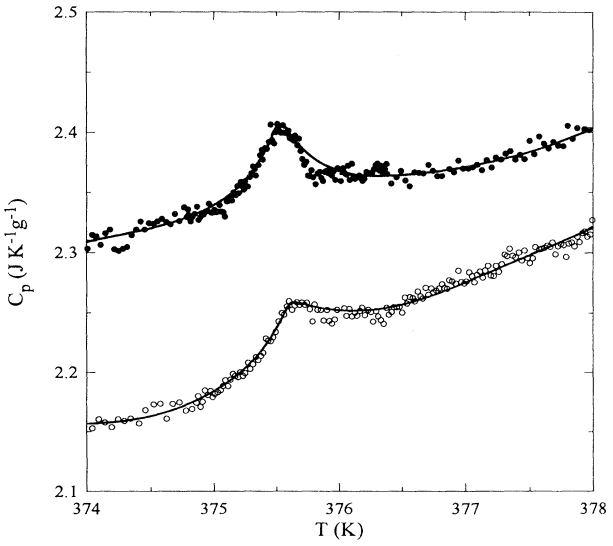

FIG. 3. Specific heat anomalies near the Cry-B–Hex-B phase transition for PIR7 heating (upper curve) and cooling (lower curve) runs. Solid lines are guides to the eye.

behavior of the hexatic-disorder phase transition. The first-order hexatic-crystallic transition in these orthogonal systems was found to be accompanied by both a small C_p anomaly and a small latent heat, as previously observed in tilted systems [5].

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