Effect of Pressure on Strongly Polar Liquid Crystals

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The effect of pressure on several mesogens which possess a strongly polar terminal group (CN or NO_2) is studied. In all cases the partially bilayer smectic A (A_d) gets bounded while the nematic phase gets more stabilised at high pressures. In the case of reentrant nematogens, the maximum pressure of smectic stability is seen to be related to the temperature range of the nematic phase at 1 bar.

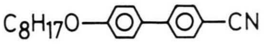
1. Introduction

Reentrant nematic behaviour is known to be exhibited by two phenyl as well as three phenyl ring systems with a strongly polar cyano group attached to one end of the molecule [1]. A few compounds with a nitro end group have also shown reentrant polymorphism, but such instances are relatively few. High pressure studies on 8 single component systems which exhibit the reentrant nematic (N_{re}) phase at atmospheric pressure were reported in an earlier paper [2]. In this paper we present results of our high pressure studies on several materials, binary mixtures as well as pure compounds, whose molecular structure is known to be favourable to the occurrence of reentrant nematic behaviour.

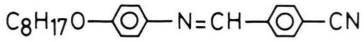
2. Materials

The substances studied are listed below:

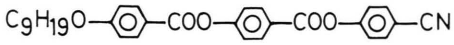
1) Binary mixtures of 4-n-octyloxy-4′-n-cyanobiphenyl (8 OCB)



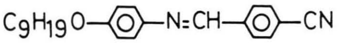
and 4-cyano benzylidene-4′-n-octyloxyaniline (CBOOA)



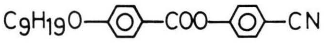
2) 4-cyanophenyl-4′-(4″-nonyloxy benzoyloxy)-benzoate (9 OCPBB)



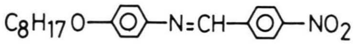
3) 4-cyano benzylidene-4′-n-nonyloxyaniline (CBNA)



4) 4-cyanophenyl-4′-n-nonyloxy benzoate (CPNB)



5) 4-nitrobenzylidene-4′-n-octyloxyaniline (NBOOA)



The transition temperatures of these substances are listed in Table 1.

The smectic A phases of CBOOA and 8 OCB have been studied by X-ray diffraction [3, 4]. For both the smectic A phase has been characterised as a partially bilayer A phase (A_d) with a d/l ratio of about 1.4, which is practically independent of tem-

Table 1. Transition temperatures in °C (at 1 bar) of the compounds studied.

Substance	K		N_{re}	S_A	N	I
8 OCB/CBOOA mixtures						
$X = 0$	+	73.0	–	+ 82.5	+ 107.2	+
$X = 0.1$	+	67.5	–	+ 81.5	+ 104.4	+
$X = 0.3$	+	59.0	–	+ 78.0	+ 98.4	+
$X = 0.5$	+	39.0	–	+ 75.1	+ 91.9	+
$X = 0.7$	+	47.0	–	+ 71.2	+ 87.3	+
$X = 0.9$	+	53.0	–	+ 67.5	+ 82.0	+
$X = 1.0$	+	55.0	–	+ 66.8	+ 79.9	+
9 OCPBB	+	120.4	+ (116.4)	+ 194.8	+ 226.4	+
CPNB	+	76.7	–	+ (58.6)	+ 81.5	+
CBNA	+	72.0	–	+ 97.5	+ 103.6	+
NBOOA	+	62.5	–	+ 74.0	+ 84.2	+

( ) denotes that the transition is monotropic; K, crystal; N_{re}, reentrant nematic; A, smectic A; N, nematic; I, isotropic.

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Table 2. *d* and *d/l* values for the substances used in the pressure study.

Compound	d (Å)	d/l
9OCPBB	37.9	1.15
CPNB	33.8	1.26
CBNA	36.5	1.35
NBOOA	31.6	1.25

perature (d is the layer thickness in the A phase as measured by X-ray diffraction, while l corresponds to the length of the molecule in its most extended configuration as obtained by a molecular model). We have determined d for compounds 2–5 at a common relative temperature of $(T_{AN}-5)$ °C. These values of d along with the d/l values are listed in Table 2. It is clear that the A phase of these compounds can be categorised as an A_d phase.

3. Experimental

An optical high pressure cell [2] was used for the experiment. The liquid crystalline sample was sandwiched between two optically polished sapphire cylinders which are enclosed in an elastomer tube (Fluran). This ensured that the sample is isolated from the pressure transmitting fluid (plexol). Transition temperatures were determined by varying the temperature at a constant pressure and monitoring the changes in the intensity of the laser light transmitted by the sample. Pressures were measured by a Heise gauge to an accuracy of ± 1 bar while transition temperatures were measured to ± 0.1 °C.

4. Results and Discussion

4.1. *8OCB/CBOOA mixture*

We have studied the effect of pressure on the smectic A-nematic (A–N) phase boundary in the P–T diagram for 5 different 8OCB/CBOOA mixtures, viz. $X = 0.1$, 0.3, 0.5, 0.7, 0.9 (where X is the mole fraction of 9OCB in the mixture). We have also studied, for the sake of completeness, the A–N boundary of both pure 8OCB and CBOOA at high pressure. The P–T diagram for the mixtures as well as the pure compounds is presented in Figure 1. It is seen that in each case the A–N phase boundary has the characteristic elliptic shape [2] and also there exists a maximum pressure of smectic stability (P_m) beyond which the A phase ceases to exist.

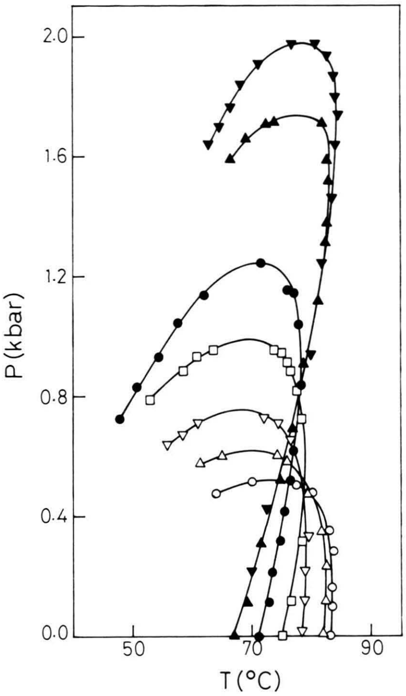

Fig. 1. P–T diagram of 8OCB (▼), CBOOA (○) and 8OCB/CBOOA mixtures, showing the smectic A-nematic phase boundary. The concentrations of the mixtures are $X = 0.9$ (▲), $X = 0.7$ (●), $X = 0.5$ (□), $X = 0.3$ (▽) and $X = 0.1$ (△), where X is the mole fraction of 8OCB in the mixture.

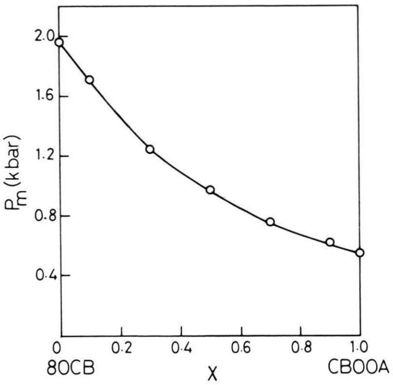

Fig. 2. Variation of the maximum pressure of smectic stability (P_m) with concentration for 8OCB/CBOOA mixtures.

The variation of P_m with X is, as to be expected from data for other binary mixtures [5–7], a smooth curve (Figure 2). It might be recalled that Herrmann [8] has also measured P_m for several mixtures of 8OCB/CBOOA. He found that P_m shows a nonlinear variation with X, there being a maximum

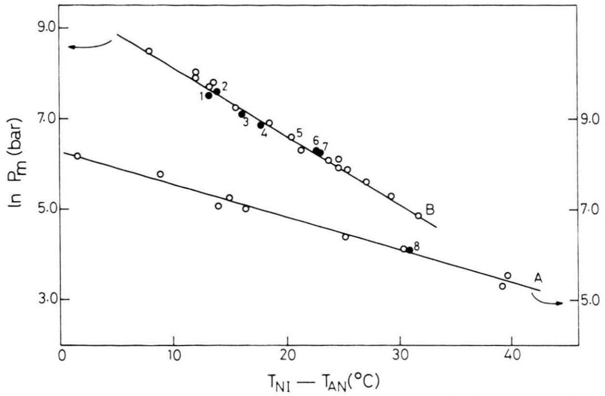

Fig. 3. Dependence of P_m on the range of the nematic phase ($T_{NI} - T_{AN}$) at atmospheric pressure. The open circles are data from [2], while the closed circles are data discussed in this paper. The points 1 and 7 correspond to 8OCB and CBOOA, respectively, while the points 2–6 are for 8OCB/CBOOA mixtures with concentrations $X = 0.9$ (2), 0.7 (3), 0.5 (4), 0.3 (5), 0.1 (6), respectively. The point 8 is for 9OCPBB, a three phenyl ring compound (see text).

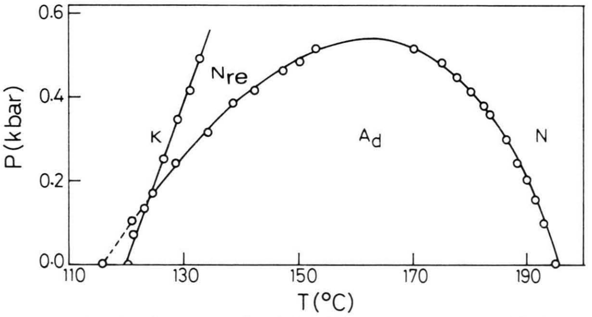

Fig. 4. P–T diagram of 9OCPBB showing the A–N phase boundary.

for $X \simeq 0.3$. Our results are in disagreement with those of Herrmann. In an earlier paper [2] we had shown that P_m is uniquely related to the range of the nematic phase, $R (= T_{NI} - T_{AN})$, at 1 bar by the relation $P_m = P_0 \exp(-mR)$ where P_0 and m are constants which depend only on the number of phenyl rings in the molecule. To check whether our present results on 8OCB/CBOOA also fit this relation we have plotted in Fig. 3 our data for the 8OCB/CBOOA mixtures along with all the earlier data given by Kalkura et al. [2]. It is seen that the 8OCB/CBOOA data indeed fit very well the line B, which is the line for two phenyl ring systems. The discrepancy of our data compared to those of [8] is perhaps attributable to the thermal degradation of CBOOA in Herrmann's measurements, conceivably caused by the sample being in direct contact with the steel gasket.

4.2. 9OCPBB

The P–T diagram of 9OCPBB, a three phenyl ring system, which exhibits reentrant nematic at atmospheric pressure, is given in Figure 4. It is seen that the A–N phase boundary again has the elliptic shape. The value of $P_m = 540$ bar fits the line A of Fig. 3 showing once more the validity of the relation discussed earlier.

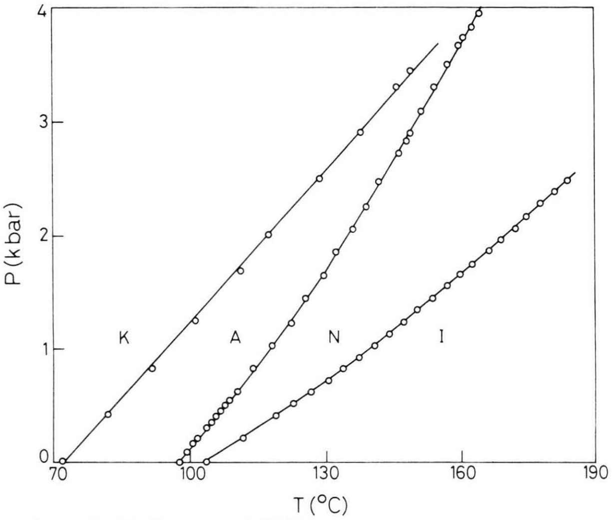

Fig. 5. P–T diagram of CBNA.

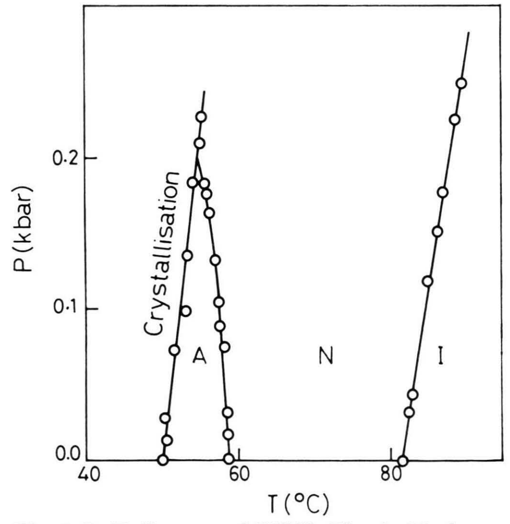

Fig. 6. P–T diagram of CPNB. The A–N phase transition is monotropic at all pressures.

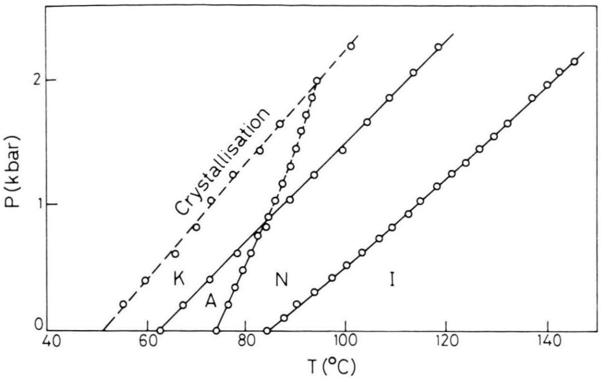

Fig. 7. P–T diagram of NBOOA. The dashed lines indicate that the transitions are monotropic.

4.3. CBNA

This compound is the next higher homologue of CBOOA. Considering that CBOOA exhibits the reentrant nematic phase at a relatively low pressure (see Fig. 1), it was expected that CBNA would also show an RN phase. But the P–T diagram (Fig. 5) shows that the A_d phase of CBNA is surprisingly stable over a wide range of pressures. There is of course a decrease of the A_d range with increase of pressure but the rate of this decrease is quite small, and also the A–N phase boundary does not show a pronounced curvature towards the pressure axis even up to 4 kbar, the highest pressure that we have reached. Extrapolating the melting and A–N boundaries to higher pressures, we expect the A_d phase to be bounded (in the heating mode) at $\approx$ 4.3 kbar.

Addition of an extra methylene group to the end chain (compared to CBOOA) therefore seems to enhance considerably the stability of the A_d phase.

4.4. CPNB

This is a two phenyl ring compound with a COO bridging group. The phase diagram of this compound is given in Figure 6. It is seen that the A–N has a negative slope throughout and A_d gets bounded at 200 bars. It is obvious that this compound would surely have exhibited the N_{re} phase at a higher pressure if crystallisation had not intervened.

4.5. NBOOA

It is relevant to recall that so far [9] only one three phenyl ring nitro compound in which the longitudinal components of the bridging dipoles are additive with respect to the dipole of the nitro end group has shown a reentrant nematic phase at high pressure. We undertook high pressure studies in order to see if such a possibility exists in this terminally nitro substituted compound which has only two phenyl rings. Figure 7 gives the P–T diagram for NBOOA. It can be seen that the A–N transition, which is enantiotropic at lower pressures, becomes monotropic beyond 1.8 kbar. Finally, at $\approx$ 2 kbar, the crystallisation line cuts the A–N line and thereby the A phase ceases to exist for pressures beyond 2 kbar. Also the A–N line is practically linear throughout, and absence of any curvature of the boundary precludes the possibility of observing the N_{re} phase.

These studies show that although pressure does have the effect of destabilizing the A_d phase in terminally polar liquid crystals, the occurence of reentrant nematic is clearly less favoured in two phenyl ring systems than in three phenyl ring systems.

Acknowledgements

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[1] Nguyen Huu Tinh, J. Chim. Phys. **80,** 83 (1983).
[2] A. N. Kalkura, R. Shashidhar, and M. Subramanya Raj Urs, J. Physique. **44,** 51 (1983).
[3] A. J. Leadbetter, J. C. Frost, J. P. Gaughan, G. W. Gray, and A. Mosley, J. Physique **40,** 375 (1979).
[4] D. Guillon, P. Seurin, and A. Skoulios, Mol. Cryst. Liq. Cryst. **51,** 149 (1979).
[5] P. E. Cladis, R. K. Bogardus, W. B. Daniels, and G. N. Taylor, Phys. Rev. Lett. **39,** 720 (1977).
[6] P. E. Cladis, in 'Liquid Crystals' – Proc. Int. Liq. Cryst. Conf., Bangalore (Ed.: S. Chandrasekhar), Heyden, London 1980, p. 105.
[7] R. Shashidhar, H. D. Kleinhans, and G. M. Schneider, Mol. Cryst. Liq. Cryst. **72** (Lett.), 119 (1981).
[8] J. Herrmann, Mol. Cryst. Liq. Cryst. **72** (Lett.), 219 (1982).
[9] B. R. Ratna, S. Krishna Prasad, R. Shashidhar, G. Heppke, and S. Pfeiffer, Presented at the X. International Liquid Cryst. Conf., York, July 1984, Mol. Cryst. Liq. Cryst. (in press).