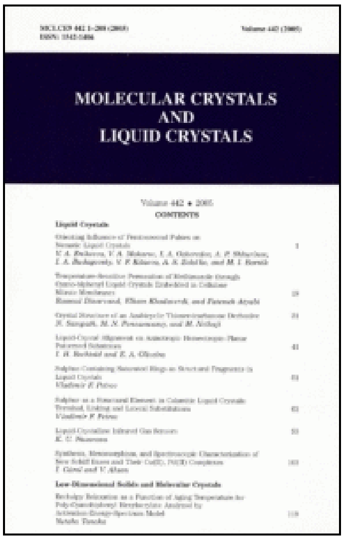

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The Topology of the P-T Diagram of DOBBCA in the Vicinity of the Reentrant Nematic–Smectic C–Smectic A Multicritical Point†

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The P-T diagram of 4(4-*n*-decyloxybenzoyloxy)-benzylidene-4′-cyanoaniline shows a new kind of multicritical point, viz., a reentrant nematic–smectic C–smectic A point, at 0.55 ± 0.01 kbar and 86.8 ± 0.1 °C. The topology of the diagram close to this point has been studied using precise optical high pressure techniques.

I. INTRODUCTION

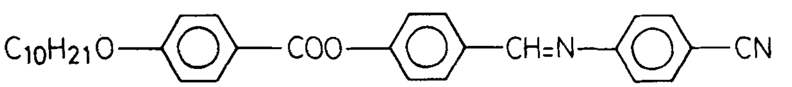
The nematic–smectic A–smectic C multicritical point (hereafter called the NAC point) was first observed in the temperature-concentration diagram of binary liquid crystal systems by Johnson *et al.*[1] in 4-*n*-pentyl-phenylthiol-4′-heptyloxybenzoate / 4-*n*-pentyl-phenylthiol-4′-octyloxy-benzoate ($\bar{7}$S5/$\bar{8}$S5) mixtures and independently by Sigaud *et al.*[2] in 2-*p*-*n*-heptyloxybenzylidene amino fluorene/4′-*n*-octyloxy-4-cyanobiphenyl (70NE/80CB) mixtures. Very recently several other binary systems have been found[3,4] which show the NAC point. There have also been high resolution a.c. calorimetric[5] and X-ray[6] studies on the $\bar{7}$S5/$\bar{8}$S5 system which have initiated explicit comparisons with theoretical predictions.[7,8] We undertook pressure studies on a number of compounds with a view to observing the NAC point in the P-T diagram of a single component liquid crystal system. In an earlier

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 1982.

paper[9] we reported our results on *N*-(4-*n*-pentyloxybenzylidene)-4′-*n*-hexylaniline (or 50.6) but the NAC point proved to be elusive. We then studied 4(4-*n*-decyloxybenzoyloxy)benzylidene-4′-cyanoaniline (hereafter abbreviated as DOBBCA)[10] and these studies led to the observation of a new kind of multicritical point, viz., the reentrant nematic–smectic C–smectic A (or RN–C–A) point.[11] However, the accuracy of the measurements was such that no definitive conclusions could be drawn about the topology of the diagram in the vicinity of this point. We have subsequently improved the precision of our measurements considerably and with this high precision set up have re-determined the P-T diagram of DOBBCA, with particular attention to the data points close to the RN–C–A point.

2. EXPERIMENTAL

The compound, which was kindly provided to us by Dr. D. Demus, has the following structural formula and exhibits the nematic, smectic A, smectic C and reentrant nematic phases, in that order, on cooling from the isotropic phase. The temperatures of the various transitions, as determined by using a polarizing microscope equipped with a Mettler FP52 hot stage, are given in Table I.



The pressure dependence of the phase transitions was studied by the optical transmission technique. An optical high pressure cell equipped with sapphire windows was used. The liquid crystalline sample was sandwiched between the two optically polished sapphire cylinders and enclosed inside a fluron tube. The transmitted light was monitored by a photocell. The experiments were always conducted along isobars, i.e., the transition temperature at any given pressure was determined by keeping the pressure constant and varying the temperature at a rate

TABLE I

Transition temperatures (at atmospheric pressure) of DOBBCA

Transition	Temperature (°C)
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

of about 1°C/min. The temperature at which there was an abrupt change in the transmitted light intensity was taken as the transition point. Further details of the experimental set up are described elsewhere.[12,13] The significant improvement in the present set up was that the pressure was measured electronically using a transducer (BLH-GP, Waltham, USA) and was continuously monitored during the experiment. The accuracy in the determination of the relative variations of pressure was ±0.3 bar (compared to the earlier accuracy of ±15 bars[11]) while that for temperature determination was ±0.025°C.

3. RESULTS AND DISCUSSION

As the aim of the experiment was to map accurately the topology of the phase boundaries in the neighbourhood of the RN–C–A point, only the RN–C, C–A and at higher pressures the RN–A transitions have been studied as functions of pressure. The P-T diagram of DOBBCA showing these transitions up to a pressure of 800 bar is given in Figure 1. It is clearly seen that the range of the C phase which is 11.1°C at 1 bar decreases with increasing pressure and is ultimately

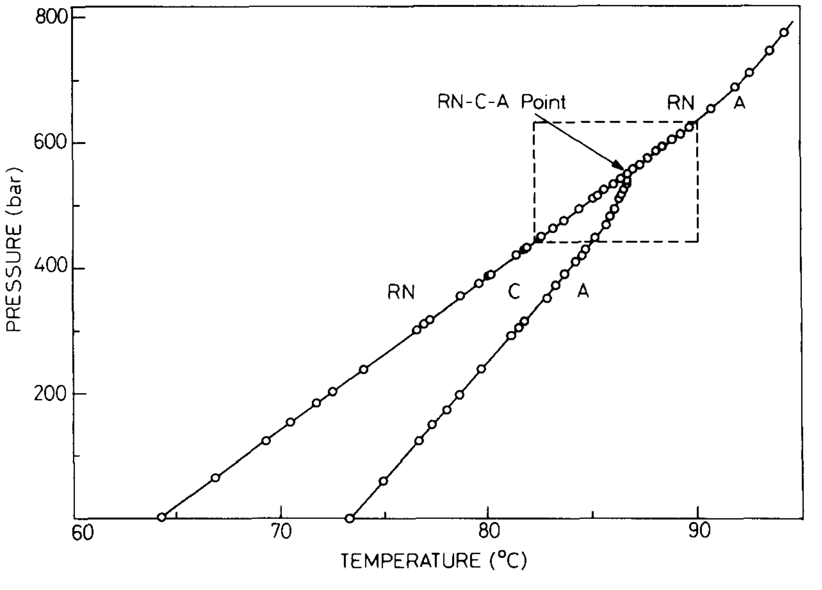


FIGURE 1 P-T diagram of DOBBCA showing the data for the reentrant nematic, smectic C and smectic A phases up to 800 bar. The section of this diagram marked within the dashed lines is shown on an enlarged scale in Figure 2.

bounded. The RN–C–A point occurs at 0.55 ± 0.01 kbar and 86.8 ± 0.1°C. We also conducted high pressure DTA experiments (see ref. 14 for details of the cell used) to determine the nature of the transitions close to the RN–C–A point. A very high gain had to be used and it was observed that both the RN–C and C–A transitions, which are second order at atmospheric pressure, remain so right up to the RN–C–A point. As regards the RN–A transition which exists only beyond 0.55 kbar, it was also found to be a second order transition with somewhat larger pretransitional effects.

We shall now consider the topology of the P-T diagram close to the RN–C–A multicritical point. Figure 2 shows an enlarged section of the P-T diagram in the vicinity of this point. It may be mentioned that the transitions become sharper as the RN–C–A point is approached and as a consequence the accuracy of the data close to the RN–C–A point is in fact better than that stated earlier. The following points are seen from the diagram: (i) The RN–C and RN–A boundaries are *collinear* at the RN–C–A point. (This is at variance with what we had stated earlier[11] on the basis of our less precise measurements which revealed only the gross features of the phase diagram.) The RN–A line

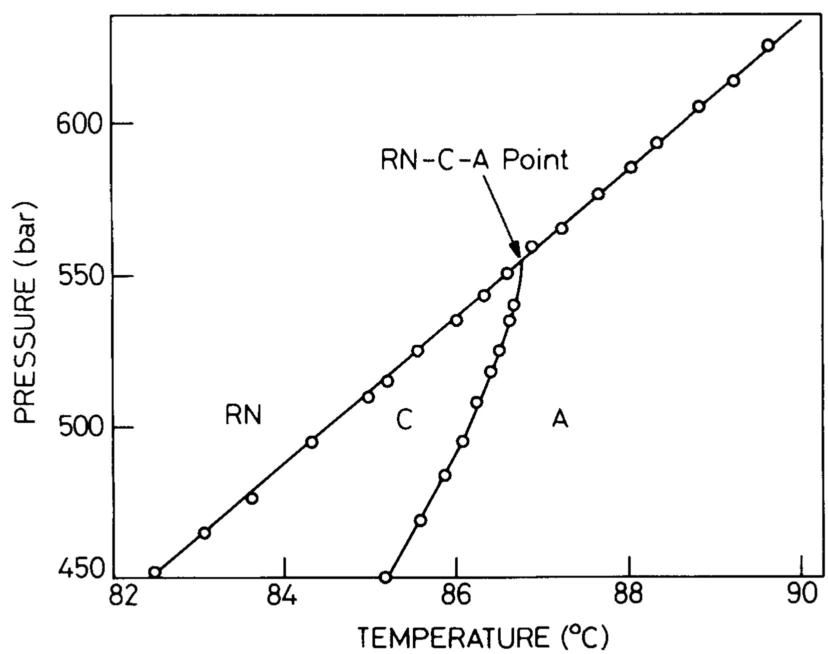


FIGURE 2 Enlarged section of the P-T diagram of DOBBCA in the vicinity of the RN–C–A multicritical point.

continues to be straight till about 620 bars beyond which it starts showing a pronounced curvature towards the pressure axis (see Figure 1). (ii) The C–A boundary is initially straight but exhibits a curvature as it approaches the RN–C–A point.

After completion of these experiments we learnt that Sigaud *et al.*[15] have observed a similar RN–C–A point (they have referred to it as the 'inverted NAC point') in the temperature-concentration (T-X) diagram of a binary liquid crystal system consisting of DOBBCA and 4-cyanobenzylidene-4′-(4″-decyloxybenzoyloxy)aniline. These two compounds are very similar in their molecular structure, the only difference being that in the latter compound the direction of the linking Schiff base group is reversed. Figure 3 shows the T-X diagram obtained by Sigaud *et al.*[15] Interestingly the topology of this diagram is very similar to that of our P-T diagram for DOBBCA.

It must also be mentioned that very recently Brisbin *et al.*[3] showed on the basis of their high resolution T-X diagrams for 4 binary liquid crystal mixtures that the topology of the NAC diagram is universal. However the RN–C–A multicritical point seems to show a different

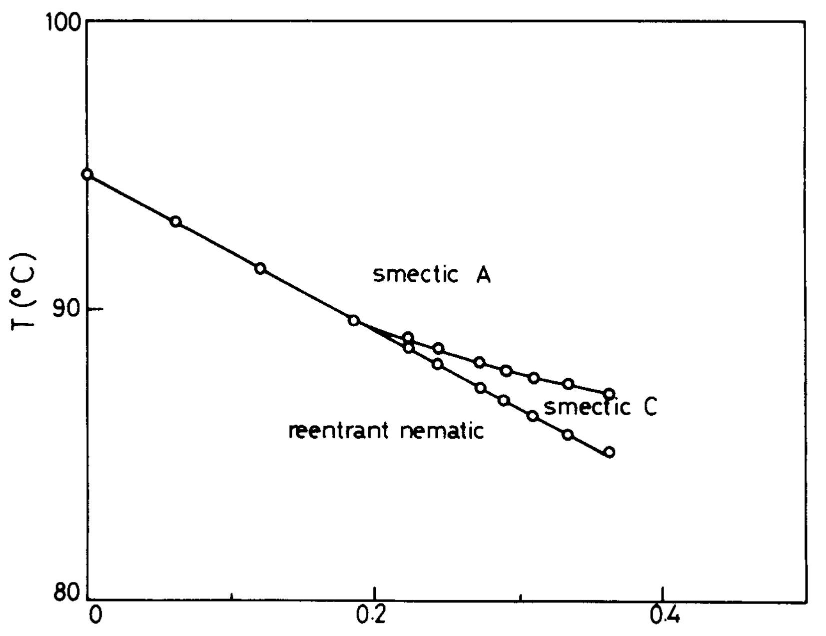


FIGURE 3 Binary phase diagram (at atmospheric pressure) of the liquid crystal mixtures of DOBBCA and 4-cyanobenzylidene-4′-(4″-decyloxybenzoyloxy) aniline. X denotes the mole fraction of DOBBCA in the mixture. (From Sigaud *et al.*[15]).

kind of topology both in the P-T and T-X diagrams. More systems exhibiting the RN–C–A point need to be studied both at high pressures and at atmospheric pressure to see if the topology of the RN–C–A diagram, which is different from that of the NAC diagram, is also universal.

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