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A NEW MULTICRITICAL POINT IN A SINGLE COMPONENT LIQUID
CRYSTAL: HIGH PRESSURE STUDY OF DOBBCA

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We report here the results of our high pressure optical and DTA studies on the compound 4(4-n-decyloxybenzoyloxy)-benzylidene-4'-cyanoaniline. The P-T diagram shows a new kind of multicritical point, viz., a reentrant nematic-smectic C-smectic A point at 0.52 ± 0.02 kbar, $86.2 \pm 0.2^\circ\text{C}$.

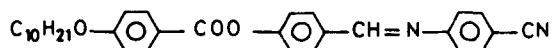
INTRODUCTION

The first observation of the nematic-smectic A-smectic C (NAC) point was reported by Johnson et al¹ in the temperature-concentration diagram of binary mixtures of 4-n-pentyl-phenylthiol-4'-heptyloxybenzoate ($\bar{7}S5$) and 4-n-pentyl-phenylthiol-4'-octyloxybenzoate ($\bar{8}S5$). Sigaud et al² also found a binary liquid crystal system which exhibits the NAC point with a slightly different topology. Although Chen and Lubensky³ had predicted that the NAC point should be a Lifshitz point, the subsequent high resolution X-ray studies of Safinya et al⁴ and AC calorimetric studies of de Hoff et al⁵ indicated that the NAC point is not a Lifshitz point but a multicritical point. We undertook pressure studies on a number of compounds with a view to observing such a point in the P-T diagram of a single component liquid crystal system. In an earlier paper⁶ we reported our results on

N-(4-n-pentyloxybenzylidene)-4'-n-hexylaniline (or 50.6) but the NAC point proved to be elusive. We now present the results of our pressure studies on 4(4-n-decyloxybenzoyloxy)-benzylidene-4'-cyanoaniline (hereafter abbreviated as DOBBCA)⁷ which have led to the first observation of a multicritical point in a single component system.

EXPERIMENTAL

The compound (kindly provided to us by Dr. D. Demus) has the structural formula



and exhibits the nematic, smectic A, smectic C and reentrant nematic (RN) phases, in that order, on cooling from the isotropic phase. The temperatures of the various transitions as measured by optical microscopy are given in Table 1.

Table 1
Transition temperatures (at atmospheric pressure)
of DOBBCA

<u>Transition</u>	<u>Temperature (°C)</u>
Reentrant nematic-smectic C (RN-C)	65.1
smectic C - smectic A (C-A)	76.2
smectic A - nematic (A-N)	231.8
nematic - isotropic (N-I)	242.3

The high pressure experiments were conducted using two types of cells, a sapphire optical cell which makes use of the light transmission technique for the detection of the phase transitions, and a DTA cell. Details of these cells are given elsewhere^{8,9} and will not be repeated here. The accuracies of pressure and temperature measurements are ± 15 bar and $\pm 0.05^\circ\text{C}$.

RESULTS AND DISCUSSION

Since the nematic-isotropic transition temperature is rather high (242.3°C) even at atmospheric pressure, this transition could not be studied as a function of pressure. This is essentially because the seals used in the pressure cell become soft and unusable at these temperatures. For the same reason the A-N transition has been followed only up to about 100 bars. On the other hand the melting transition as well as the C-A, and RN-C transitions all occur at relatively low temperatures and could therefore be followed easily. Figure 1 shows the P-T diagram of DOBBCA determined up to 240°C , while Figure 2 gives the data for the RN, C and A phases up to 800 bars only on an enlarged scale. The interesting result emerges that the range of the smectic C phase which is 11.1°C at 1 bar decreases rapidly with increase of

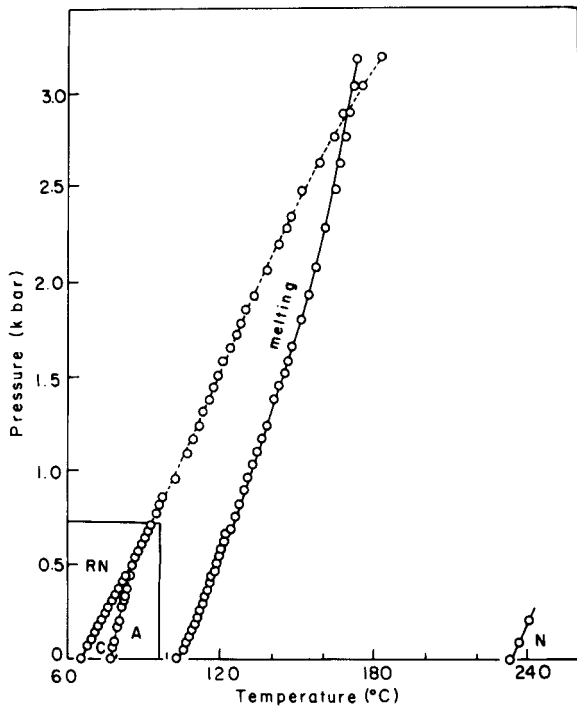


FIGURE 1
P-T diagram of DOBBCA determined up to about 240°C .

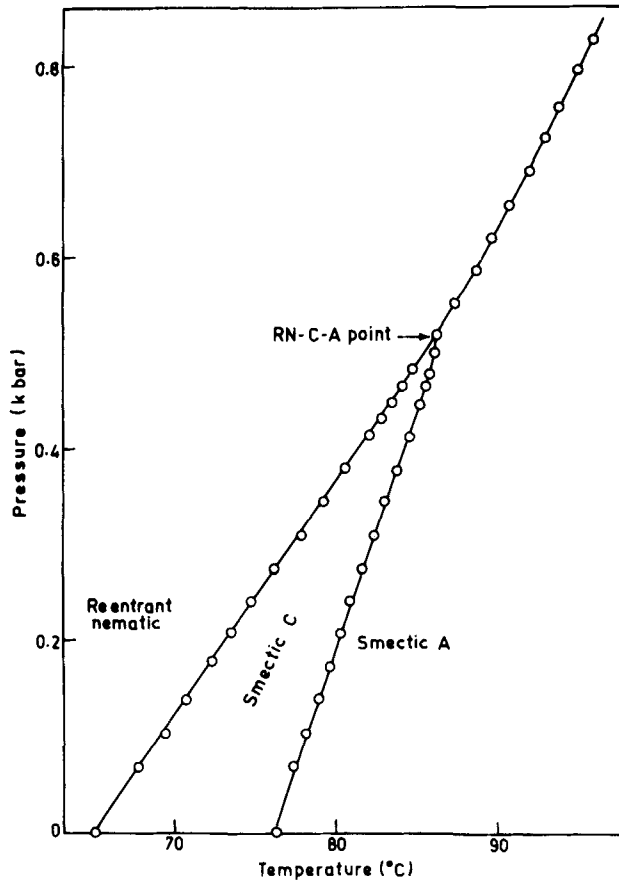


FIGURE 2: P-T diagram of DOBBCA (on an enlarged scale) showing the data for the reentrant nematic, smectic C and smectic A phases up to 800 bars.

pressure and is ultimately bounded. The RN-C-A point occurs at 0.52 ± 0.02 kbar, $86.2 \pm 0.2^\circ\text{C}$. Experiments have also been conducted using the DTA cell to determine the nature of the transitions close to the RN-C-A point. It was observed that the RN-C and C-A transitions which are second-order-like⁷ remain so even at high pressures while the RN-A transition, which exists only beyond 0.52 kbar, is always first order. In other words, it appears that the two

second order phase boundaries (RN-C and C-A) culminate and continue as a first order (RN-A) phase boundary in the P-T plane. We have thus obtained a new kind of multicritical point.

As regards the topology of the P-T diagram, the following results may be seen from the enlarged section of the diagram (Figure 2). (i) Neither the RN-C nor the C-A line is collinear with the RN-A line through the RN-C-A point, (ii) the C-A boundary is straight till very close to the RN-C-A point and exhibits a curvature near it, and (iii) the RN-A phase boundary, particularly beyond 1.7 kbar, starts curving towards the temperature axis as is indeed expected, since the AN phase boundary has generally an elliptic shape. It must be mentioned that on the basis of topology alone we are unable to make any definitive conclusions regarding the nature of the RN-C-A point. Experiments like measurements of elastic constants, high resolution X-ray studies are required to be conducted at high pressures in order to provide more information concerning the nature of this point.

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