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STUDY OF THE SMECTIC A NEMATIC TRANSITION IN OCTYL AND NONYL CYANOBIPHENYL

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ABSTRACT: A new DSC method is used to study a smectic A to nematic transition. The measurement of the height of the DSC transition peak gives the order of the transition. The smectic A to nematic transition of octyl cyanobiphenyl was found to be second order while the same transition was found to be first order for nonyl cyanobiphenyl.

Characterization of the nematic (N) to smectic A (S) transition in liquid crystals is a problem of current interest. Several theoretical studies[1-3] have shown that the width of the nematic temperature range may determine the order of the S→N phase transition. The alkyl cyanobiphenyl series has recently been used to confirm this theory and a tricritical point in which a phase transition passes from second to first order was found to occur for $n=9$, where n is the number of carbon atoms in the alkyl chain.[4-5] In spite of the fact that the cyanobiphenyl series has been known for nearly ten years, the second order nature of the S→N transition in octyl cyanobiphenyl (8CB) has been discovered only recently.[6-9] The reason for this is mainly that up to the present the order could only be determined by adiabetic calorimetry, a time consuming technique not often used when compared to DSC. Differentiation between first and second order transitions by DSC has not been possible due to the similarity of the peaks for each of these types of transition and the S→N transition of 8CB determined by DSC had always been regarded as first order, with a latent heat in the range of 0.1 to 0.3 cal/mole.[10-13] Later work however, using abiabatic calorimetry has shown no latent heat.[4,7] This was later confirmed by measurements of X-ray scattering.[5]

A method for differentiation between first and second order transitions for pure single components has recently been proposed.[14] This consists of measuring the height of the transition peak (H) at two heating rates, one being twice the other as illustrated in Fig. 1.

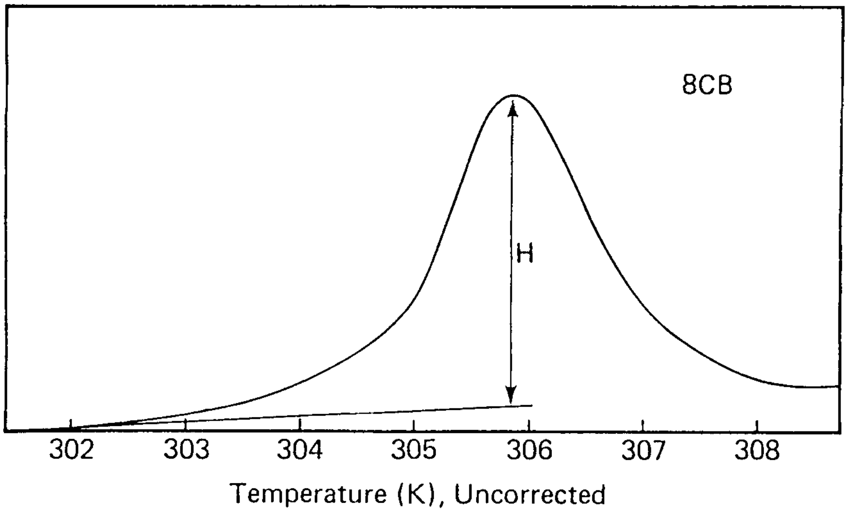

FIGURE 1. DSC trace of a 19 mg sample of 8CB Smectic-Nematic transition. Heating rate 10K min^{-1}. Temperature scale not corrected. H is the height of the peak.

The ratio (N) of the measured heights is $1<N\sqrt{2}$ for an isothermal first order transition and $N=2$ for a second order transition. A problem arises because an impurity in a compound may change the value of N so that a first order transition may have $N>\sqrt{2}$, and an independent determination of purity thus becomes necessary. Many liquid crystalline compounds have multiple transitions, and it has been established that at least two of these, the crystal to smectic (K→S), and the nematic to isotropic (N→I) are first order. Thus by running DSC's the application of our theory to liquid crystals exhibiting several transitions can readily be checked.

The aim of the present work is, therefore, to measure the value of N in the octyl and nonyl cyanobiphenyls for the K→S, S→N, and N→I transitions and to see if the transition orders as determined by these measurements are the same as those found recently by abiabatic calorimetry.

8CB was purchased from British Drug House Ltd., and was used without further purification. Nonyl cyanobiphenyl (9CB) was prepared at the IBM Laboratories and was found to be 99% pure.[13] Both samples were studied using a Perkin Elmer DSC2 controlled by a Model 3600 Data Station. The measured enthalpies and transition temperatures of these two materials agreed with the DSC literature values.[10-13]

The values of N for the K→S, S→N, and N→I transitions for 8CB and 9CB are reported in Table 1.

TABLE 1. N ratio for the three transitions (K→S, S→N, N→L) of 8CB and 9CB. The heating rates were 5 and 10K min^{-1}.

	Crystal-Smectic	Smectic Nematic	Nematic-Liquid
8CB	1.29	2.05	1.32
9CB	1.40	$1.1<N<1.4$	1.36

N for these materials is below 2 for both the K→S and N→I transitions, as predicted for first order transitions. We can therefore interpret with confidence, the values of N for the other transitions occurring in these compounds. N for the S→N transition of 8CB is 2, indicating a second order and is between 1.1 and 1.4 for the same transition in 9CB, indicating first order for this transition. The reason for the large experimental discrepancy in the latter case is due to the difficulty in defining a proper baseline, and we have reported the two extreme possibilities. The result nevertheless, indicates unambiguously that the transition is first order. As found by adiabatic calorimetry and x-ray scattering,[4,5] 8 CB has a second order S→N transition, as also found by our method. 9 CB, according to the same two techniques, is at the tricritical point and thus should rigorously be second order. This result was found for very slow heating rates. We found a first order character for this transition. This contradiction may be due to the large difference in heating rate between DSC and the other techniques and to the fact that 9 CB is just at the frontier between second and first order. Confusion between the occurrence of a DSC peak and the first order nature of such a transition can therefore be resolved as seen for 8 CB. This new technique for determination of transition order is very sensitive, and moreover does not require that the DSC measurements be made with any special degree of care. It is a fast and convenient method for determination of the tricritical point in a homogeneous liquid crystalline series, and can be used to select the particular compound of choice in such a series when one wishes to study tricritical phenomena in detail using adiabatic calorimetry.

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