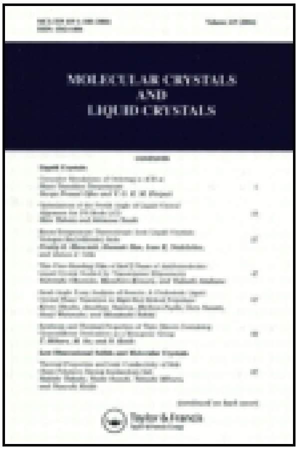

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Heat Capacity and Enthalpy Behavior Near Phase Transitions in Some Alkylcyanobiphenyls

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Heat Capacity and Enthalpy Behavior Near Phase Transitions in Some Alkylcyanobiphenyls[†]

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An adiabatic scanning calorimeter has been used in a calorimetric investigation of alkylcyanobiphenyl (nCB) liquid crystals. Measurements near solid to smectic (KA), smectic A to nematic (AN) and nematic to isotropic (NI) or smectic A to isotropic (AI) phase transitions have been carried out for scanning rates as low as a few μKs^{-1}. Results for the temperature dependence of the heat capacity as well as for the enthalpy (including latent heats) have been obtained for 8CB, 9CB, 10CB and 11CB. Latent heat values are reported for the different KA, NI and AI transitions. For the two compounds 8CB and 9CB, which show a AN transition, it was found that, within the resolution of the experiments, these transitions are second-order. The anomalous heat capacity observed near the AN transition is much larger for 9CB than for 8CB. The critical exponent α obtained from power law fits to the heat capacity data is 0.31 ±0.03 for 8CB and 0.50 ±0.05 for 9CB. It is suggested that the AN transition in 9CB must be very close to a tricritical point, and that the α value for 8CB should be considered as an effective value, reflecting crossover between the tricritical and XY critical behavior.

1. INTRODUCTION

Calorimetric investigations have always played an important role in the study of phase transitions and critical phenomena in condensed matter. This has also been the case in the field of liquid crystals. Differential scanning calorimetry (DSC) has been a major tool in localizing phase transition points in liquid crystals. The detailed investigation of pretransitional effects

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in liquid crystals has, however, only rather recently reached a high level of sophistication by applying ac calorimetric techniques.[1] This technique is very well adapted for measuring the pretransitional heat capacity behavior but has an important drawback: it is not possible to measure latent heats which are quite often present at liquid crystal phase transitions.

During the last two years, we have used an adiabatic scanning calorimeter to study phase transitions in liquid crystals. We have previously used this apparatus to study critical phenomena in fluids belonging to the universality class of the three-dimensional Ising model.[2] With this apparatus we can obtain detailed information on the heat capacity near the phase transitions as well as on the enthalpy behavior, including latent heats. The liquid crystals which we have investigated so far are the following four compounds of the alkylcyanobiphenyl homologous series: octylcyanobiphenyl (8CB), nonylcyanobiphenyl (9CB), decylcyanobiphenyl (10CB) and undecylcyanobiphenyl (11CB). For all these compounds, we have investigated in detail the region around the phase transition temperatures which occur between the solid phase and the isotropic liquid state. The results for 8CB have been described recently.[3] In this paper we present new results for the three other compounds and make a comparison with the 8CB data. Much emphasis will be put on the smectic A to nematic (AN) transition and in particular on the intriguing differences in critical behavior for the NA transitions for 8CB and 9CB.

2. EXPERIMENTAL

The cyanobiphenyls used in these studies were obtained from BDH Chemicals Ltd. (Poole, Dorset, U.K.). No further purification of the samples was attempted. The liquid crystal materials were transferred directly from their sealed containers into our sample cell.

The adiabatic scanning calorimeter and its possible modes of operation are described in detail elsewhere.[4] A small modification has been made between the 8CB work and the present measurements on the other three compounds: instead of a sample holder with a maximum content of 25 cm^3, we now use one of 10 cm^3. Also for this sample holder it is possible to stir the sample (for details see Ref. 3). For the purposes of this paper, a very brief account of the principal working conditions of the calorimeter will be given.

The calorimeter consists of four stages: a central stage 1 containing the sample and three outer shielding stages. All stages are thermally insulated from each other and made of copper to avoid temperature gradients in the stages. All inner stages contain heaters and thermistors as temperature sensing elements. The free space between the stages is evacuated.

Starting with the defining relation for the specific heat

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{dQ}{dT}\right)_p \tag{1}$$

different measuring procedures may be considered. The simplest one is to supply a known amount of heat ΔQ to the sample and measure the corresponding temperature rise ΔT. There is also some heat required to increase the temperature of the sample holder. Since this can, however, be separated from the sample contribution by proper calibration,[3,4] we will not take it into account further and concentrate on the sample only. The heat pulse method is a rather time-consuming method with limited resolution near phase transitions. It is, however, also possible to operate in dynamic modes by continuously applying (or extracting) heating power P to (or from) the sample. In that case the heat capacity can be written in this way:

$$C_p = P/\dot{T}. \tag{2}$$

By keeping P or $\dot{T}$ constant, combined with increasing or decreasing the temperature of stage 1, four practical modes of operation can be realized with our calorimeter.[4] In the four cases, different setting conditions are required for the shielding stages. In the constant heating rate mode, our principal mode of operation, a constant heating power P is applied to the sample, and $\dot{T}$ is then derived from a detailed measurement of the temperature (T) *vs* time (t) evolution of the sample. Essential in the whole procedure is a very low heat leak from stage 1 to the surroundings. This is achieved by very sensitive servo-systems controlling the temperature of the shielding stages. We measure the temperature of the sample by means of a thermistor. The resistance of the thermistor was previously[3,4] measured every 20 s by means of a six-digit, self-balancing ac-potentiometer, giving a temperature resolution of 0.1 mK. Our temperature resolution has been improved by an order of magnitude by using now a seven-digit, self-balancing ac-bridge, which is connected to a minicomputer for handling and storing the data. $\dot{T}$ (which is typically of the order of 10 mK/h) can then be obtained by numerical differentiation of the $T(t)$ curve. The $T(t)$ results can also be converted directly in an enthalpy curve:

$$H(T) = H(T_s) + P(t - t_s), \tag{3}$$

where the index s refers to the starting conditions of the run. If a first-order transition occurs at T_{tr} between T_s and T, we can write Eq. (3) as follows:

$$\begin{aligned} H(T) - H(T_s) &= P(t_{tr}^{(i)} - t_s) + P(t_{tr}^{(f)} - t_{tr}^{(i)}) + P(t - t_{tr}^{(f)}) \\ &= \int_{T_s}^{T_{tr}} C_p dT + \Delta H_L(T_{tr}) + \int_{T_{tr}}^{T} C_p dT \end{aligned} \tag{4}$$

Because of the latent heat $\Delta H_L(T_{tr})$ the temperature will be constant for a time interval $t_{tr}^{(f)} - t_{tr}^{(i)} = \Delta H_L/P$. With the heating-rate method, it is thus possible to obtain detailed information on the pretransitional heat capacity behavior near the transitions, but it allows us also to measure the latent heats if present. This is of course a great asset in the study of liquid crystal phase transitions where quite often small latent heats have to be separated from large pretransitional effects.

3. RESULTS

In Table I, the latent heat values for all the transitions investigated so far have been summarized. The heat of fusion increases gradually with the alkyl chain length. The latent heat for the transition to the isotropic phase is quite strongly dependent on the chain length. The most interesting result is, however, obtained for the AN transitions for 8CB and 9CB, which we find to be continuous within our experimental resolution. We will come back to that later. It should also be noted that in our calorimetric measurements we did not observe the small (0.5°C) nematic range reported preciously[5] for 11CB; instead we found a direct transition from the smectic A phase to the isotropic phase. Optical observation under the

TABLE I

Latent heats (kJ/mol)

	K-S_A	S_A-N	N-I	S_A-I
8CB	25.7 ±1.0 (23)[a]	$\leq 4 \times 10^{-4}$ (0.04)	0.612 ±0.005 (0.67)	—
9CB	34.5 ±1.0 (31)	$\leq 5 \times 10^{-3}$ (0.25)	1.20 ±0.03 (1.0)	—
10CB	36.0 ±1.0 (34)	—	—	2.83 ±0.05 (2.7)
11CB	43.2 ±1.0 (38)	—	—	3.8 ±0.1 (3.4)

[a] The values in parenthesis are from DSC results by H. J. Coles and C. Strazielle (Ref. 6).

polarizing microscope gave the same result.[†] The values in parenthesis are from DSC results by Coles and Strazielle.[6] There is reasonable agreement for most of the transitions. In the cases of 8CB and 9CB, the rather large DSC values should not be considered as true latent heats, but as overall enthalpy changes over a small temperature interval around the AN transition temperature.[3]

In Figure 1 the enthalpy changes involved at the NI and AN transitions are compared on the same energy and temperature scales. The zeros for H have, however, been chosen at different reference temperatures T_s for the two transitions. The NI transition is clearly first-order with a latent heat of 1.20 ±0.03 kJ/mol and a two-phase region of 52 mK. The enthalpy change at the AN transition is appreciably smaller. In the case of 8CB's AN transition,[3] there was no indication of a latent heat in the enthalpy curve. For 8CB we obtained,[3] as an upper limit for a possible latent heat, a value of 0.4 J/mol (or 1.4×10^{-3} J/g). In Figure 2 the temperature dependence of the enthalpy is given for a 23 mK temperature range around T_{AN}. These results have been obtained with a very slow scanning rate of 0.6 mK/h (at T_s). As can be observed from Figure 2, the enthalpy for 9CB changes smoothly from the S_A phase to the nematic phase. Heat capacities per mol C_p calculated with Eq. (2) from these enthalpy results give values (in units of R) between 3×10^2 (at T_s) and 2×10^3 (at T_{AN}) (cf. also Fig. 5). There is an uncertainty of about 0.5 mK in the precise location of T_{AN} (indicated by the error bars for the arrow indicating T_{AN} in Figure 2). The C_p behavior in this range also shows some rounding-off effect. If one would interpret the enthalpy change over this 0.5 mK range as a latent heat, an upper limit for ΔH_{AN} of about 5 J/mol would be obtained. This is about ten times the value for 8CB, but the total enthalpy change over the temperature range $T_{AN} \pm 10$ mK is, however, a factor of five larger for 9CB than for 8CB.

The temperature dependence of the heat capacity C_p (which corresponds to the slope of the enthalpy curve at a given temperature) for the four compounds in the liquid crystalline and isotropic phases is given in Figure 3. The different transition temperatures are also indicated along the

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[†] It has subsequently also been confirmed at BDH that recent high purity 11CB batches do not give a nematic phase and show only an AI transition around 57°C. The discrepancy with the figures quoted in the BDH catalogue is ascribed to the greater purity of recent batches of materials compared with that of the first sample which was used to obtain the original information.

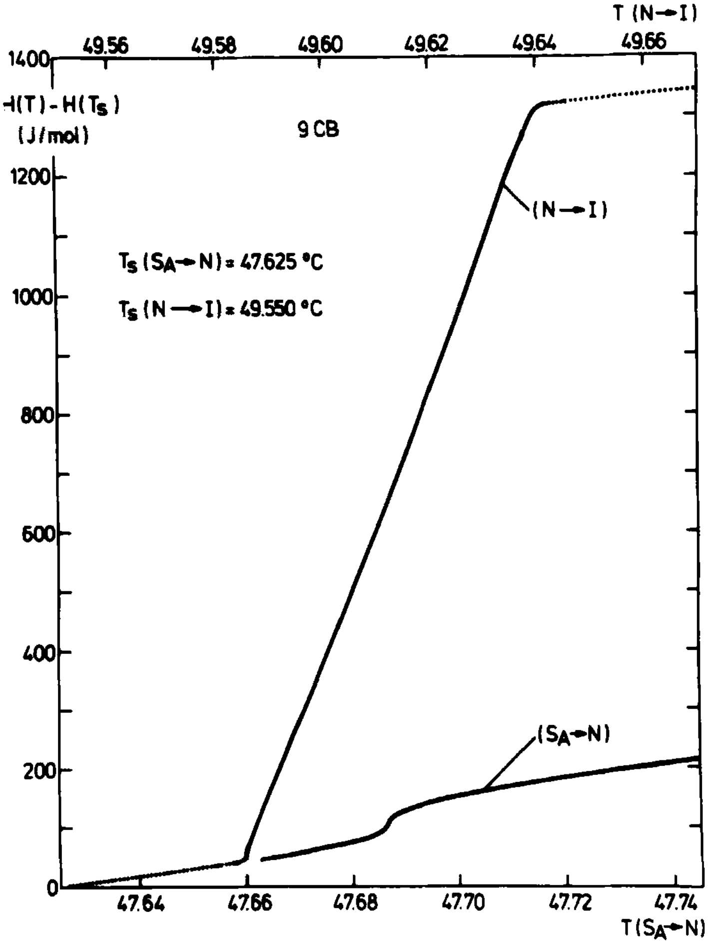

FIGURE 1 Temperature dependence of the enthalpy near the smectic-A to nematic and the nematic to isotropic phase transitions for nonylcyanobiphenyl (9CB).

temperature axis. The dashed lines at some of the transitions indicate that they are first-order; the separation of the lines indicate the width of the two-phase region which seems to decrease with decreasing chain length. On the other hand, the pretransitional effects in the I and the N or A phase near T_{NI} or T_{AI} increase with decreasing chain length. These two effects are consistent with the fact that the latent heat grows with the length of the molecules. In Fig. 4, a more detailed plot of the C_p behavior for the S_A, N and I phases near T_{AN} and T_{NI} is given for 9CB. From Figures 3 and 4 it is quite clear that the NA peak in C_p is much larger for 9CB than for 8CB.

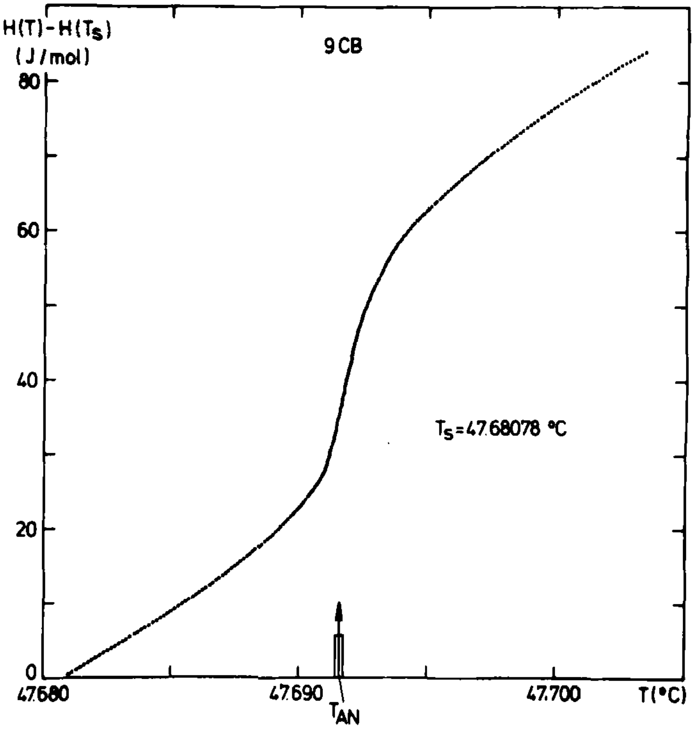

FIGURE 2 Detailed temperature dependence of the enthalpy of nonylcyanobiphenyl (9CB) near the smectic-A to nematic phase transition.

4. ANALYSIS AND DISCUSSION

In this section, we will discuss the analysis and the interpretation of the C_p anomaly at T_{AN} for 8CB and 9CB. As already pointed out above, for both compounds, we are apparently dealing with second-order phase transitions for which we can analyse the heat capacity data, given in detail in Figure 5 for 9CB and in Ref. 3 for 8CB, in terms of asymptotic power laws:

$$C_p = \frac{A}{\alpha}\varepsilon^{-\alpha} + B, \qquad (T > T_{\mathrm{AN}}) \tag{5a}$$

$$C_p = \frac{A'}{\alpha'}(-\varepsilon)^{-\alpha'} + \beta' \qquad (T < T_{\mathrm{AN}}), \tag{5b}$$

with α and α' the critical exponents, and A and A' the critical amplitudes. $\varepsilon \equiv (T - T_{\mathrm{AN}})/T_{\mathrm{AN}}$ and B and B' represent the noncritical background contributions. Information on the parameters in Eqs. (5), in particular

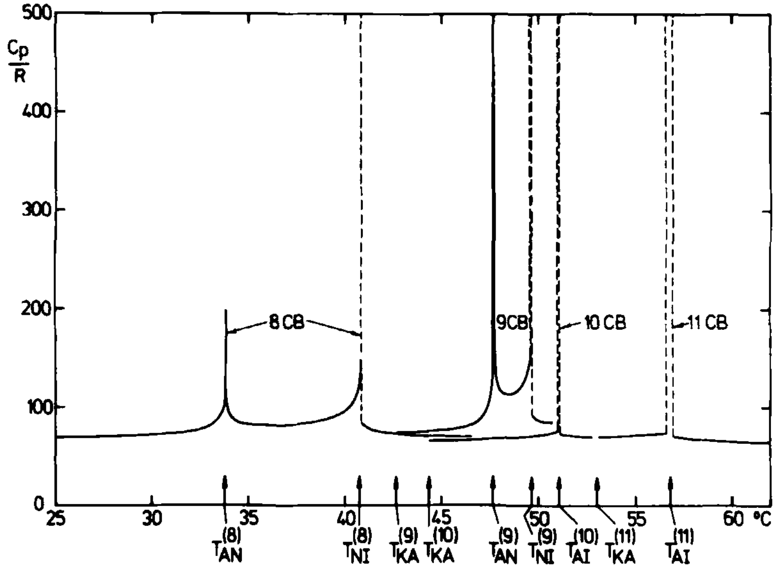

FIGURE 3 Reduced heat capacity per mol (R is the gas constant) for four different alkylcyanobiphenyls (nCB) in the liquid crystalline and the isotropic phases as a function of temperature. The vertical dashed lines indicate the first-order nature of the transition, and the separation between the lines for a given transition corresponds with the two-phase region. The transition temperatures are indicated along the temperature axis (KA: solid to smectic; AN: smectic-A to nematic; NI: nematic to isotropic; AI: smectic-A to isotropic). The superscripts between parenthesis give the number of carbon atoms in the alkyl chain of the relevant alkylcyanobiphenyl.

about α and α', can be deduced from the C_p data by means of nonlinear least-squares procedures. We have done that in detail for 8CB in Ref. 3. But as pointed out there also, there is a much more attractive way of arriving at the α and α' values. This can be done by introducing the following experimental quantity (for $T > T_{AN}$):

$$C(T) \equiv \frac{H(T) - H(T_{AN})}{T - T_{AN}} = \frac{P(t - t_{AN})}{T - T_{AN}}, \tag{6}$$

with T_{AN} the transition temperature and t_{AN} the time during the constant heating run at which T_{AN} is reached. It can be easily verified[3] that if Eq. (5a) applies for the heat capacity C_p, it follows that:

$$C(T) = \frac{A}{(1 - \alpha)\alpha}\varepsilon^{-\alpha} + B \tag{7}$$

Thus $C(T)$ diverges with the same critical exponent α, but with an amplitude modified by a factor $(1 - \alpha)^{-1}$. Similar results for $T < T_{AN}$ with

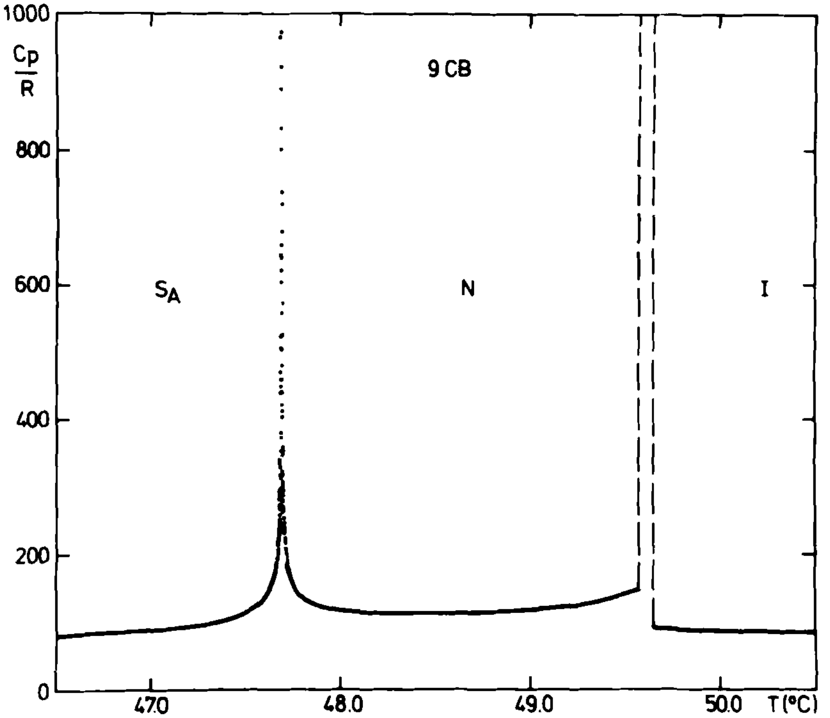

FIGURE 4 Reduced heat capacity per mol for nonylcyanobiphenyl (9CB) near the phase transitions in the smectic-A (S_A), the nematic (N) and the isotropic (I) phases. The width of the two-phase region for the NI transition is indicated by the two vertical dashed lines.

primed symbols can be derived. Combining Eqs. (5a) and (7) gives also the following interesting result:

$$C - C_p = \frac{A}{1-\alpha}\varepsilon^{-\alpha} \tag{8}$$

This way of presenting the $C(T)$ and $C_p(T)$ data has the great advantage that the adjustable parameter B is eliminated and that in a double logarithmic plot, a linear relationship is found between $(C - C_p)$ and ε. In Figure 6 $(C - C_p)$ results for 9CB are given on a double logarithmic scale. In Figure 6, our data for a run with $\dot{T} \simeq 25$ mK/h at $T_{AN} - T = 0.05$°C are given. For comparison purposes, the previously[3] obtained results for 8CB with a comparable scanning rate are also given in Figure 6. In the case of 8CB, we obtained for the critical exponents α and α' as a best value $\alpha = \alpha' = 0.32$. For 9CB the much larger value $\alpha = \alpha' \simeq 0.50$ is obtained.

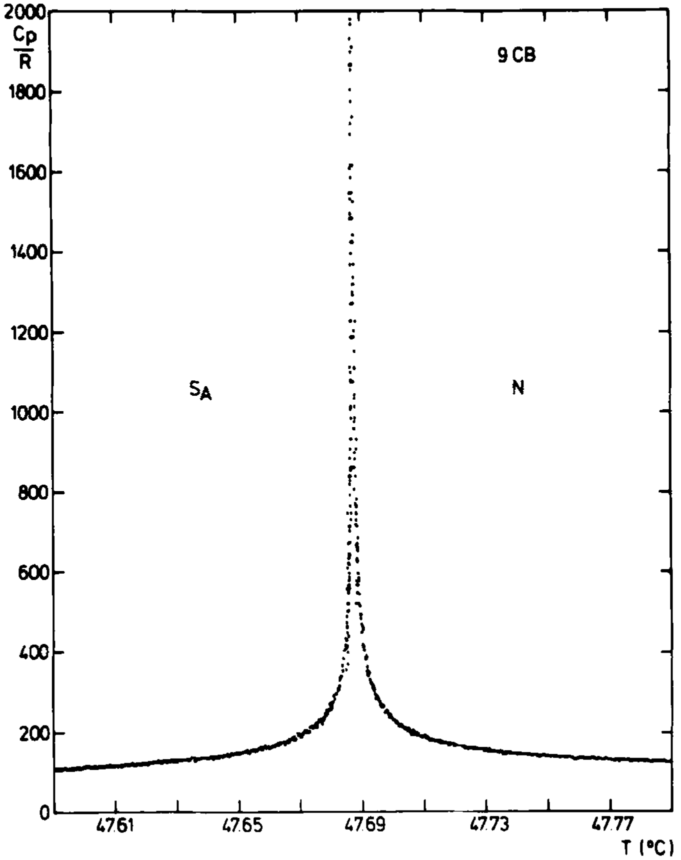

FIGURE 5 Detailed plot of the reduced heat capacity per mol for nonylcyanobiphenyl near the smectic-A to nematic phase transition.

If the above α values coincide with the asymptotic values at the critical point, one would have a different universality class for the 8CB and the 9CB AN phase transitions. However, these α values are also quite different from the theoretically expected value. Indeed, on the basis of the dimensionality of the order-parameter and considering the analogy with the λ-transition in helium and with the normal to superconducting transition, it was suggested[7] that one should observe XY-critical behavior (with $\alpha = \alpha' = -0.02$) for second-order AN transitions in liquid crystals. It has been pointed out by de Gennes[7] that this transition can be first-order as well, depending on the width of the nematic range. Large nematic ranges would give second-order transitions, while small N-ranges result in first-

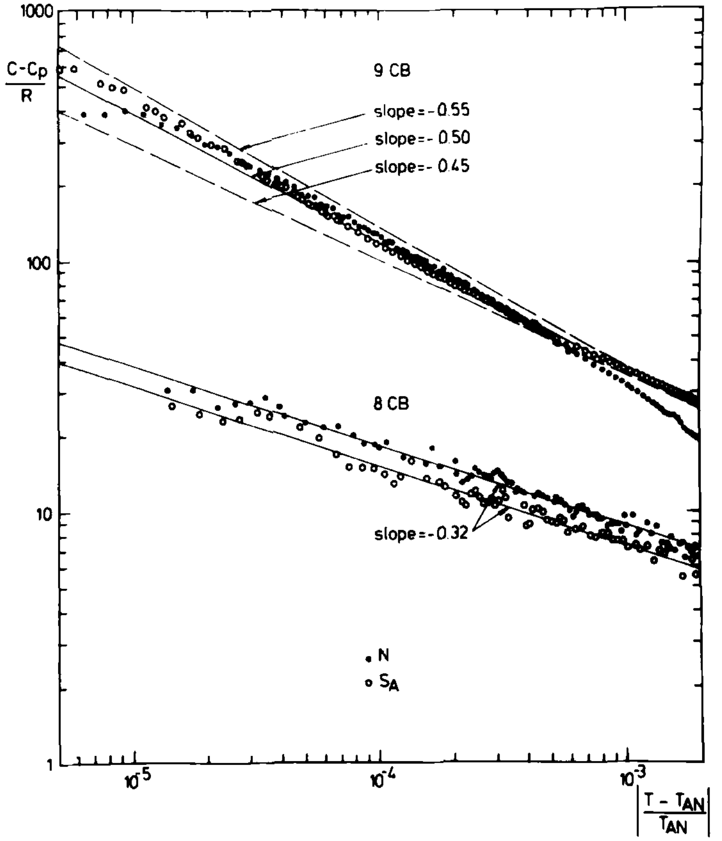

FIGURE 6 Double logarithmic plot of $(C-C_p)/R$ *vs* the reduced temperature difference with the smectic-A to nematic phase transition temperature T_{AN} for octylcyanobiphenyl (8CB) and nonylcyanobiphenyl (9CB). C and C_p are, respectively, the quantity defined in Eq. (6) and the heat capacity per mol. Open symbols are for the smectic-A phase and solid ones for the nematic phase.

order transitions. A tricritical point occurs at the change from first to second order. This picture is consistent with the result of a molecular model[8] where a tricritical point is obtained for $T_{AN}/T_{NI} = 0.88$. An $\alpha = \alpha'$ value of 0.5 is expected at a tricritical point.[9]

From the fact that the transition is second-order for 8CB (with $T_{AN}/T_{NI} = 0.978$) and also for 9CB (with $T_{AN}/T_{NI} = 0.994$), where the N-range is only 1.90°C, it is clear that the predicted tricritical point must occur for very narrow nematic ranges, or T_{AN}/T_{NI} values much closer to 1 than the model[8] value of 0.88. The fact that for 9CB the exponent α is consistent with the tricritical value of 0.5 indicates, however, that this AN-transition is very close to the tricritical point and suggests that the experimental data have been measured in the tricritical region. It follows then that for 8CB, where the AN transition point is farther from the tricritical point, the α value should be considered as an effective one, reflecting a crossover behavior between tricritical and XY critical behavior. This decrease in effective α value with decreasing T_{AN}/T_{NI} ratio is consistent with a general trend in the available literature values for different liquid crystals (see *e.g.* Figure 12 of Ref. 3). It is certainly very much in agreement with the results obtained by Brisbin *et al.*[10] for three compounds of the 4-n-pentylphenyl 4′-n-alkylthiolbenzoate ($\bar{n}$S5) homologous series. For $\bar{8}$S5 (with $T_{AN}/T_{NI} = 0.936$) a nearly logarithmic singularity ($\alpha \simeq 0$) was obtained, for $\bar{9}$S5 (with $T_{AN}/T_{NI} = 0.966$) α was 0.22, and finally for $\overline{10}$S5 (with $T_{AN}/T_{NI} = 0.988$) they found $\alpha \simeq 0.45$.

From the existing calorimetric information, the conclusion seems to arise that in order to observe the theoretically predicted XY-behavior for second-order AN transitions, systems should be chosen with $T_{AN}/T_{NI} < 0.94$. As far as the tricritical point is concerned, one can conclude that it could possibly be found for systems with very narrow nematic ranges. If T_{AN}/T_{NI} is the only relevant parameter for all the different systems, and assuming that our 9CB results prove the absence of a first-order effect for 9CB, the tricritical T_{AN}/T_{NI} value should be closer to 1 than 0.994. In order to clarify this question and to locate the tricritical point, measurements with mixtures of alkylcyanobiphenyls with very narrow nematic ranges are in progress.

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References

1. D. L. Johnson, C. F. Hayes, R. J. DeHoff and C. A. Schantz, *Phys. Rev. B*, **18**, 4902 (1978); C. W. Garland, G. B. Kasting and K. J. Lushington, *Phys. Rev. Lett.*, **43**, 1420 (1979).
2. J. Thoen, E. Bloemen and W. Van Dael, *J. Chem. Phys.*, **68**, 735 (1978); E. Bloemen, J. Thoen and W. Van Dael, *J. Chem. Phys.*, **73**, 4628 (1980); E. Bloemen, J. Thoen and W. Van Dael, *J. Chem. Phys.*, **75**, 1488 (1981).
3. J. Thoen, H. Marynissen and W. Van Dael, *Phys. Rev. A*, **26**, 2886 (1982).
4. J. Thoen, E. Bloemen, H. Marynissen and W. Van Dael, *Proceedings of the 8th Symposium of Thermophysical Properties*, Natl. Bur. Stand., Maryland, 1981, (American Society of Mechanical Engineers, New York, 1982).
5. BDH Chemicals Ltd Catalogue (Poole Dorset, U.K., 1979).
6. H. J. Coles and C. Strazielle, *Mol. Cryst. Liq. Cryst.*, **55**, 237 (1979).

7. P. de Gennes, *Solid State Commun.*, **10**, 753 (1972); *The Physics of Liquid Crystals*, Clarendon, Oxford, (1974).
8. K.K. Kobayashi, *Phys. Lett. A*, **31**, 125 (1970); *J. Phys. Soc. Jap.*, **29**, 101 (1970); W.L. McMillan, *Phys. Rev. A*, **4**, 1238 (1971).
9. R. Bausch, *Z. Physik*, **254**, 81 (1972); R.B. Griffiths, *Phys. Rev. B*, **7**, 545 (1973).
10. D. Brisbin, R. DeHoff, T.E. Lockhart, and D.L. Johnson, *Phys. Rev. Lett.*, **43**, 1171 (1979).