

CHAPTER IV

HIGH PRESSURE STUDIES ON TERMINALLY CYANO SUBSTITUTED COMPOUNDS

4.1 Introduction

For a long time it was presumed that the general sequence of phase transition on cooling a polymeric compound should be

Isotropic \longrightarrow Nematic \dashrightarrow Smectic \longrightarrow Solid

But in 1975, Cladis¹ reported an exciting departure from this sequence. She found that in certain mixtures of n-p-cyanobenzylidene-p'-octyloxyaniline (CBOOA) and p-[(p'-hexyloxy benzylidene)-amino]benzonitrile (HBAB) the nematic-smectic A transition temperature becomes multivalued, the nematic phase occurring at higher as well as at lower temperature relative to the smectic A phase. The phase diagram for this binary system obtained by Cladis¹ is given in fig. 4.1. It is seen that for the mixtures in a certain concentration range, the sequence of phase transition on cooling from the isotropic phase is

Nematic \longrightarrow Smectic A \dashrightarrow Nematic \longrightarrow Solid

The lower temperature phase was later designated as "reentrant nematic phase".

The appearance of a higher symmetry phase at a lower temperature compared to a less symmetric one is not special to liquid crystals. There are quite a few examples in other fields of condensed matter physics. The pressure dependence

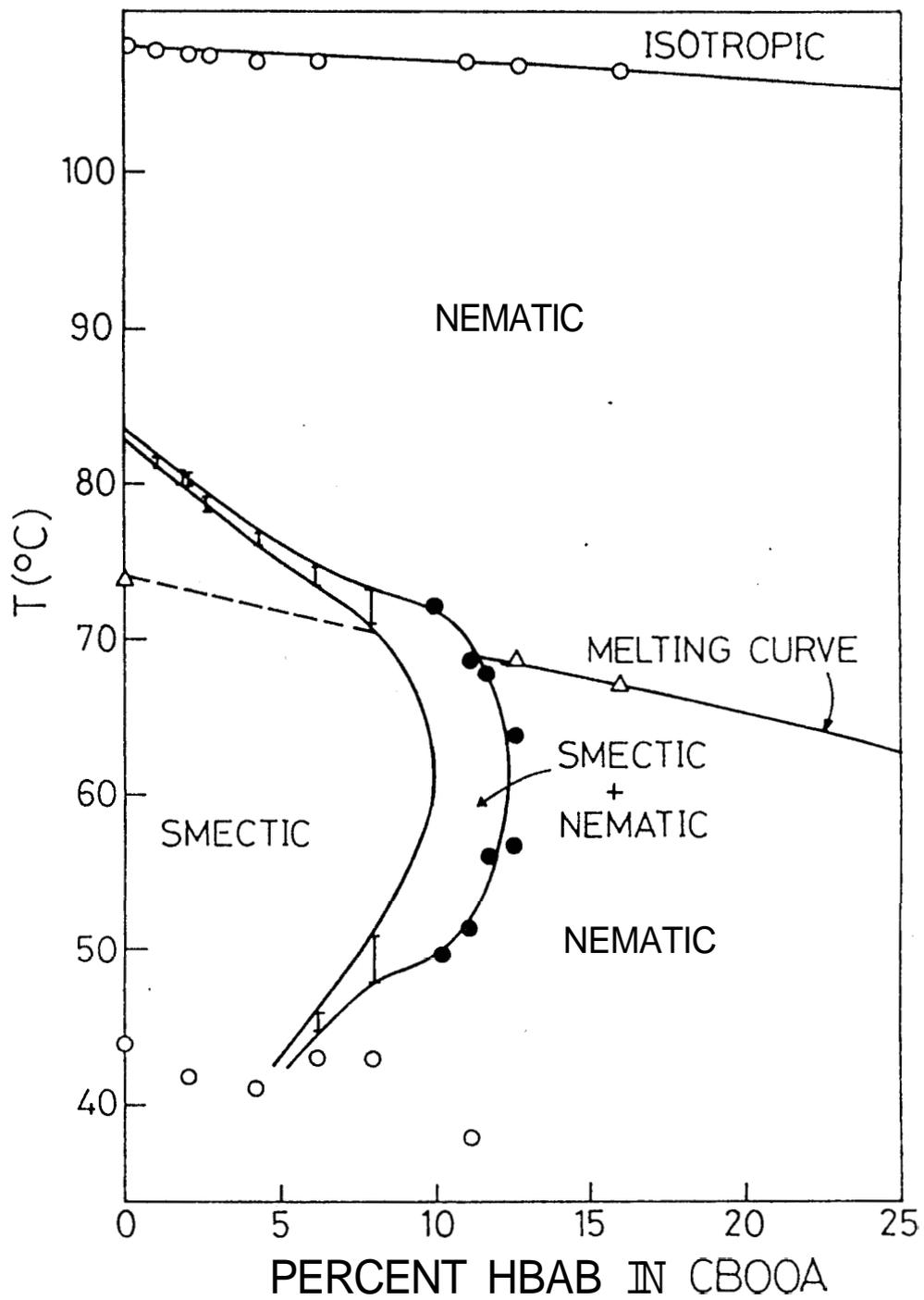


Figure 4.1 Isobaric phase diagram (T - X) for mixtures of CBOOA and HBAB (from ref. 1)

of the ^3He melting temperature² is an early example of reentrant behaviour. Some other systems exhibiting the reentrant phenomena are, superconductors doped with magnetic impurities³, rare earth superconducting materials which order magnetically at a temperature below the superconducting transition⁴ and lyotropic systems showing reentrant isotropic phase.⁵

Cladis¹ also measured the bend elastic constant (K_{33}) for the CBOOA/HBAB mixtures. It showed a similar pretransitional increase on either side of the smectic A phase. It was therefore concluded that no macroscopic difference exists between the normal i.e., high temperature nematic and the reentrant nematic phases.

Subsequently, Cladis et al⁶ found the reentrant nematic (N_{re}) phase in a pure compound at elevated pressures. The pressure-temperature diagram of .4-n-octyloxy-4'-cyanobiphenyl (8OCB) is shown in fig. 42. It shows the following features:

- i) the nematic-smectic A phase boundary curves towards the pressure axis resembling the arc of an ellipse.
- ii) the reentrant nematic phase exists in the pressure range 1.6-1.8 kbar.
- iii) beyond a pressure P_m (about 1.8 kbar) the smectic A phase ceases to exist and there is only a nematic phase.

Further high pressure studies⁷ on CBOOA, mixtures of 8OCB/6OCB and mixtures of CBNA/CBHA also revealed the existence of the N_{re} phase in these systems.

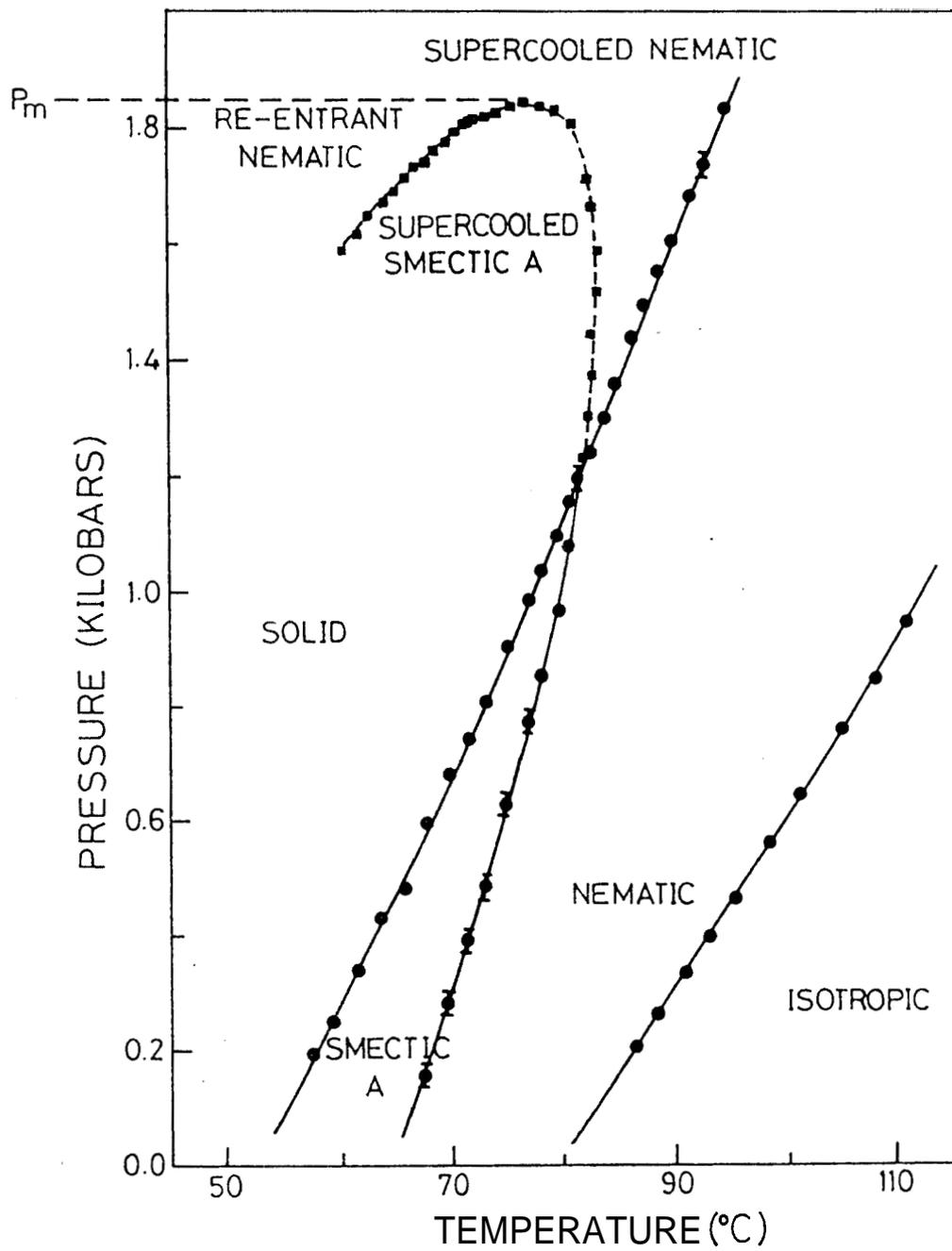


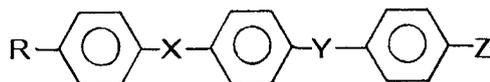
Figure 4.2 P-T diagram of 80CB (from ref. 6)

Until the beginning of 1979, the N_{re} phase was seen either in mixtures at atmospheric pressure or in single component systems at high pressures. In early 1979, Madhusudana et al⁸ reported the observation of the reentrant nematic phase in three pure compounds at atmospheric pressure. The compounds, 10 OMCP, 11 CPMBB and 12 CPMBB showed the N_{re} phase on supercooling the smectic A phase. Almost simultaneous with this report, Hardouin et al⁹ and Tinh and Gasparoux¹⁰ made a similar observation on some other compounds. Interestingly, these two systems - 4-n-octyloxy-benzoyloxy-4'-cyanostilbene⁹ and 4-nonyloxy-benzoyloxy-4'-cyanotolane¹⁰ - show not only a reentrant nematic phase but also a reentrant smectic A phase. Considering de Gennes analogy¹ between the normal-superconductor system and the nematic-smectic A transition, we may note that E.Muller-Hartmann and J.Zittartz¹² have predicted a double reentrant behaviour in superconducting alloys containing Kondo impurities. But the occurrence of the third phase transition at low temperatures corresponding to the re-appearance of superconductivity on cooling from reentrant normal state has not been confirmed experimentally.

The observation of the N_{re} phase in pure compounds at atmospheric pressure initiated a tremendous activity in the synthesis of reentrant nematogens (For the latest review see Ref.13). Presently a large number of three phenyl ring single component systems are known which exhibit the reentrant behaviour at atmospheric pressure. The occurrence of reentrant nematic behaviour in two phenyl single component systems is relatively rare, although binary mixtures of such systems commonly exhibit the reentrant nematic phase.

On the basis of molecular structure of the compounds the following generalisations can be made.

1. For the occurrence of reentrant nematic behaviour, the molecules should have a strongly polar end group CN or NO₂ (the reentrant nematic phase in NO₂ compounds was first observed by Pelzl et al¹⁴. . An exception to this has been seen by Pelzl et al¹⁵ in a terminally non polar binary system.
2. The appearance of the N_{re} phase is highly favoured if the maximum electron density is located on the terminal polar group, the positive site being on the rigid core at the farthest extremity from the polar end group.
3. An alkoxy chain is more favourable for reentrance than the alkyl chain.
4. A typical molecular structure of a three phenyl ring compound which is likely to show reentrance would be



where R is the end chain, X and Y are the bridging groups and Z is the polar end group.

For Z = CN , to obtain the N_{re} phase, the longitudinal component of the dipole moment of "X" linkage must be in the same sense as that of the CN end group. The direction of the longitudinal component of

the dipole of "Y" linkage appears to have no effect.

For $Z = \text{NO}_2$, the N_{re} phase is observed only when the dipole moment of "X" opposes that of the terminal NO_2 group. Here also the direction of "Y" seems to have very little effect. We shall give evidence of an exception to this in Chapter V.

5. The dimensions of the conjugated part of the molecule can also play an important role. The N_{re} phase is seen at 1 bar if the conjugated part of the molecule (core length) satisfies the following condition

$$16\text{\AA} \leq d_c \leq 22.4 \text{\AA}$$

(d_c is the length of the conjugated part)

This is a necessary but not sufficient condition. It is seen that for molecules with two phenyl rings, the core is relatively short (about 10-15 \AA) and reentrance is hence obtained only at high pressures and at low temperatures while in the case of three phenyl ring systems the core size is about 20 \AA and the reentrant phases are quite stable at room pressure.

6. The lateral dimension of the core also seems to have some effect on the appearance of the N_{re} phase. When the core contains a lateral group such as Cl, CH_3 , CH_3O etc., the N_{re} phase is observed only with longer chains. So bulkier the lateral group, less stabilized is the N_{re} phase.
7. The occurrence of the reentrant behaviour at 1 bar is more commonly

observed in three phenyl systems than those with two phenyl rings.

Compounds which exhibit a reentrant nematic phase, have a strong polar group attached to one end of the molecule. Minimising the mutual interaction energy, Madhusudana and Chandrasekhar¹⁶ theoretically postulated that neighbouring molecules with strong longitudinal dipoles should form an antiparallel arrangement. Xray studies¹⁷ on alkyl cyanobiphenyls showed that the smectic A phase in these compounds is characterised by a layer spacing which is about 1.4 times the molecular length. In such a situation the attractive interaction between neighbouring molecules would favour mutual overlapping and an antiparallel correlation as shown in fig. 4.3. Such correlation in turn leads to a "bilayer structure".. Madhusudana and Chandrasekhar¹⁶ also predicted that the antiparallel local order should manifest itself in the dielectric properties of the medium. Indeed it has been shown experimentally that the mean dielectric constant in the nematic phase $\bar{\epsilon} = [\epsilon_{\parallel} + 2\epsilon_{\perp}] / 3$ is less than the extrapolated isotropic value ϵ_{is} , because of the increased antiparallel associations in the nematic phase.

As already mentioned the observation of reentrant behaviour in single component systems at atmospheric pressure not only initiated a surge of activity in the synthesis of a large number of compounds exhibiting the N_{re} phase, but also led to a variety of experiments¹⁸⁻²⁴ which were conducted to understand the properties of the N_{re} phase. We shall summarise here some important observations arising out of these experiments:

1. The layer spacing shows only a very small variation with pressure or temperature in the A_d phase¹⁸⁻²⁰

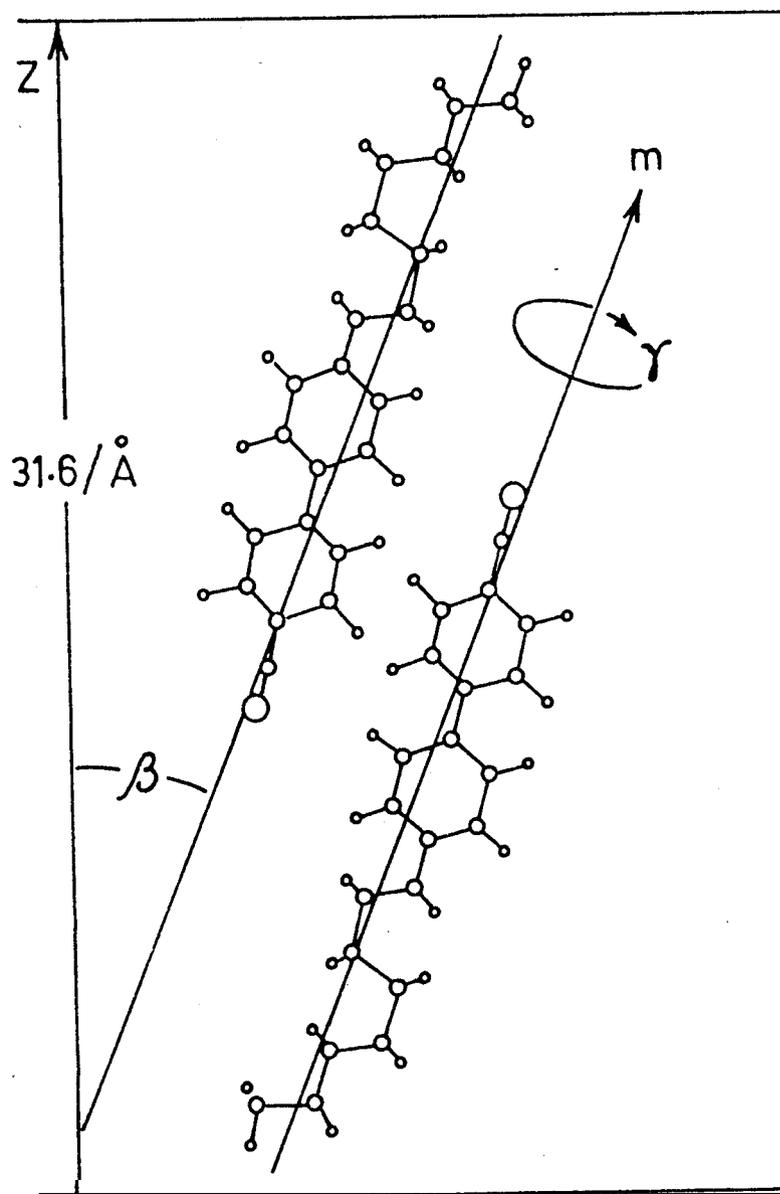


Figure 4.3 Schematic representation of the antiparallel arrangement of bimolecular unit cell for 8CB (from ref. 17)

2. The in-planar local ordering and the in-plane structure factor is - within the experimental uncertainties - the same in the nematic, smectic A_D and reentrant nematic phases²¹.
3. The dielectric anisotropy shows a continuous increase with decrease of temperature right upto the lowest temperature in the reentrant nematic phase.²²⁻²⁴
4. The activation energy associated with the low frequency dielectric relaxation of ϵ_r is greater in the reentrant nematic phase than in the nematic phase.^{22,24}

Very recently Kalkura et al²⁵ conducted detailed high pressure experiments on eight compounds exhibiting reentrant nematic phase at room pressure. On the basis of these experiments, they showed that

- a) the S_A -N phase boundary has an elliptic shape.
- b) where the S_A -N transition is monotropic at 1 bar, it becomes enantiotropic at higher pressures.
- c) the maximum pressure of stability of the smectic A phase is related to the range R of the nematic phase at atmospheric pressure by the relation $P_m = P_0 \exp(-mR)$ where P_0 and m are empirical constants which only depend on the number of phenyl rings in the constituent molecules.

By fitting the data to the relation mentioned above they found that the stability of the smectic A phase in compounds with two phenyl rings is higher than the

smectic stability of the three phenyl ring compounds. Hence it was concluded that the formation of the reentrant nematic phase is more favourable in compounds with three benzene rings.

In this chapter we present the results of our studies on compounds, three benzene as well as two benzene ring systems, all of which possess a cyano group at one end of the molecule.

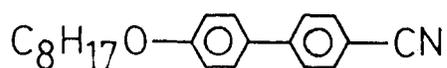
4.2 Materials

The substances studied are listed in Table 4.1 together with their chemical formulae and acronyms. The transition temperatures are tabulated in Table 4.2. All the compounds have a cyano group attached to one end of the molecule. Three of them (9 OCPBB, 8 OBCAB and 9 OBCAB) are three phenyl ring systems, the rest having two phenyl rings.

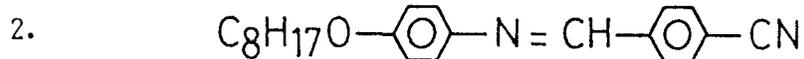
9 OCPBB has a monotropic reentrant nematic phase while 8 OBCAB and 9 OBCAB belong to a series of compounds which were among the first to show the reentrant nematic and reentrant smectic phases. Fig.4.4 shows a plot of transition temperature versus alkyl chain length for the series.²⁶ It is seen that the N-A₁ transition temperature increases with increasing chain length for $n < 6$ but decreases for the higher homologues. For the 9th homologue another smectic A phase (S_{Ad}) becomes stabilized. In this compound the two smectics are separated by a reentrant nematic phase. For $n \geq 10$ the low temperature smectic A i.e., A₁ is not to be observed.

TABLE 4.1

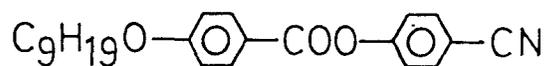
Chemical formulae of the compounds studied



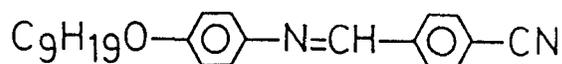
4-n-octyloxy-4'-n-cyanobiphenyl (8OCB)



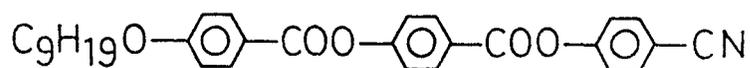
4-cyanobenzylidene-4'-n-octyloxyaniline (CBOOA)



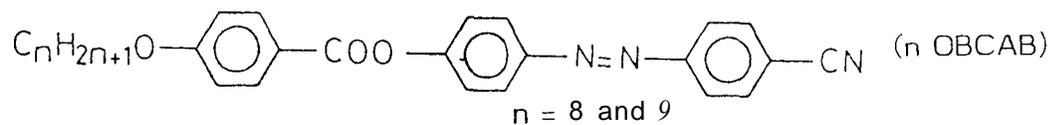
4-cyanophenyl-4'-n-nonyloxybenzoate (CPNB)



4-cyanobenzylidene-4'-n-nonyloxyaniline (CBNA)



4-cyanophenyl-4'-(4"-nonyloxybenzoyloxy)benzoate (9 OCPBB)



4-alkyloxybenzoyloxy-4'-cyanoazobenzene

TABLE 42

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

Substance	K	S _{A1}	N _{re}	S _{Ad}	N	I
8OCB/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	.
CPNB	▪ 76.7	-	-	▪ (58.6)	. 81.5	.
CBNA	▪ 72.0	-	-	▪ 97.5	. 103.6	.
8 OBCAB	▪ 93.0	▪	-	- 97.0	. 257.5	.
9 OBCAB	▪ 94.0	▪ (70.9)	▪ 116.0	▪ 212.4	. 242.9	.
9 OCPBB	▪ 120.4	-	▪ (116.4)	▪ 194.8	. 226.4	.

() denotes a monotropic transition

- shows that the phase exists and
- represents the phase is absent

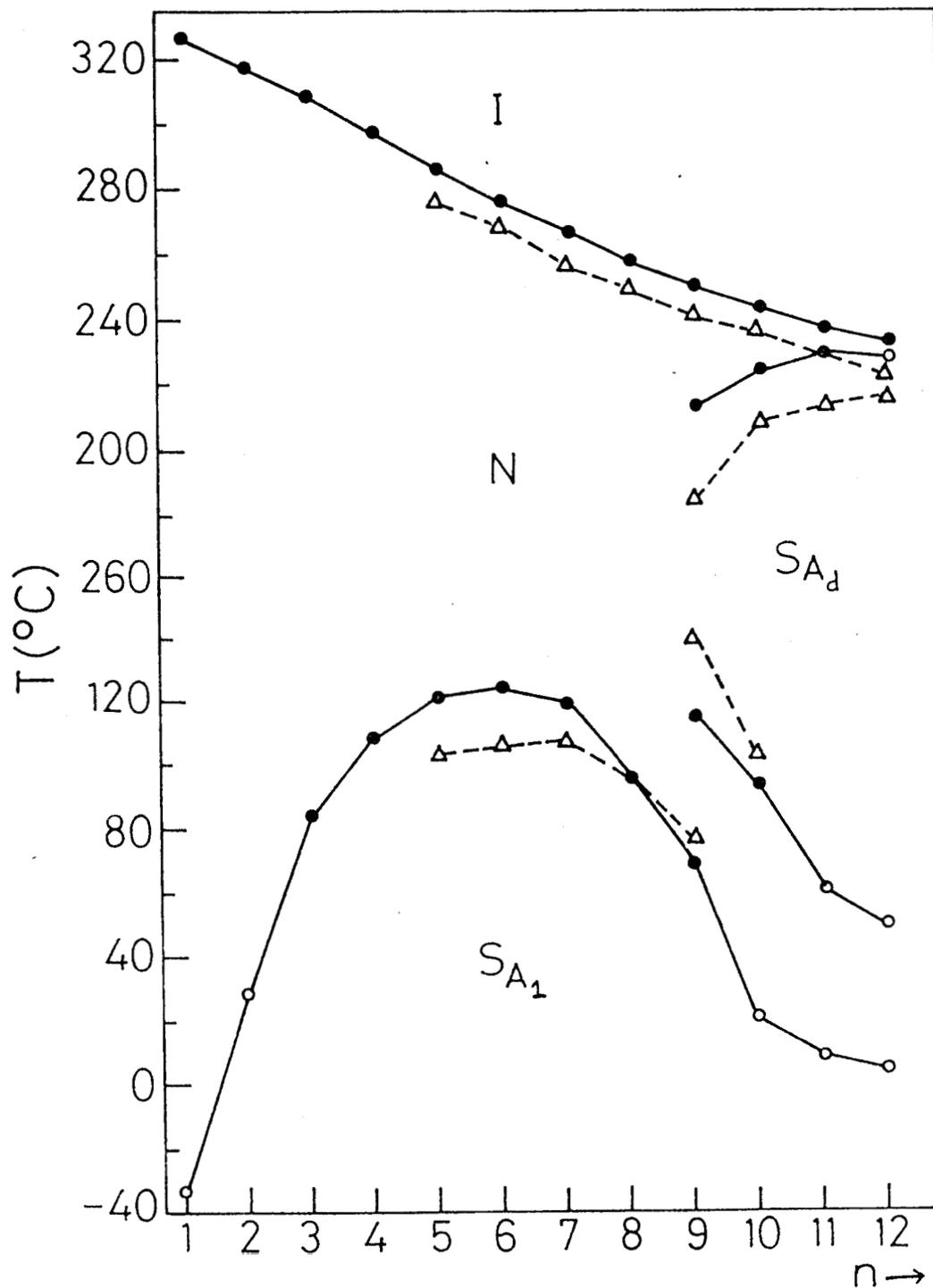


Figure 4.4 Plot showing transition temperature (●) versus chain length for the 4-alkyloxybenzoyloxy-4'-cyanoazobenzene series (●) are extrapolated values (Δ) are for the compounds of the 4-alkyloxy benzoyloxy-4'-cyanotolanes (from ref. 26)

4.3 Experimental

High pressure experiments were done using an optical cell. A brief description of the cell as well as the technique used to determine the transition temperatures have already been given in Chapter II and will not be repeated here. Pressure was measured using a Heise gauge to an accuracy of ± 1 bar, while the temperature was measured with a precision of $\pm 0.1^\circ\text{C}$.

The apparatus used for Xray diffraction experiments has also been described in Chapter II. The samples were irradiated with monochromated Xrays obtained using a bent quartz crystal monochromator. The temperature of the sample was maintained constant to within $\pm 0.25^\circ\text{C}$ during an exposure. The relative accuracy in the layer spacing determination is reckoned to be $\pm 0.1\text{\AA}$

4.4 Results and Discussion

4.4.1 Two Phenyl Ring Systems

a) Xray Results: The layer thickness (d) in the smectic A phase for the compounds CPNB and CBNA was determined at a common relative temperature of $(T_{AN} - 5)^\circ\text{C}$. It was also ascertained that the layer spacing hardly varies with temperature in the A phase. The length of the molecule (l) in its most extended configuration was measured using Dreiding model. The values of d along with the d/l ratios are given in Table 4.3. It is clear from the table that the A phase of these two compounds can be characterised as the partially bilayer A phase (A_D phase). The smectic A phase of 8OCB as well as CBOOA

TABLE 4.3

d and d/l values for compounds 2 and 3 of Table 4.1

Compound.	d Å	d/l
CPNB	33.8	1.26
CBNA	36.5	1.35

have been studied using Xray diffraction by Leadbetter et al¹⁷ and Guillon et al¹⁸ respectively. For both the substances the smectic A phase has been characterised as an A_d phase. Thus the A phase exhibited by all the two phenyl ring systems has been classified as the (partially bilayer) A_d phase. The results of our Xray studies on the 3 phenyl ring systems will be discussed later.

b) Pressure Results:

8OCB/CBOOA Mixtures: We have studied the effect of pressure on the smectic A-nematic (A-N) phase boundary for 5 different 8OCB/CBOOA mixtures viz., $x = 0.1, 0.3, 0.5, 0.7$ and 0.9 (where X is the mole fraction of 8OCB in the mixture). For the sake of completeness, we have also studied the A-N boundary of both pure 8OCB and CBOOA at high pressure. The P-T diagrams of the mixtures as well as those of the pure compounds presented in fig. 4.5 clearly show the existence of the N_{re} phase at high pressure. *It* is seen that in each case the A-N phase boundary has the characteristic elliptic shape and also there exists a maximum pressure of smectic stability (P_m) beyond which the A phase ceases to exist. The variation of P_m with X is, as to be expected from data for other binary mixtures, a smooth curve (see fig. 4.6). It might be recalled that Herrmann²⁷ has also measured P_m for several mixtures of 8OCB/CBOOA. He observed that P_m shows a nonlinear variation with X , there being a maximum for $X \approx 0.3$ see fig.4.7. Our results are in disagreement with those of Herrmann.

As mentioned in the introductory part of the chapter, Kalkura et al²⁵, on the basis of their studies on eight reentrant nematogens showed that P_m

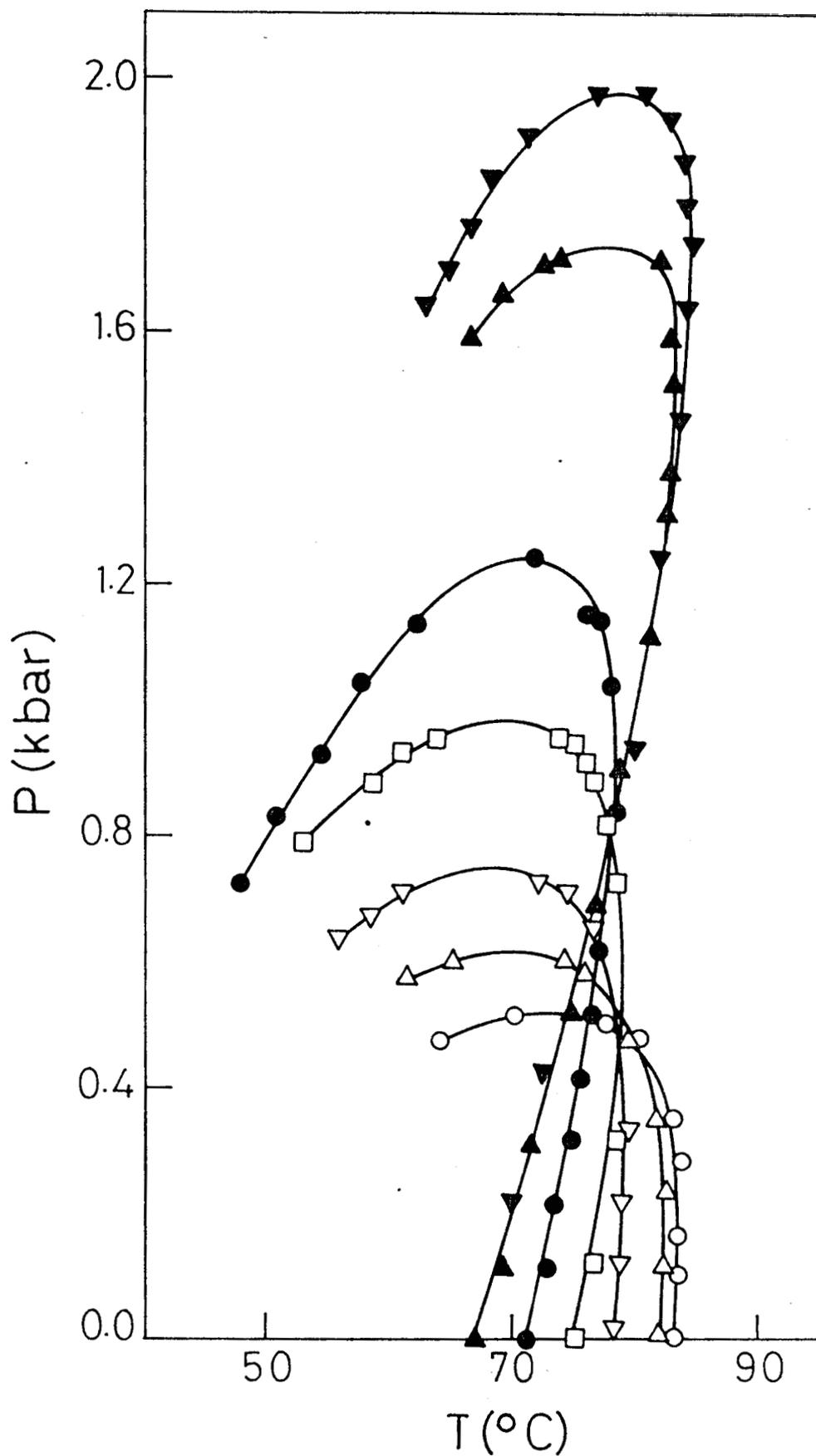


Figure 4.5 P-T diagram of 8OCB (\blacktriangledown), CBOOA (\circ) and 8OCB/CBOOA mixtures showing the S_A^A -N boundary. The concentrations of the mixtures are $X = 0.9$ (\blacktriangle), $X = 0.7$ (\bullet), $X = 0.5$ (\square), $X = 0.3$ (\triangledown) and $X = 0.1$ (\triangle) [where X is the mole fraction of 8OCB in the mixture]

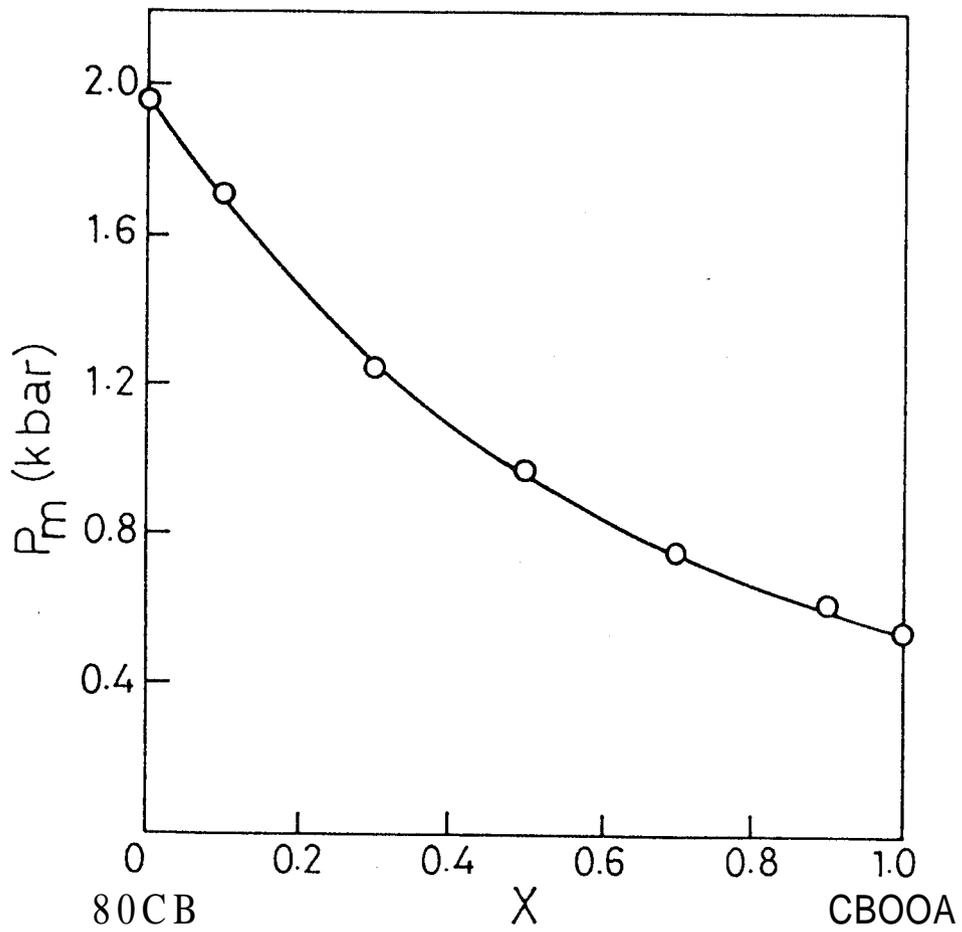


Figure 4.6 Variation of the maximum pressure of smectic stability (P_m) with concentration (X) for 80CB/CBOOA mixtures

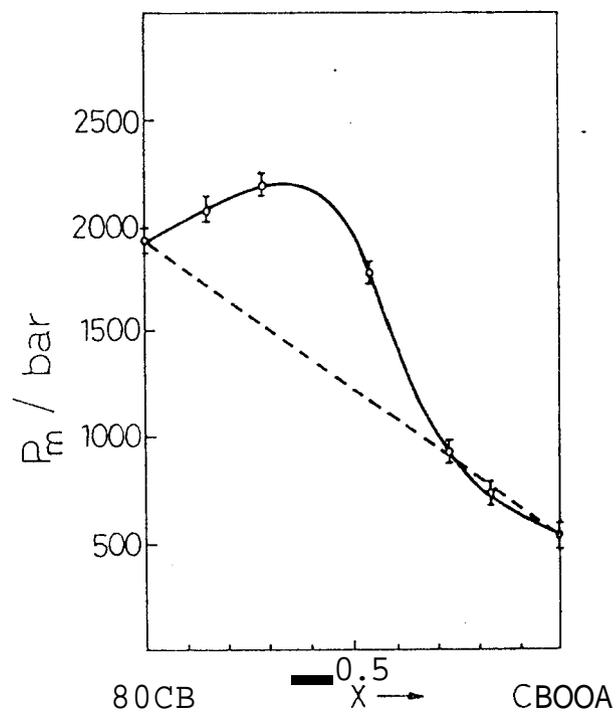


Figure 4.7 Variation of P_m with X for 80CB/CBOOA mixtures obtained by Herrmann (ref. 27)

is uniquely related to the range of the nematic phase- $R(=T_{NI} - T_{AN})$ by

$$P_m = P_0 \exp(-mR)$$

Here P_0 and m are empirical constants which depend only on the number of phenyl rings in the molecule. The values of P_0 and m for two phenyl ring systems obtained from a least square fit of the data to a straight line are 15891 bar and 0.151/°C respectively. To check whether our present results on 8OCB/CBOOA also fit this relation, we have plotted in fig. 4.8 our data for the 8OCB/CBOOA mixtures alongwith all the earlier data given by Kalkura et al.²⁵. It is seen that the 8OCB/CBOOA data indeed fit very well with the line.

It is relevant to recall here that experiments on CBOOA by Cladis et al.⁷ showed that the P_m for this compound is extremely sensitive to impurities.

We therefore believe that the discrepancy of our data compared to those of reference²⁷ 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.

We shall now discuss the individual phase diagrams of the single component systems in some detail.

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. 4.5), it was expected that CBNA would also show a reentrant nematic

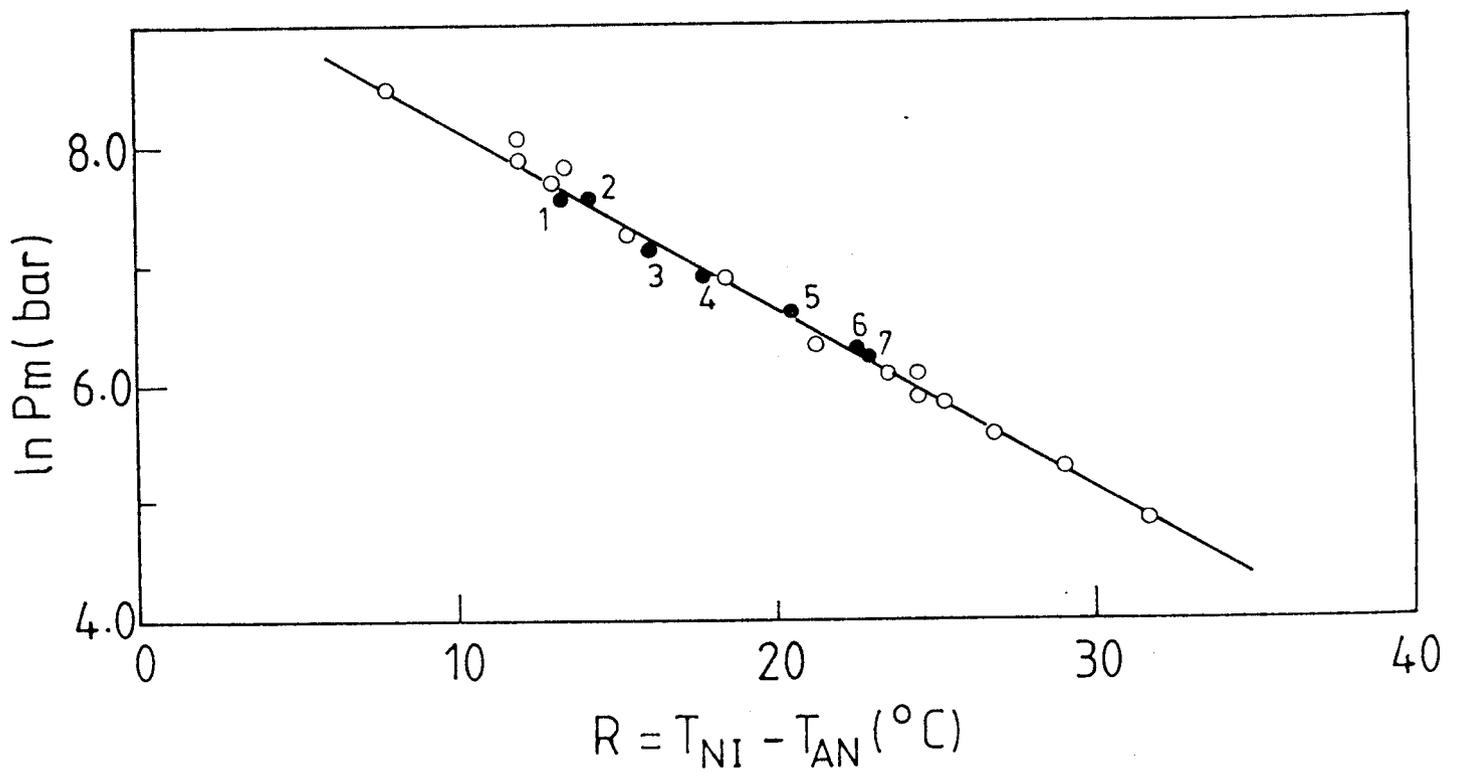


Figure 4.8 Dependence of P_m on the range R of the nematic phase at 1 bar. The open circles are data from ref. 24. Closed circles with numbers 1 to 7 correspond to 8OCB/CBOOA mixtures with concentrations $X = 1, X = 0.9, X = 0.7, X = 0.5, X = 0.3, X = 0.1$ and $X = 0$ respectively.

phase. But the P-T diagram of CBNA (fig. 4.9) shows that the A_d phase is surprisingly stable over a wide range of pressures. There is of course a decrease in 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 exhibit a pronounced curvature towards the pressure axis even upto 4 kbar, the highest pressure that we have studied. Extrapolating the melting and A-N phase boundaries to higher pressures, we expect the A_d phase to be bounded (in the heating mode) at ≈ 4.3 kbar. Addition of an extra methyl group to the end chain (compared to CBOOA) therefore seems to enhance considerably the stability of the A_d phase. This result is in agreement with the observation of Kalkura et al.²⁵ that P_m increases with increasing chain length.

CPNB : This compound is identical to CBNA except that the linkage group is an ester (-COO-) instead of a schiff base (-N = CH-). The pressure-temperature diagram is given in fig. 4.10. The A-N boundary has a negative slope throughout and intersects the crystallization line at about 200 bar and thereby the A_d phase is suppressed. Beyond this pressure, it is obvious that this compound would most likely have exhibited the N_{re} phase at a higher pressure if crystallization had not intervened. Changing the bridging group from N = CH to COO has brought down the smectic stability substantially.

4.4.2 Three Phenyl Ring Systems

a) 8 OBCAB and 9 OBCAB

As seen in Table 4.2, 8 OBCAB exhibits one smectic A phase while 9

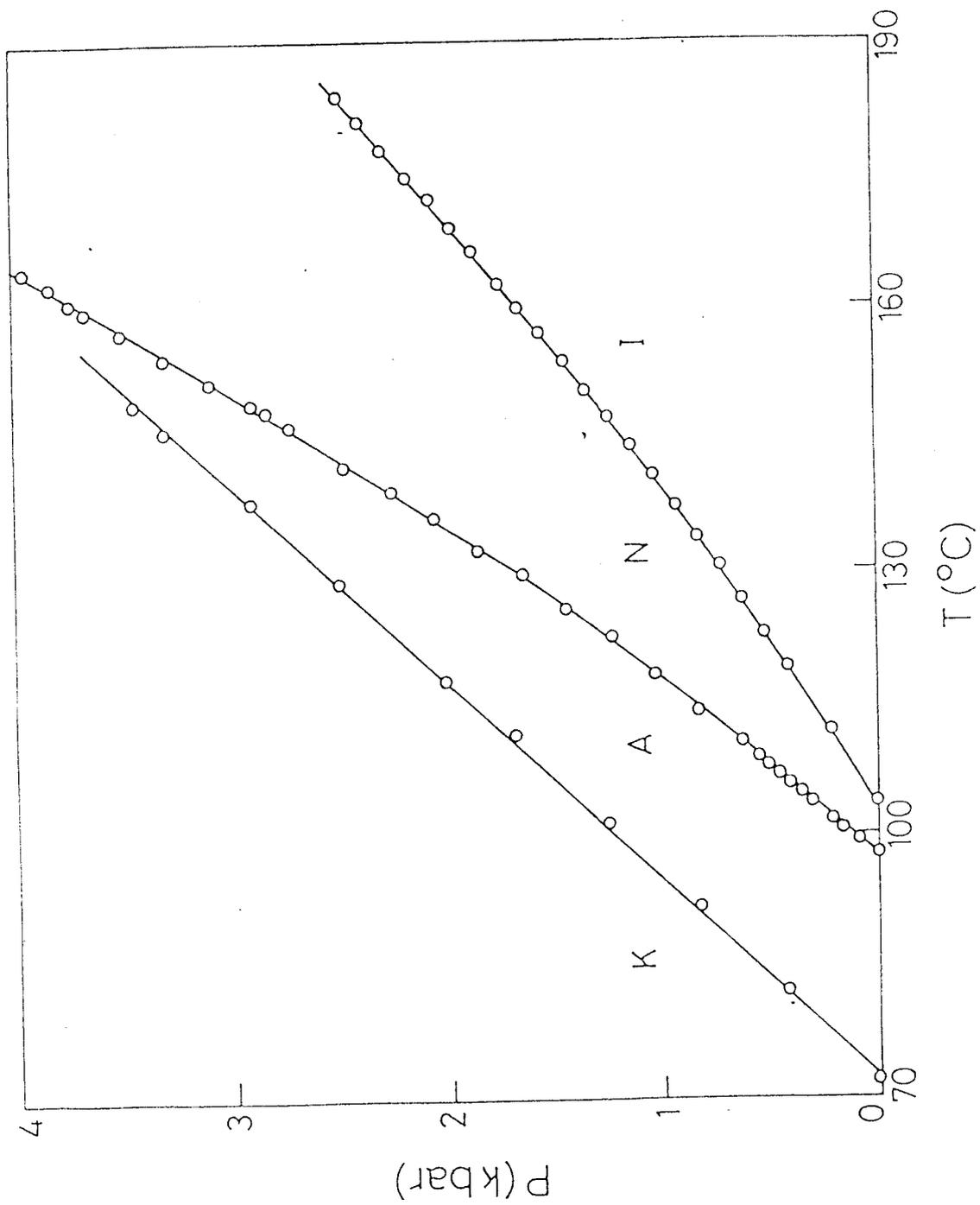


Figure 4.9 P-T diagram of CBNA

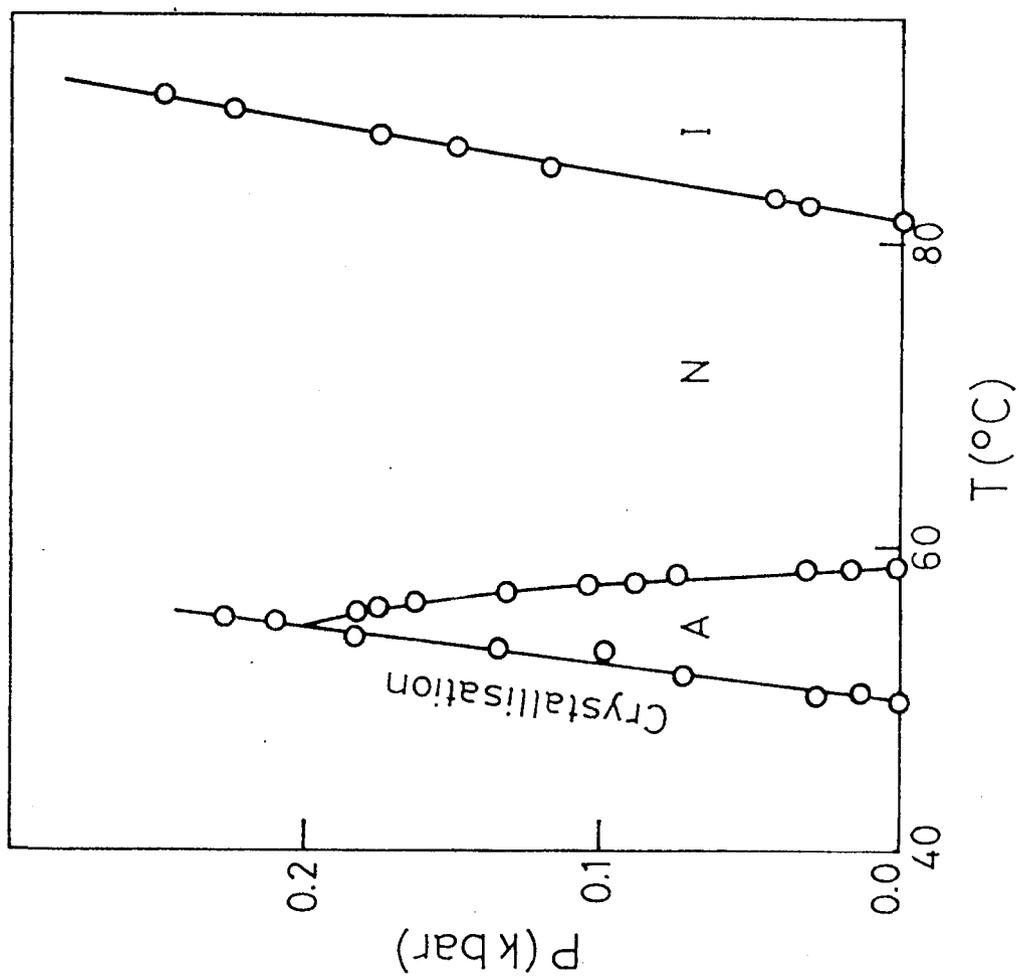


Figure 4.10 P-T diagram of CPNB

OBCAB has two such phases. We have studied the binary phase diagram of these compounds (fig. 4.11). 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.

Xray Studies. We have determined the layer spacing in the S_A phases of both the compounds and in the reentrant nematic phase of 9 OBCAB.

8 OBCAB: The value of d in the smectic A phase is 30.6\AA and is hardly temperature dependent (see fig. 4.12). The length of the molecule (l) measured in its most extended configuration (using Dreiding model) is 32.3\AA . Hence the smectic A phase can be classified as a monolayer A (A_1) phase with a d/l ratio of about 0.95, which is temperature invariant. It may be recalled that Levelut et al.²⁸ had observed a similar behaviour in the lower temperature monolayer A phase of 4-n-octyloxybenzoyloxy-4'-cyanostilbene (T8) in which reentrant behaviour was first observed at atmospheric pressure.

9 OBCAB : Fig. 4.13 shows our Xray measurements carried out in the high and low temperature smectic phases as well as in the reentrant nematic phase. In the high temperature smectic A phase the layer spacing decreases with decrease in temperature. The value of the d/l ratio ($l = 33.4\text{\AA}$) which is 1.08 at the highest temperature of measurement decreases steadily to about 1.06 at the smectic A-reentrant nematic transition. From the value of d/l (> 1) one can deduce that it is a partially bilayer A (A_d) phase. The low temperature smectic A phase on the otherhand has a layer thickness which is invariant

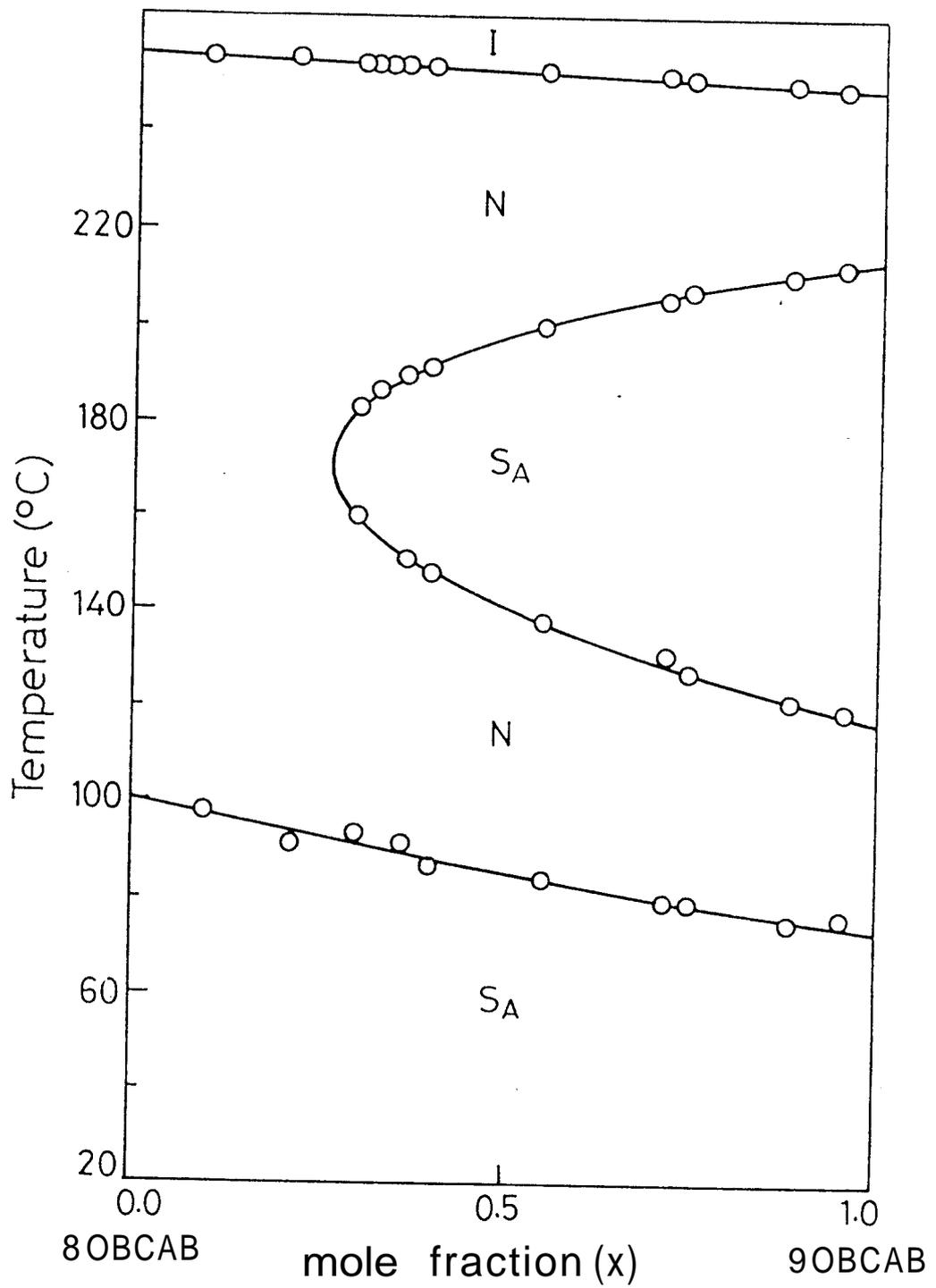


Figure 4.11 Isobaric binary phase diagram of 8 OBCAB and 9 OBCAB

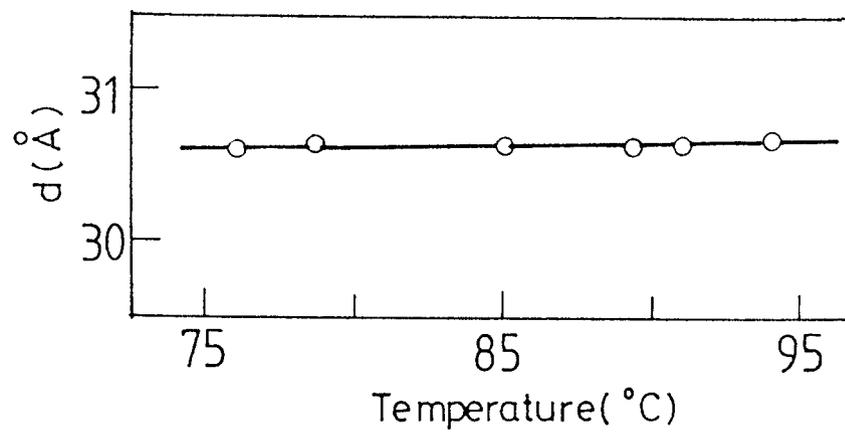


Figure 4.12 Thermal variation of the layer spacing for 8 OBCAB

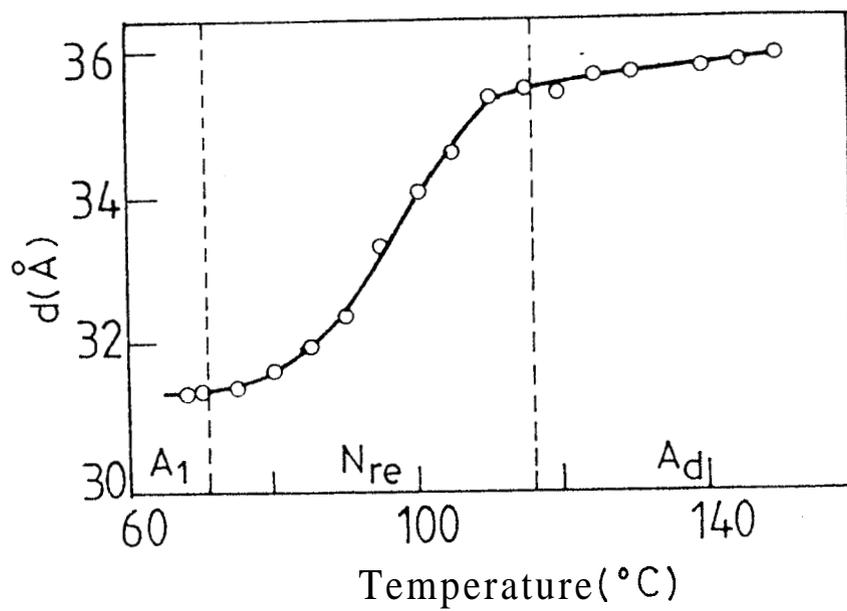


Figure 4.13 Temperature variation of the layer spacing for 9 OBCAB. The vertical dashed lines indicate the transition temperature

to the change in temperature. The d/l ratio of 0.95 indicates that it is a monolayer A (A_1) phase just like the S_A phase of 8 OBCAB. The change from the partially bilayer A_D phase to the monolayer A_1 phase is a continuous process which commences at the A_D-N_{re} phase transition and goes right through the N_{re} phase. We may recall that a similar behaviour in the A_D and A_1 phases of a pure compound has been reported by Levelut et al.²⁸ Though some measurements were done in the reentrant nematic phase also, they were restricted to temperatures very close to A_D-N_{re} and $N_{re}-A_1$ transitions (fig. 4.14). Hence it was not clear whether the development of the monolayer order from the partially bilayer one is a continuous process or an abrupt change; our measurements show that this development takes place continuously. It must also be remarked that Levelut et al.²⁸ observed the existence of two modulations (corresponding to the A_D and A_1 periodicities) in the reentrant nematic phase. However, we have not observed such coexisting periodicities - only one set of diffraction spots were observed at all temperatures in the N_{re} phase. Also these spots were quite condensed indicating a strong smectic-like local ordering in the reentrant nematic phase. Our studies like those of Levelut et al.,²⁸ indicate that the reentrant nematic phase appears as a consequence of the competition between two distinctly different smectic A phases - the A_D phase has a density modulation whose wavelength is incommensurate with respect to the molecular length, while that of the A_1 phase is commensurate with it. As far as we are aware, our results represent the first detailed layer spacing measurements in the reentrant nematic phase.

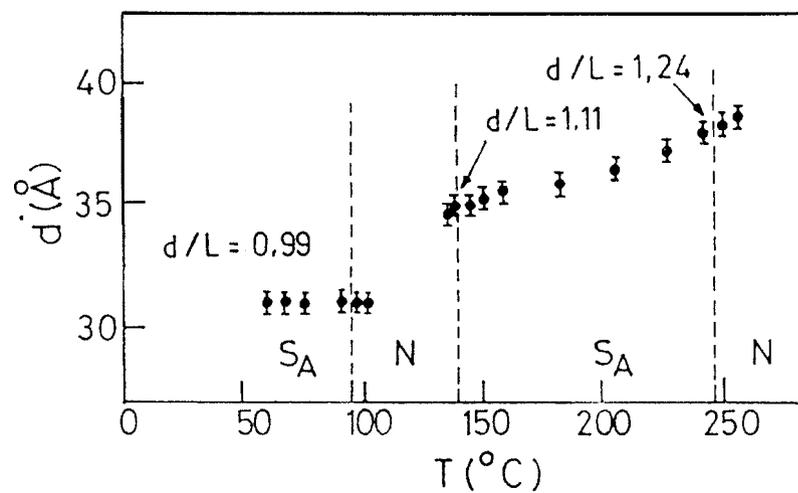


Figure 4.14 Thermal variation of the layer spacing for T8. The vertical dashed lines indicate the various transition temperatures (from ref. 28)

Pressure Studies

The nematic-isotropic transition temperature at 1 bar for both 8OBCAB and 9 OBCAB is quite high (257.5°C and 242.9°C respectively). Since the seals used in our optical high pressure cell become soft and unusable beyond about 230°C, it was not possible to follow the nematic-isotropic transition as a function of pressure. All the other transitions including highly supercooled $N_{re}-A_1$ transition in 9 OBCAB, could be followed at high pressure.

8 OBCAB: The pressure-temperature phase diagram is given in fig. 4.15. It is seen that both the melting and the A_1 -N transition boundaries are straight lines. The range of the monolayer A phase increases with increasing pressure. This trend is similar to that seen in other monolayer smectic A systems²⁹. The dT/dP for the A_1 -N transition is 30.6°C/kbar.

9 OBCAB : The pressure-temperature phase diagram is given in fig. 4.16. It is seen that the two smectic A phases behave very differently under pressure. The A_d -N phase boundary is elliptic in shape, the A_d phase getting bounded in the P-T plane. The maximum pressure (P_m) of smectic stability is 0.51 kbar. As already mentioned P_m is related to the range $R(= T_{NI} - T_{AN})$ of the nematic phase at atmospheric pressure by the relation $P_m = P_o \exp(-mR)$; P_o and m being empirical constants. For three phenyl ring systems the values of the constants are 3769 bar and -0.071/°C respectively. The P_m data for 9 OBCAB fits this relation very well (see fig. 4.17). The behaviour of the A_1 - N_{re} phase boundary is similar to the A-N boundary of 8 OBCAB. Interestingly, dT/dP for the transition involving the A and reentrant nematic phases

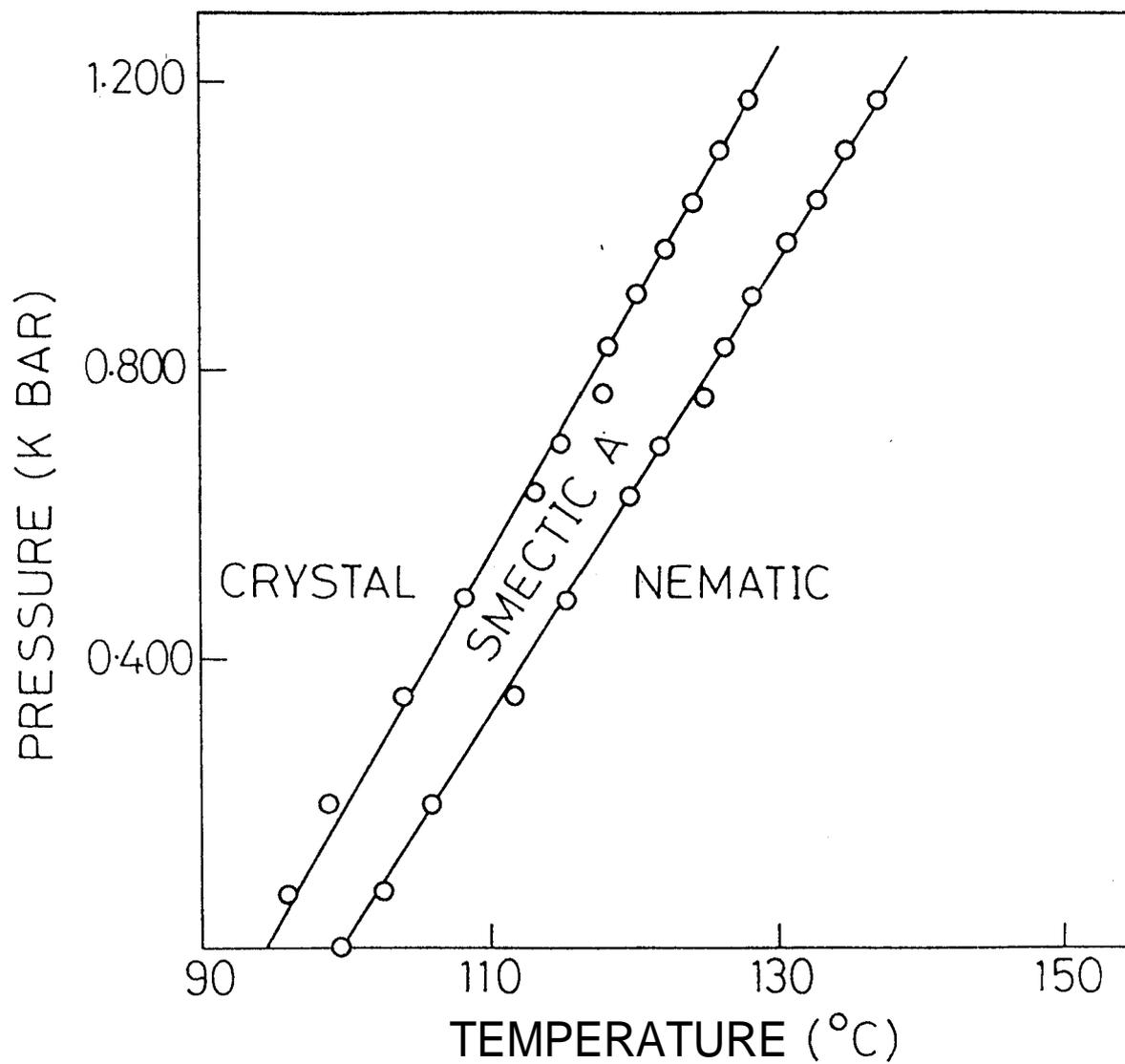


Figure 4.15 P-T diagram of 8 OBCAB

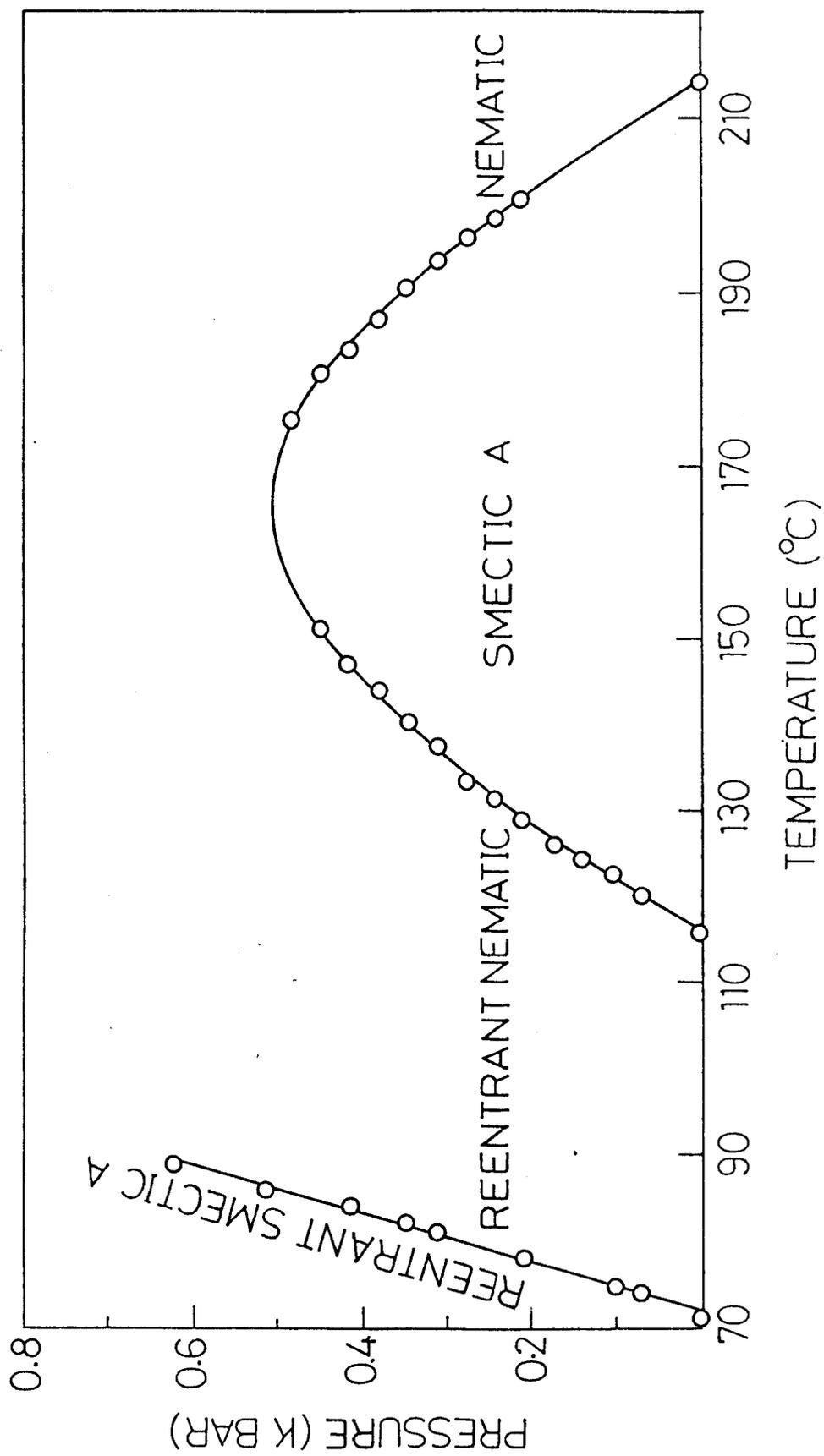


Figure 4.16 P-T diagram of 9 OBCAB

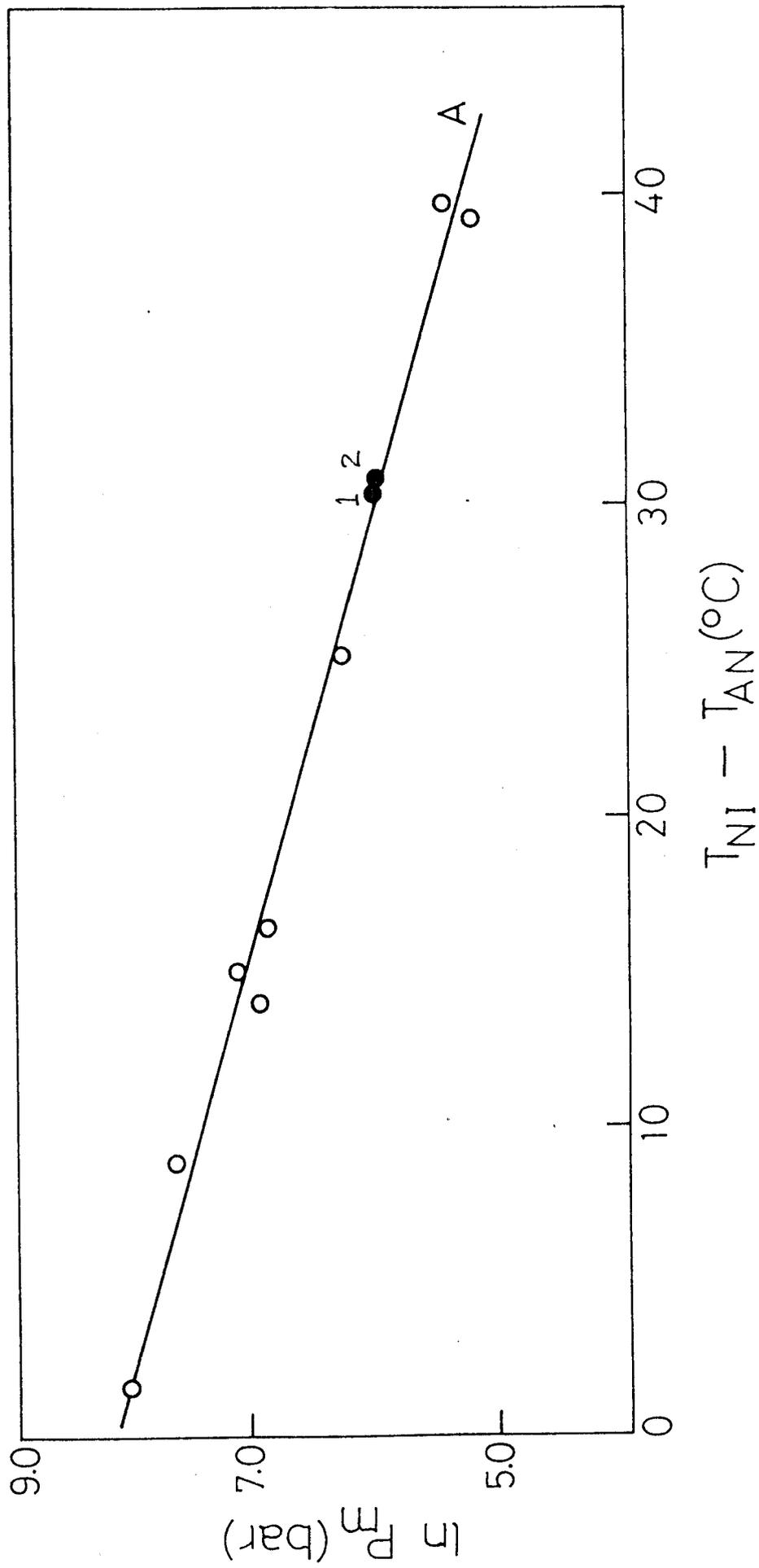


Figure 4.17 Dependence of P_m on the range of the nematic phase for three phenyl ring compounds. Open circles are data from reference 25. Closed circles with numbers 1 and 2 correspond to 9 OBCAB and 9 OCPBB respectively.

is exactly the same ($30.6^{\circ}\text{C}/\text{kbar}$) in both the cases.

9 OCPBB: The P-T diagram is shown in fig. 4.18. At atmospheric pressure, the reentrant nematic phase is monotropic i.e., appears only in the cooling mode (with respect to the solid phase). But at about a pressure of 200 bar, it cuts the melting line and above that pressure becomes enantiotropic. The A-N line takes a negative curvature throughout and the A_d phase having a temperature independent d ($d/l = 1.15$) gets bounded at a pressure of 540 bar. In fig. 4.17 we have also represented the P_m value obtained for this compound and it is seen that the data fits very well.

From these results it is seen that 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. For the A_1 phase, on the otherhand, the stability increases with increasing pressure in both 8 OBCAB and 9 OBCAB. A similar effect was observed even in the monolayer A phases of compounds whose molecules do not possess a strong polar end group.²⁹ It may be mentioned here that the results of the pressure studies on 9 OBCAB agree with those obtained by Cladis in a similar system.³⁰

Our studies show that although pressure does have the effect of destabilizing the A_d phase in all terminally polar liquid crystals, the occurrence of reentrant nematic is clearly less favoured in two phenyl ring systems. The results also demonstrate that the pressure behaviour of the smectic A phases is closely related to the extent of interdigitation of molecules. The latter point is nicely demonstrated in our experiments on binary mixtures (Chapter VI).

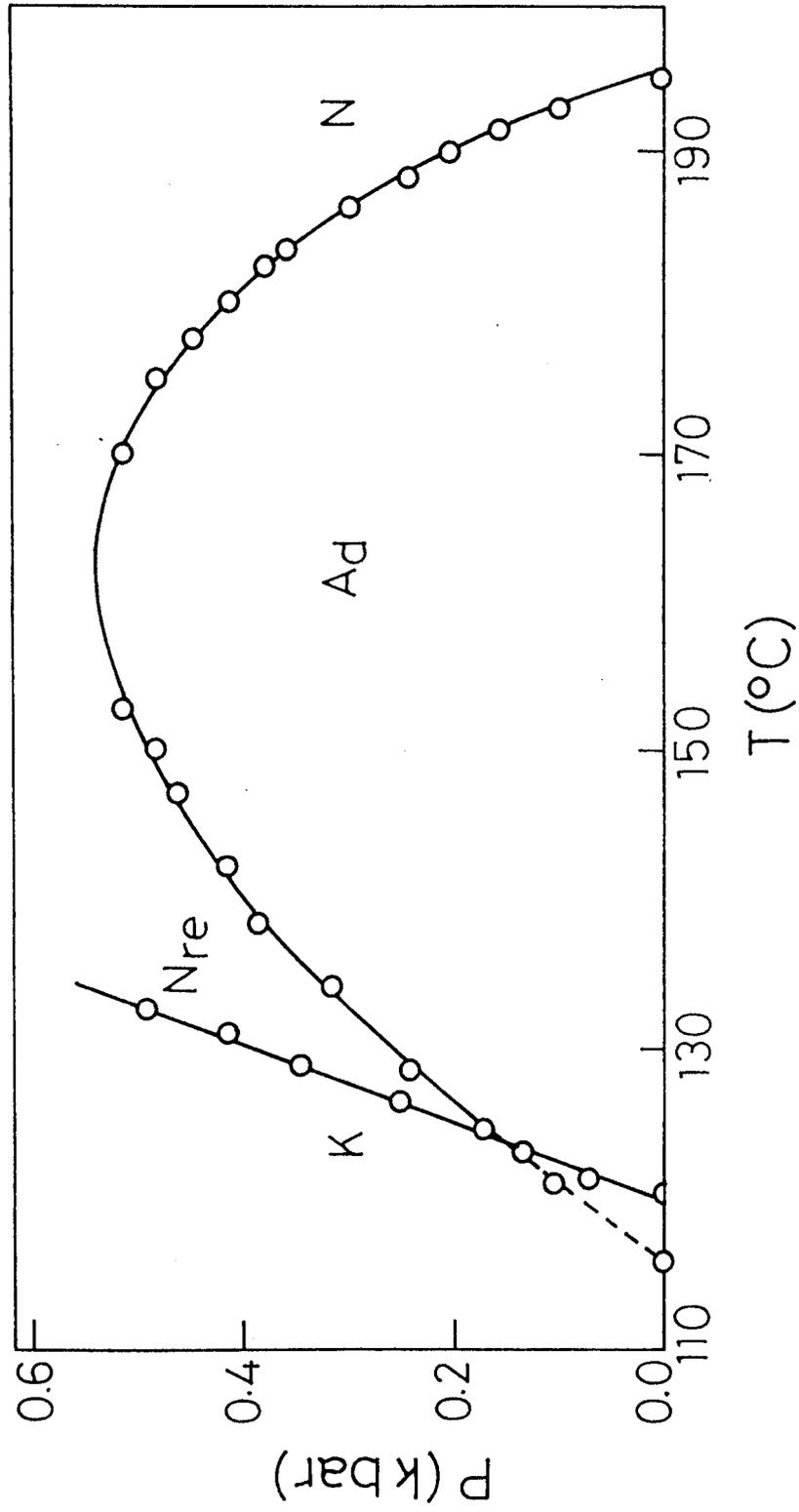


Figure 4.18 P-T diagram of 9 OCPBB showing the melting line and the A-N boundary. Dashed line indicates that the transition is monotropic

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