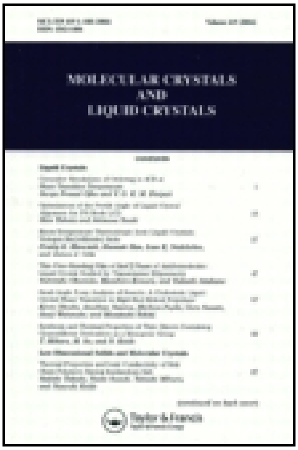

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Smectic C-Nematic Transition in the Mixtures 5_x6_{1-x}BABA[†]

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We describe DSC investigations of the (S_C-N) transition in the mixtures 5_x6_{1-x}BABA, for $0 \leq x < 1$. This transition could only be observed for $x \leq 0.8$. A marked difference was found in the chain length dependences of both the transition temperature, T_{CN}, and the transition entropy, ΔS_{CN}, between the pure and mixed compounds. This might be related to the difference between end hydrocarbon chain conformations of 5BABA and 6BABA. Specific heat measurements show (i) for $x = 0$, a first order transition with hardly any fluctuations, (ii) for $x = 0.59$, an almost continuous transition, but again with weak fluctuations. The fact that the fluctuations remain weak near T_{CN} even when ΔS_{CN} is very small, is attributed to large bare coherence lengths.

INTRODUCTION

The higher homologues ($n \geq 6$)* of the compounds, *p-n*-Alkoxy*b*enzylidene-*p*-*A*mino*B*enzoic *A*cid (*n*BABA) exhibit both smectic C(S_C) and nematic (N) phases,[1] while the lower members exhibit only a nematic phase. For $6 \leq n \leq 9$, ΔS_{CN} increases linearly with increasing *n*, and extrapolates to zero for $n \approx 4.1$. DeHoff *et al.*[2] have found that in mixtures of $\bar{7}$S5 and $\bar{8}$S5 the (S_C-N) transition is first order right up to the NAC point and they have argued that this could be as a result of the large bare coherence lengths. In the present work, we have studied the (S_C-N) transi-

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* n = numbers of carbon atoms in the alkoxy group.

tion in mixtures of 5BABA and 6BABA (5_x6_{1-x}BABA) by differential scanning calorimetry, in order to investigate whether this transition becomes continuous for any x or region of x, and if the latter be true, whether a multicritical point could be predicted.

EXPERIMENTAL DETAILS

A Perkin-Elmer DSC-2C instrument was used for our measurements. The transition temperatures T_{CN} and T_{NC} and the transition enthalpies, ΔH_{CN} and ΔH_{NC} were measured for BABA mixtures having $0 \leq x \leq 1.0$. The specific heat, C_p, was measured only for two samples having $x = 0$ and 0.59. The scanning speed was varied from 2.5°/min to 20°/min for measurements of transition temperatures, and the values reported here were obtained by extrapolating the measured temperatures to zero scanning speed. For the specific heat measurements, scanning speeds down to 0.31°/min were used. Sample weights ranged from 2 to 7 mg, and the sensitivity used was in the range 5 mCal/s to 0.2 mCal/s (the noise level was rather high for the high sensitivity limit). It was found that for many of the samples $T_{CN}(S_C \rightarrow N) \approx T_{NC}(N \rightarrow S_C)$ and $\Delta H_{CN} \approx \Delta H_{NC}$. Most of the results presented here are those obtained while heating. However, the transition entropies for $x > 0.6$ were obtained from the cooling data since the temperature resolution was better in this case. The specific heat measurements were made using a sapphire sample as a standard.

RESULTS AND DISCUSSION

The values of the transition temperatures, T_{PC} and T_{CN} are given for some values of x in Table I. T_{PC} is the temperature of the transition ($P \rightarrow S_C$), preceding the $S_C \rightarrow N$ transition, where P refers to a phase of unknown nature. The ($P \rightarrow S_C$) transition has a large transition enthalpy compared with ΔH_{CN}. It is seen from Table I that for $x > 0.4$, the temperature separation between these two transitions becomes small, making it difficult to resolve the (S_C-N) transition especially because of the neighboring

TABLE I

Transition temperatures for the systems 5_x6_{1-x}BABA

x	0	0.2	0.4	0.55	0.7	0.8
T_{PC}(K)	436	424	433	439	440	440
T_{CN}(K)	459	446.5	443.5	442	442	443

(P-S_C) transition which is very strong. This feature is clearly seen in Figure 1 which shows heating scans for 6BABA and $5_{0.55}6_{0.45}$ BABA. This factor combined with the small values of ΔH_{CN} for $x > 0.5$, have led to rather large errors in our measurements of the transition entropy, $\Delta S_{CN}(=\Delta H_{CN}/T_{CN})$ for $x > 0.5$.

The extrapolated temperatures, T_{CN}, are plotted as a function of x in Figure 2. Following a rapid decrease for $0 \leqslant x \leqslant 0.3$, T_{CN} remains almost constant for $x > 0.3$. Since a S_C-N transition could not be observed for $x > 0.8$, it has not been shown in the figure. The inset shows T_{CN} as a function of n. For $5 < n < 6$, n is taken to be equal to $[5x + 6(1 - x)]/2$. A marked change is observed in the T_{CN} variation as one passes from the pure compounds ($n \geqslant 6$) to the mixtures ($5 < n < 6$), especially for $n < 5.8$ ($x > 0.2$). This could point to a difference in the end hydrocarbon (hc) chain conformations between 5BABA and 6BABA.

The dependence of the transition entropy, ΔS_{CN} on x is shown in Figure 3. ΔS_{CN} is almost constant for $x \leqslant 0.3$ but decreases for larger x. For $x \geqslant 0.6$, the error bars on the experimental points give only a lower limit since they represent only the error made in measuring transition peak areas and not those involved in marking the baseline of the peak. The variation of ΔS_{CN} with n can also be seen in the inset. For the pure compounds, ΔS_{CN} varies linearly with n, but this dependence changes in the

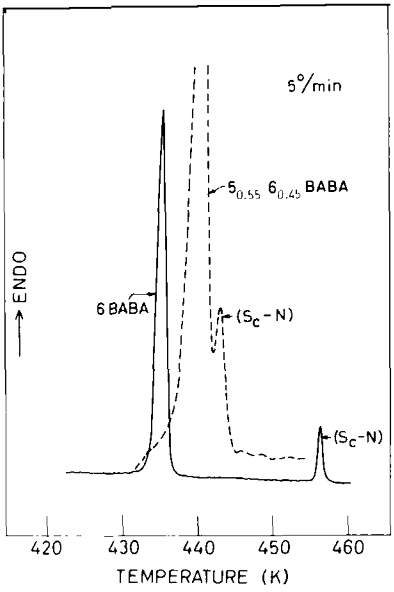

FIGURE 1 DSC heating scans for 6BABA and 5_x6_{1-x} BABA (x = 0.55).

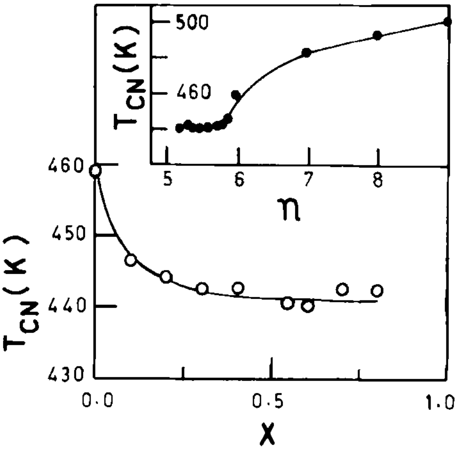

FIGURE 2 T_{CN} as a function of x.

case of mixed compounds. This change could also be due to differences in the end chain conformation of 5BABA and 6BABA.

The specific heats for compounds with $x = 0$ and $x = 0.59$, measured in the vicinity of T_{CN} while heating are shown in Figure 4 as a function of the reduced temperature, $t = (T - T_{CN})/T_{CN}$. In the case of 6BABA, the specific heat clearly shows the first order nature of the (S_C-N) phase tran-

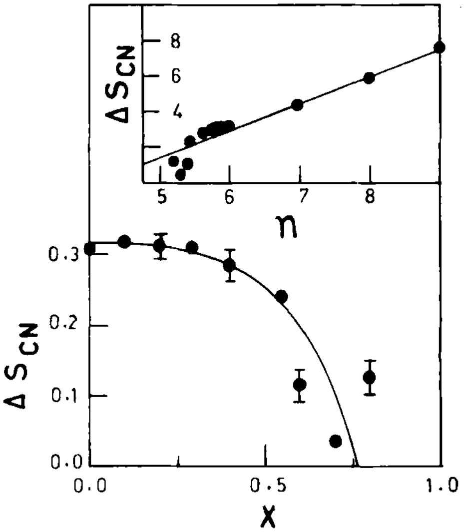

FIGURE 3 ΔS_{CN} (in units of R_0, the gas constant) as a function of x.

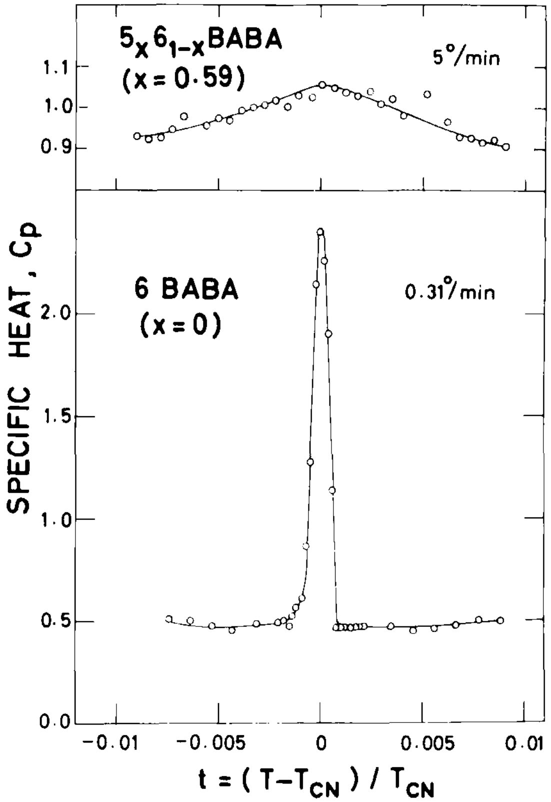

FIGURE 4 Specific heat, C_p (Cal/g K) for 6BABA and 5_x6_{1-x} BABA ($x = 0.41$) as a function of the reduced temperature, t.

sition, with very weak fluctuations. A small pretransitional effect is seen for $T < T_{CN}$, but for $T > T_{CN}$, the specific heat is almost independent of temperature. This is typical of mean-field behavior which is also seen for (S_C-N) transitions in other mixtures.[2] A very approximate estimate of the specific heat jump, ΔC_P at T_{CN} turns out to be $\approx 20R_0$ where R_0 is the gas constant. The specific heat data for $5_{0.41}6_{0.59}$ BABA seems to indicate that the S_C-N transition is continuous. However, since these data were taken at a scanning speed of 5°/min, we believe that the poor temperature resolution has smeared the peak at T_{CN} to a large extent, making the transition look second order, although it is in reality a first order transition. The nearness of the (P-S_C) and (S_C-N) transitions necessitated the use of samples of low weight in order to resolve the (S_C-N) transition, which in turn led to high scanning speeds being used in order to obtain a reasonable intensity of the transition peak. It is, therefore, obvious that the values of ΔS_{CN} presented in Figure 3 for $x \geqslant 0.5$ can only be an upper limit to ΔS_{CN}, whereas the actual value could be smaller. Thus we cannot say with certainty whether the (S_C-N) transition for $x \geqslant 0.6$ is continuous or first order, though it appears to be very weakly first order.

Our results on T_{CN} and ΔS_{CN} show that there is a change in n-dependence when one goes from pure nBABAs to mixtures. This could be due to the difference in the end chain conformation in 5BABA and 6BABA, which in turn could be related to the odd and even number of C atoms in their chains. To date, there is no theory of the (S_C-N) transition which takes explicitly into consideration the length of the end hydrocarbon chains of the molecules. The only theory which takes this into account is McMillan's theory,[3] which, however, only treats the (S_A-N) transition. This theory predicts that T_{AN}/T_{NI} increases with increasing molecular length and that for $T_{AN}/T_{NI} \leqslant 0.87$, one should have continuous (S_A-N) transitions. We can examine our results in the light of McMillan's theory, if we assume that as far as this aspect is concerned, one can apply this theory to the (S_C-N) transition. For 6BABA, it is found that $T_{CN}/T_{NI} = 0.861$, and for 5_x6_{1-x} BABA this ratio is smaller, so that one should expect continuous (S_C-N) transitions in them. But this is not observed.

Several theories exist which predict the (S_C-N) transition. Of these, the Chu-McMillan theory[4] which predicts a second order (S_C-N) transition and Wulf's theory[5] which sets an upper limit of 49.1° to the tilt angle, θ_t (in 6BABA, θ_t is measured[6] to be about 60°), cannot explain our results. No comparison with Chen-Lubensky theory[7] was possible since a measurement of correlation lengths was not done. Swift and Mulvaney,[8] using Brazovskii's perturbation method,[9] have calculated ΔS_{NC} for a binary mixture of liquid crystals having an NAC point. They find that,

$$\Delta S_{NC} \sim \frac{q_\perp^0}{(\xi_\parallel^0 \xi_\perp^0)}, \tag{1}$$

where $q_\perp^0 = q_0 \tan \theta_t$ and $q_0 = 2\pi/\text{smectic layer spacing}$ and $\xi_\parallel^0$ and $\xi_\perp^0$ are bare coherence lengths defined by,

$$\xi_\parallel \sim \xi_\parallel^0 t^{-\nu} \quad \text{and} \quad \xi_\perp \sim \xi_\perp^0 t^{-\nu}. \tag{2}$$

$\xi_\parallel$ and $\xi_\perp$ are correlation lengths, parallel and perpendicular respectively to the nematic director, and ν is a critical exponent. X-ray diffraction[10] reveals the presence of skewed cybotactic groups in both 5BABA and 6BABA for $T = T_{tr} + 0.5$°C, where T_{tr} is the transition temperature to the nematic phase ($T_{tr} = T_{CN}$ for 6BABA) while heating. From these results $q_\perp^0$ is found to be 0.24 Å^{-1} and 0.22 Å^{-1} for 5BABA and 6BABA respectively. If we assume that, (a) $q_\perp^0$ remains almost constant for $0 \leqslant x \leqslant 1$, since it is nearly the same for 5BABA and 6BABA, and (b) no large change occurs in $q_\perp^0$ as $T \rightarrow T_{CN}$, we can conclude from Eq. (1) that the observed change of ΔS_{CN} with x would be primarily due to the x-dependences of the bare coherence lengths. The very weak fluctuations observed near T_{CN}, even when ΔS_{CN} is quite small, can be accounted for if one uses the arguments given in Ref. 2. This uses a Ginzbung criterion,

$$t_G \sim \frac{1}{(\Delta C_p)^2 \xi_0^6} \tag{3}$$

where t_G (width of the critical regime) is the reduced temperature at which a crossover from a strong to a weak fluctuation regime occurs. ΔC_p is the specific heat jump at T_{CN} and $[\xi_0^6 \rightarrow (\xi_\parallel^0)^2(\xi_\perp^0)^4]$ for uniaxial systems.[10]

Since ΔC_p for the mixed compounds is very small for $x \geqslant 0.5$, it must be the large bare coherence lengths which reduce t_G making it impossible to observe strong fluctuations in our experiments. Preliminary X-ray diffraction measurements[11] with 5BABA do seem to indicate that $\xi_\parallel^0$ and $\xi_\perp^0$ are large for this compound.

CONCLUSIONS

(1) Our T_{CN} and ΔS_{CN} measurements show a marked difference in their n-dependence for pure and mixed BABAs which might be related to the difference in conformations of the hc chains in 5BABA and 6BABA. A theory which uses a potential which is not only dependent on the chain length but also on the chain conformation will be required to explain our results. (2) The dependence of ΔS_{CN} on x seems to be due to the variation with x of the bare coherence lengths. (3) The weak fluctuations near T_{CN}, even when ΔS_{CN} is small, could be due to large bare coherence lengths.

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