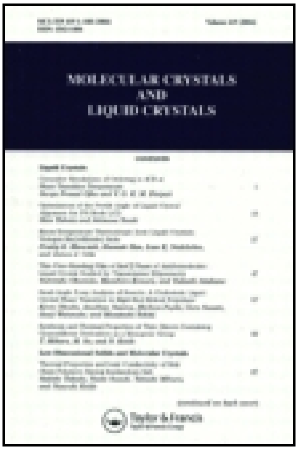

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High Pressure Studies on Partially Bilayer and Monolayer Smectics

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High Pressure Studies on Partially Bilayer and Monolayer Smectics[†]

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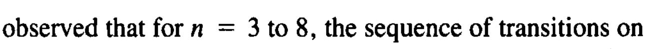
We have carried out pressure studies on the eighth and ninth members of the homologous series 4-alkoxybenzoyloxy-4′-cyanoazobenzene (nOBCAB). It is found that the pressure behavior of the monolayer smectic A (A_1) phase is entirely different from that of the partially bilayer smectic A (A_d) phase. The A_1-nematic phase boundary is a straight line at all pressures and the range of the A_1 phase increases with increasing pressure. On the other hand, the A_d-nematic phase boundary is elliptic in shape and the A_d phase gets bounded. These results emphasize the fact that the pressure behavior of the A phase is strongly related to the extent of overlap of the molecules in the layer.

INTRODUCTION

After the first observations of the reentrant nematic phase in pure compounds at atmospheric pressure[1,2] there has been a surge of activity in synthesizing more such compounds.[3] Among the first substances to be synthesized were those belonging to the homologous series 4-alkoxybenzoyloxy-4′-cyanoazobenzenes[4,5] (nOBCAB) which have the following structural formula



It was observed that for $n = 3$ to 8, the sequence of transitions on cooling was: isotropic → nematic → smectic A → solid. For the 9th and 10th

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

homologues the sequence was isotropic → nematic → smectic A → reentrant nematic → reentrant smectic A → solid. Several experimental studies[6–9] have been made on the 8th and 9th homologues, in particular, to compare the properties of the two nematic and the two smectic A phases. We have conducted high pressure studies on 8 OBCAB and 9 OBCAB to see if there is any difference in the pressure behavior of the two smectic A phases.

EXPERIMENTAL

The compounds were synthesized as described in an earlier paper.[4] The transition temperatures, as determined by optical microscopy, are given in Table I. The heats associated with the nematic-smectic A, smectic A-reentrant nematic and the reentrant nematic-reentrant smectic A transitions were too small to be determined accurately by DSC. In order to ascertain the nature of the A phases at atmospheric pressure, X-ray diffraction studies have been made on both 8 OBCAB and 9 OBCAB. The X-ray photographs were taken using quartz crystal monochromated copper K_α radiation. The sample, sealed in a Lindemann capillary, was aligned in a ~5 KG magnetic field (applied along the axis of the capillary tube). The relative accuracy in the layer spacing determination is ±0.1 Å, the temperature being maintained during the exposure to an accuracy of ±0.25°C.

The transition temperatures at high pressure were determined by the optical transmission technique using a high pressure optical cell. There was, however, a difficulty in that for both the compounds the molecules have a natural tendency for homeotropic alignment which makes the de-

TABLE I

Transition temperatures (in °C) of 8 OBCAB and 9 OBCAB

Compound	Transition	Temperature
8 OBCAB	*K* – *A*	93.0
	A – *N*	97.0
	N – *I*	257.5
9 OBCAB	*K* – *RN*	94.0
	RN – *A*	116.0
	A – *N*	212.4
	N – *I*	242.9
	RN – *RA*	(70.9)

K–crystal, *A*–smectic A, *N*–nematic, *I*–isotropic, *RN*–reentrant nematic, *RA*–reentrant smectic A; ( ) denotes monotropic transition.

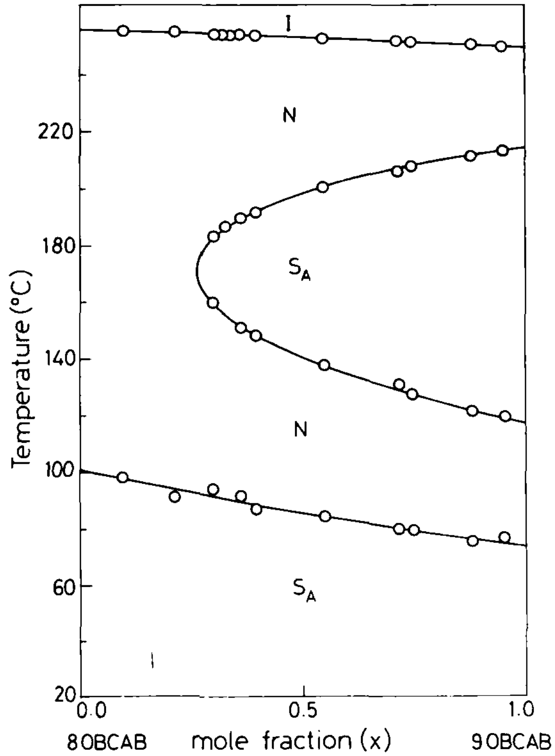

FIGURE 1 Binary diagram of 8 OBCAB/9 OBCAB mixtures. X corresponds to the mole fraction of 9 OBCAB in the mixture.

tection of the transition by the optical transmission technique rather difficult. To avoid such an alignment it was necessary to deposit SiO at an oblique angle on the surfaces of the sapphire rods in contact with the sample. Further details regarding the pressure cell have already been described elsewhere[10,11] and are therefore not repeated here. Pressures were measured to an accuracy of ± 10 bars and temperatures to ±0.025°C.

RESULTS AND DISCUSSION

(a) *Miscibility Studies*: As mentioned earlier, 8 OBCAB exhibits one smectic A phase while 9 OBCAB shows two such phases. We have studied the binary phase diagram of these compounds (Figure 1). It is seen that the lower temperature (i.e., the reentrant) smectic A phase of 9 OBCAB is completely miscible with the smectic A phase of 8 OBCAB. The higher temperature smectic A phase of 9 OBCAB is completely bounded and does not exist for mixtures with less than 0.28 mole fraction of 9 OBCAB. These results are in accord with the preliminary studies reported earlier.[12]

(b) *X-ray studies*: We have also determined the layer spacing (d) in the smectic A phases of both compounds. The value of d in the A phase of 8 OBCAB is 30.2 Å and is temperature independent. The length of the molecule (1) measured in its most extended configuration (using the Dreiding model) is 32 Å. Hence the smectic A phase of 8 OBCAB is a monolayer A (A_1) phase with a $d/1$ ratio of 0.95 which does not vary with temperature. In the case of 9 OBCAB we have found that the lower temperature A phase is again a monolayer A phase ($d/1 = 0.95$) with a temperature independent layer spacing of 31.4 Å. On the other hand, for the higher temperature A phase of 9 OBCAB, the $d/1$ ratio is temperature dependent, decreasing with decrease of temperature to a value of 1.08 close to the smectic A-reentrant nematic transition showing thereby that the higher temperature phase of 9 OBCAB is a partially bilayer A phase (A_d). Essentially similar results have been obtained on another reentrant polymorphic substance by Levelut *et al.*[13,14] Further details of our X-ray results including the measurements in the reentrant nematic phase are given elsewhere.[9]

(c) *Pressure Studies*: For both the compounds the nematic-isotropic transition temperature at atmospheric pressure is rather high (257.5°C and 242.9°C). Since the seals used in our optical high pressure cell become soft and unusable beyond about 240°C, it was not possible to follow the nematic-isotropic transition as a function of pressure. All the other transitions could be followed at high pressures, including the highly supercooled reentrant nematic-reentrant smectic A transition in 9 OBCAB. The P–T diagrams of 8 OBCAB and 9 OBCAB are given in Figures 2 and 3 respectively.

8 OBCAB: Both the melting and the A_1–N transitions are straight lines. The range of the monolayer A phase increases with increasing pressure. The dT/dP for the A_1–N transition is 30.6°C/kbar.

9 OBCAB: The two smectic A phases behave very differently under pressure. The A_d–N phase boundary has an elliptic shape, the A_d phase being bounded in the P–T plane. The maximum pressure (P_m) of occurrence of the A_d phase is 0.51 kbar. In an earlier paper[10] it was shown that P_m is related to the range $R = (T_{NI} - T_{AN})$ of the nematic phase at atmospheric pressure by the relation $P_m = P_o \exp(-mR)$, where P_o and m are empirical constants which for three phenyl ring compounds are 3769 bars and 0.071/°C respectively. The P_m data for 9 OBCAB fits this relation

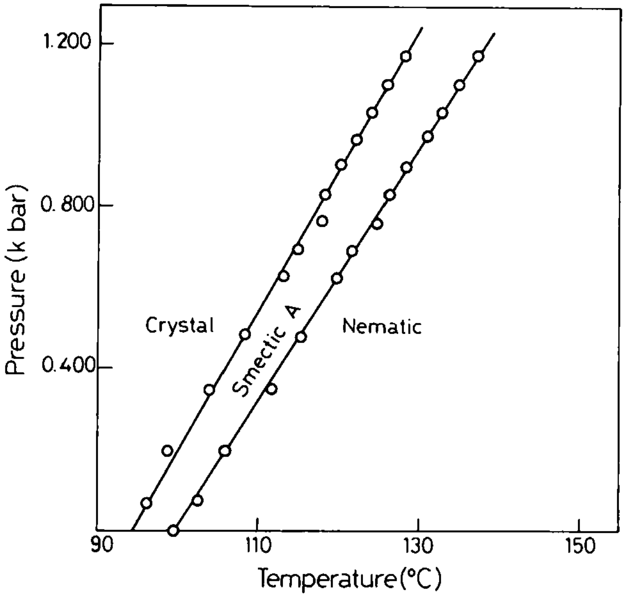

FIGURE 2 P–T diagram of 8 OBCAB.

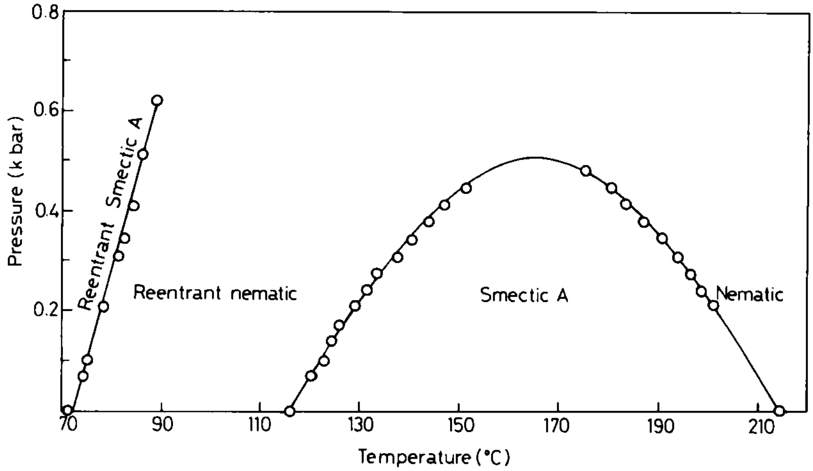

FIGURE 3 P–T diagram of 9 OBCAB.

very well (Figure 4). The A_1-reentrant nematic phase boundary on the other hand is a straight line at all pressures. Interestingly the dT/dP for this transition is 30.6°C/kbar which is exactly the same as that of the A_1–N transition in 8 OBCAB.

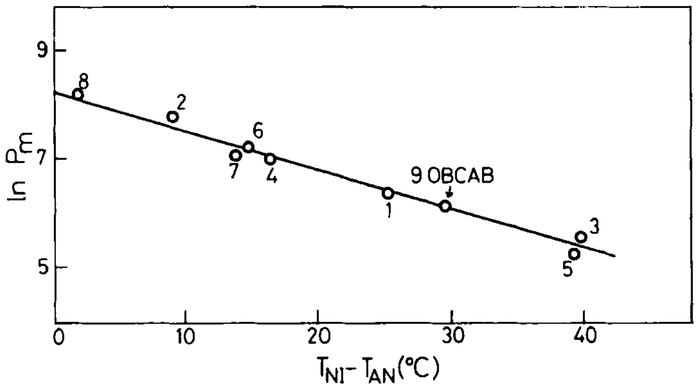

FIGURE 4 Plot of ln P_m vs $(T_{NI} - T_{AN})_{1\,bar}$ for reentrant nematogens with three phenyl rings. P_m is the maximum pressure of smectic stability. Circles marked 1, 2, etc. represent the P_m data for compounds studied earlier (see Ref. 10), P_m for 9 OBCAB is shown by the arrow (see text).

Summarizing, pressure influences the A_d and A_1 phases differently. It destabilizes the A_d phase causing the nematic phase to reenter at a lower temperature. (The mechanism of formation of the reentrant nematic phase at high pressure in bilayer systems has already been discussed by Cladis *et al.* on the basis of a molecular model.)[15,16] On the other hand, pressure increases the stability of the A_1 phase in both 8 OBCAB and 9 OBCAB. It may be recalled that a similar effect has been observed even in compounds whose molecules do not possess a strong dipolar end group.[17] It can, therefore, be concluded that the pressure behavior of the smectic A phases must be closely related to the extent of overlap of the molecules.

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