

CHAPTER V

EXPERIMENTAL STUDIES ON TERMINALLY NITRO SUBSTITUTED COMPOUNDS

5.1 Introduction

As we saw in the last chapter a large number of compounds with a terminal cyano group exhibit reentrant behaviour. But rather surprisingly the reentrant nematic phase was not observed till recently in compounds having a nitro group at one end of the molecule. The Xray investigations on cyano compounds have shown that an essential condition for the appearance of reentrant phases is the presence of a bilayer structure.¹ Even in the nitro compounds presence of such bilayer structure has been observed;² but reentrant phases were not found in these.³ This is rather intriguing because the magnitude of the longitudinal component of the terminal dipole - which plays a highly dominant role in inducing re-entrance - is almost the same for both the cyano and nitro groups (about 4.2 Debye⁴). According to Sigaud et al⁵ the absence of reentrant phases in substances with a terminal nitro group should be due to the larger size of the nitro group as compared with the cyano one.

The first observation of occurrence of reentrant nematic phase in terminally nitro substituted compounds was by Pelzl et al.⁶ They found that three binary systems - both the constituents being nitro compounds in each case - exhibit the N_{re} phase. Phase diagrams obtained by them are given in figs. 5.1, 5.2 and 5.3. Curiously, every constituent compound of these binary systems

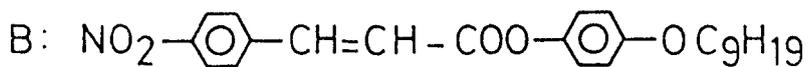
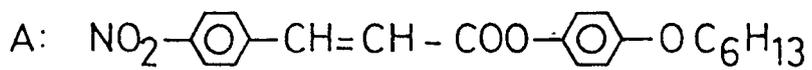
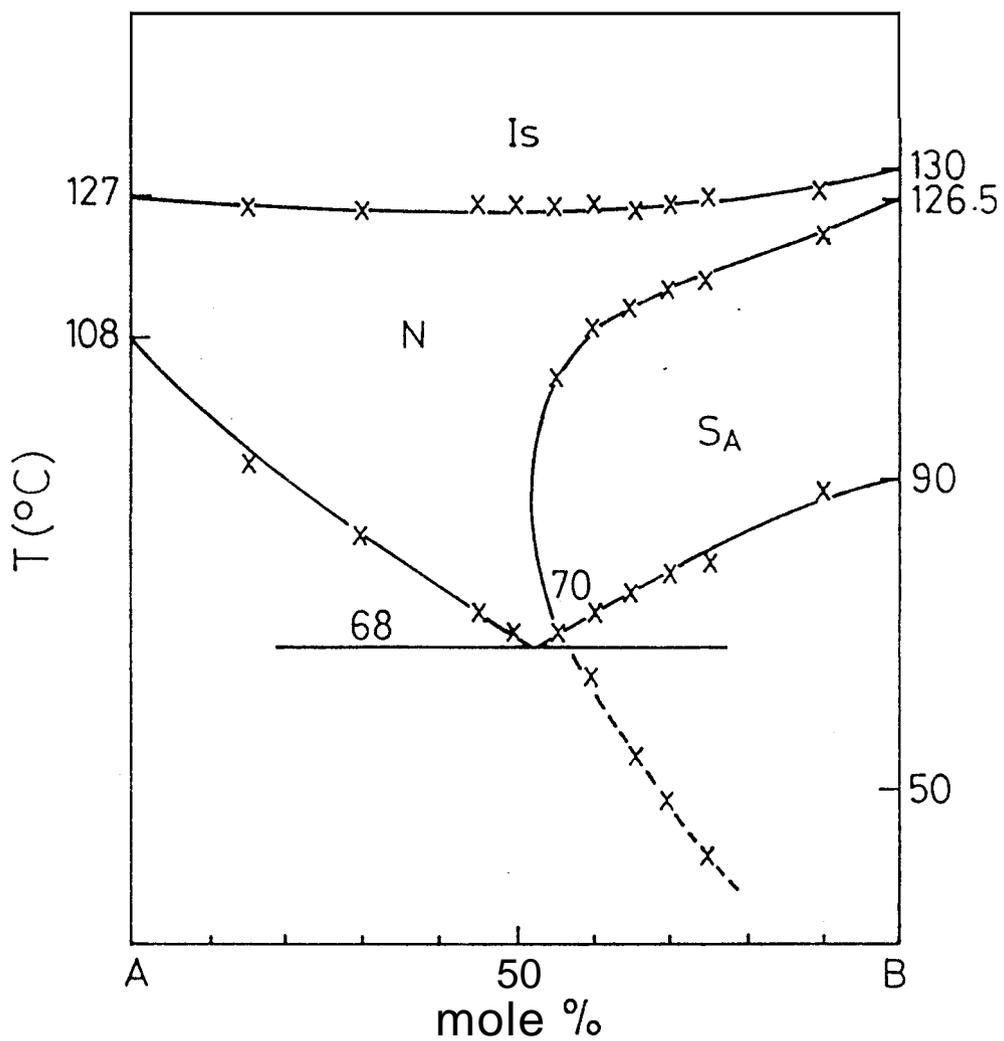


Figure 5.1 Isobaric binary phase diagram of the 6th and 9th homologues of 4-n-alkyloxyphenyl-4'-nitrocinnamates (from ref. 6)

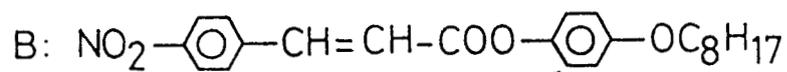
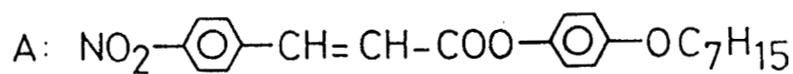
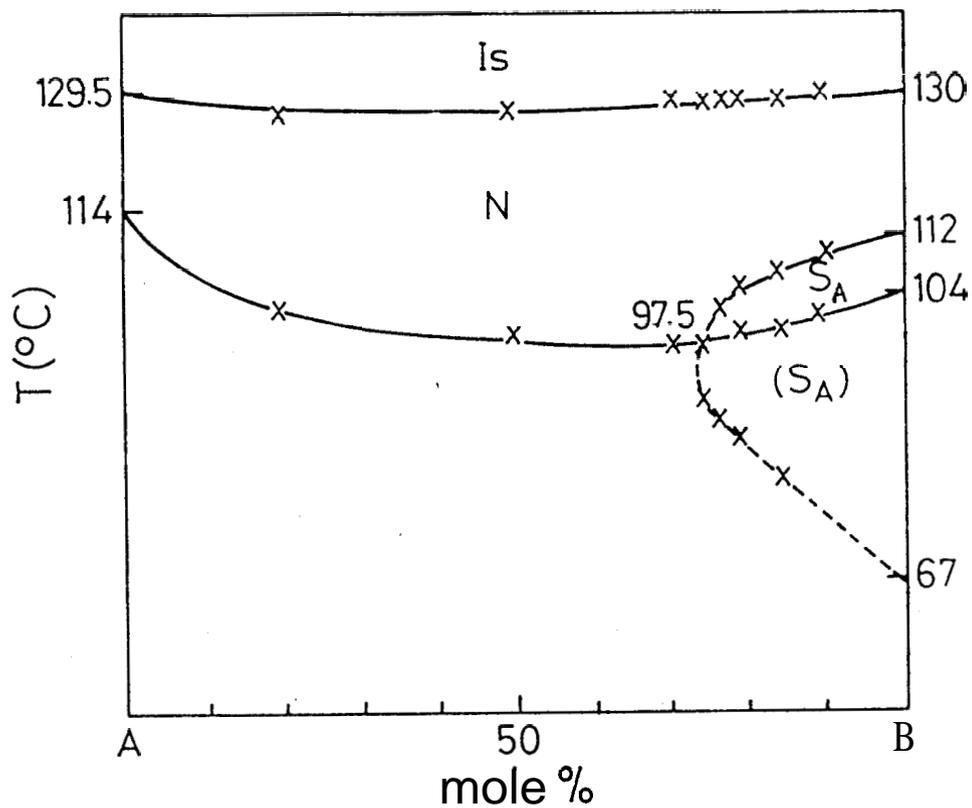
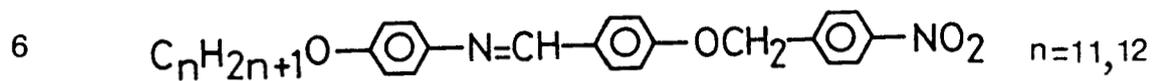
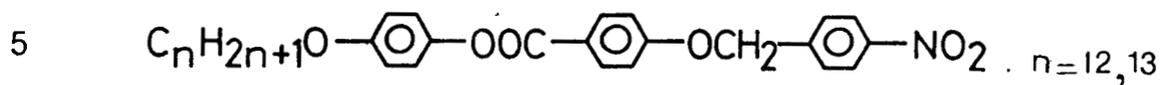
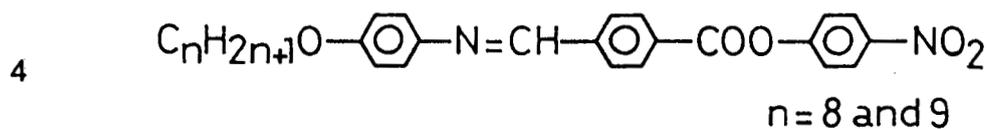
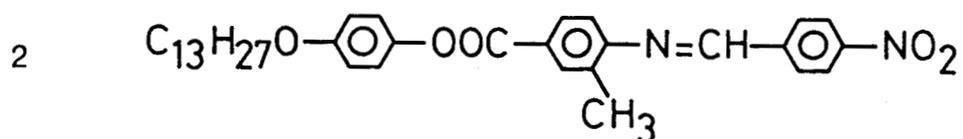


Figure 5.2 Temperature-concentration phase diagram of the mixtures of 7th and 8th homologues of 4-n-alkoxyphenyl-4'-nitrocinnamate (ref. 6)

has two aromatic rings with the longitudinal component of the bridging dipole being disposed in a direction opposite with respect to the nitro end dipole. This was followed by the first observation of reentrant phenomenon in a single component nitro system by Tinh et al.⁷ Here again the dipole moments of bridging groups opposed that of the terminal NO₂ group. After this quite a few nitro compounds showing N_{re} phase have been synthesised (for example, see ref. 8-10). The chemical formulae of all the three phenyl ring single component nitro compounds that are known⁷⁻¹⁰ to exhibit the N_{re} phase are listed in Table 5.1. It is obvious that in every one of these, the longitudinal component of the bridging dipole closest to the aliphatic chain of the molecule opposes that of the nitro end dipole. On the basis of these it has been repeatedly⁷⁻¹⁰ stated that a terminally nitro substituted compound in which both the bridging group dipoles are additive with respect to the nitro end dipole should not show reentrance.

In this chapter we present the results of our high pressure, Xray and miscibility studies on a triaromatic terminally substituted nitro compound, namely, 4-nitrophenyl-4'-(4"-n-hexyloxy benzoyloxy)benzoate (or 6 ONPBB for short) in which all the dipoles are additive with respect to the nitro end group. These results show that this compound has a latent reentrant nematic phase. We also present in this chapter the results of our dielectric studies on this compound. Finally, for the sake of comparison, this chapter also gives the results of our studies on a biaromatic nitro compound, namely, 4-nitrobenzylidene-4'-n-octyloxy aniline (NBOOA) in which the linkage group dipole opposes the terminal nitro dipole. The results of the latter studies support one of the generalizations quoted earlier, viz., that reentrance is more favoured in three aromatic compounds than in two aromatic ones.

Chemical structures of some single component nitro systems which exhibit N_{re} phase



5.2 Materials

Fig. 5.4 shows the chemical structures of the two compounds studied, viz., 6 ONPBB and NBOOA while their transition temperatures are listed in Tables 5.2 and 5.3 respectively. Both the compounds exhibit smectic A and nematic phases at 1 bar.

5.3 Results and Discussion

5.3.1 6 ONPBB

a) Xray Results

The variation of the layer spacing (d) as a function of temperature is shown in fig. 5.5. It is seen that within the experimental limits the value of d remains unchanged throughout the smectic A phase. The length of the molecule (l) in its most extended configuration as measured using a Dreiding model is 28.9 \AA . Thus the d/l ratio turns out to be about 1.04 and hence the smectic A phase can be classified as partially bilayer (A_d) phase.

b) Pressure Studies

As the maximum working temperature of our high pressure cell was about 230°C , the nematic-isotropic transition could not be followed under high pressure. Fig. 5.6 shows the P-T diagram of 6 ONPBB. The smectic A-nematic phase boundary has a negative slope even at 1 bar and curls towards the pressure axis with increasing pressure. This results in the appearance of a reentrant nematic

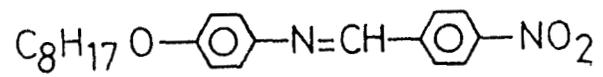
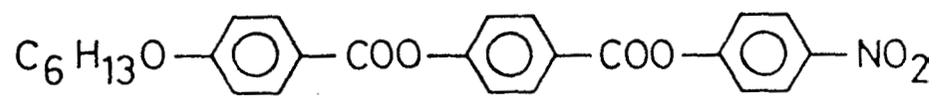


Figure 5.4 Chemical structures of 6 ONPBB (top) and NBOOA (bottom)

TABLE 5.2

Transition Temperatures of 4-nitrophenyl-4'-(4"-n-hexyloxy benzoyloxy)benzoate
(6 ONPBB)

Transition	Short Form	Temperature (°C)
Solid - Smectic A	K - S _A	124.0
Smectic A - Nematic	S _A - N	151.5
Nematic - Isotropic	N - I	238.4

TABLE 5.3

Transition Temperatures of 4-n-nitrobenzylidene-4'-octyloxy aniline
(NBOOA)

Transition	Short Form	Temperature (°C)
Solid - Smectic A	K - S _A	62.5
Smectic A - Nematic	S _A - N	74.0
Nematic - Isotropic	N - I	84.2

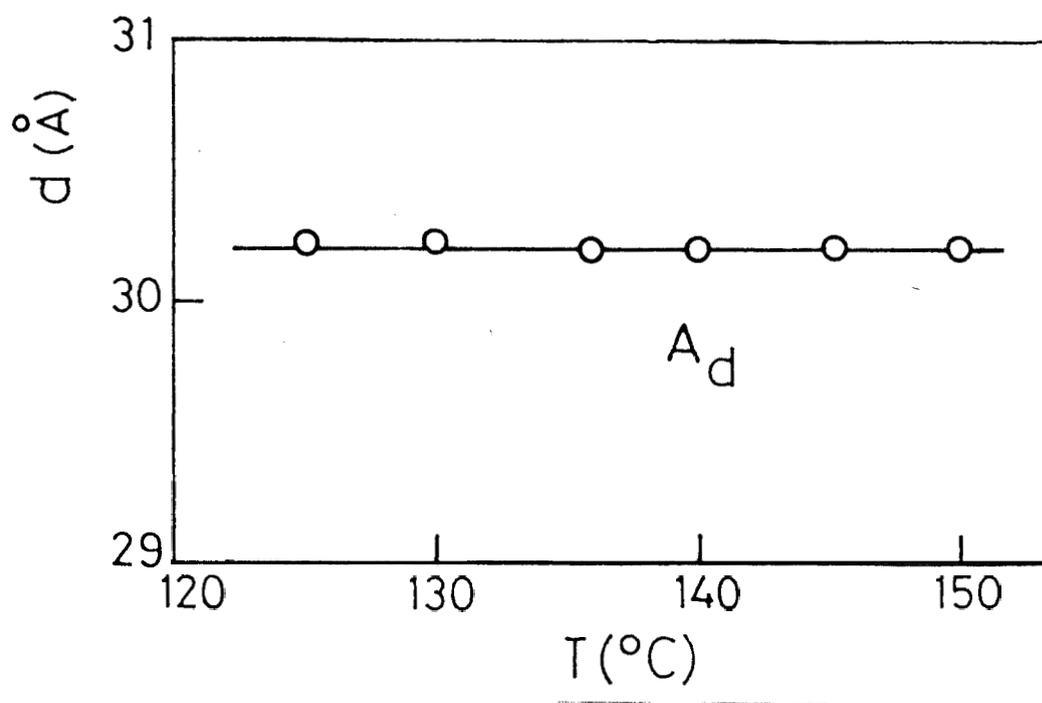


Figure 5.5 Temperature variation of layer spacing (d) in the smectic A phase of 6 ONPBB

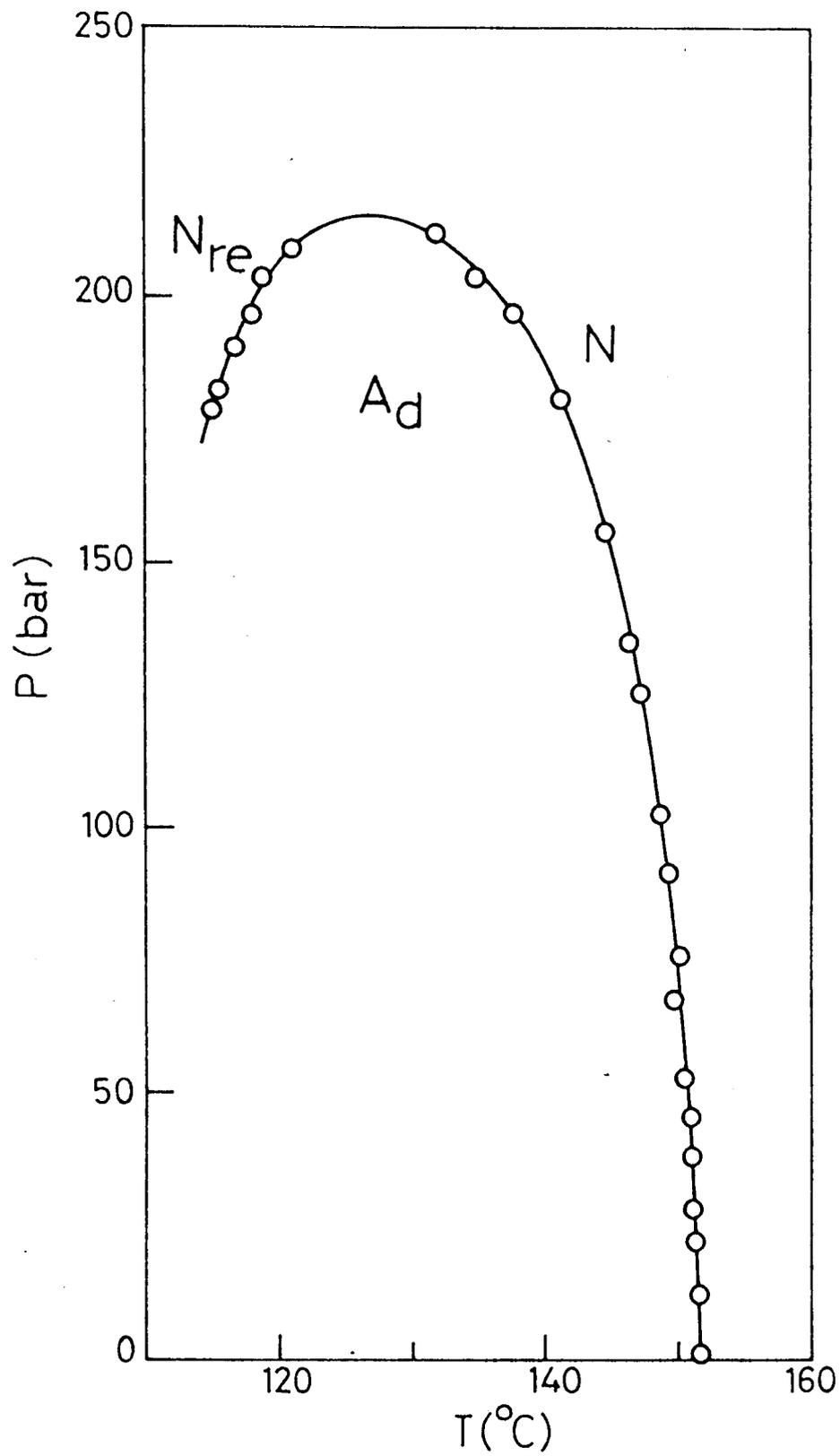


Figure 5.6 P-T diagram of 6 ONPBB showing the A-N phase boundary

phase in the pressure range 175-214 bar. Above a pressure of 214 bar, the smectic A phase is completely suppressed. The observation of the N_{re} phase below 175 bar is prevented by the onset of crystallization. The existence of N_{re} phase at high pressure was confirmed by optical microscopic observations of the sample.

The fact that this compound exhibits the reentrant nematic phase at high pressure supports the Xray results, namely, the smectic A phase of this compound is a partially bilayer phase.

We shall now analyse the shape of the P-T boundary.

Thermodynamic analysis of the A-N boundary of 6 ONPBB in the P-T plane

It might be recalled that soon after the observation of reentrant nematic phase at high pressure by Cladis et al¹³ attempts were made to conduct a thermodynamic analysis of the slope of the A-N phase boundary. This was carried out by Clark¹⁴ and independently by Klug and Whalley¹⁵. We shall briefly summarise the approach of Clark.

The P-T diagram of 8OCB used by Clark¹⁴ is shown in fig. 5.7. Along the phase boundary, the molar Gibbs free energy difference between the nematic and smectic A phases, viz., $\Delta G = G_N - G_A$ is zero and the Clausius-Clapeyron equation may be applied (assuming the transition to be first order). Therefore, we have

$$\left(\frac{\delta P}{\delta T} \right)_{\Delta G=0} = \frac{S_N - S_A}{V_N - V_A} = \left(\frac{\Delta S}{\Delta V} \right)_{\Delta G=0} \quad [1]$$

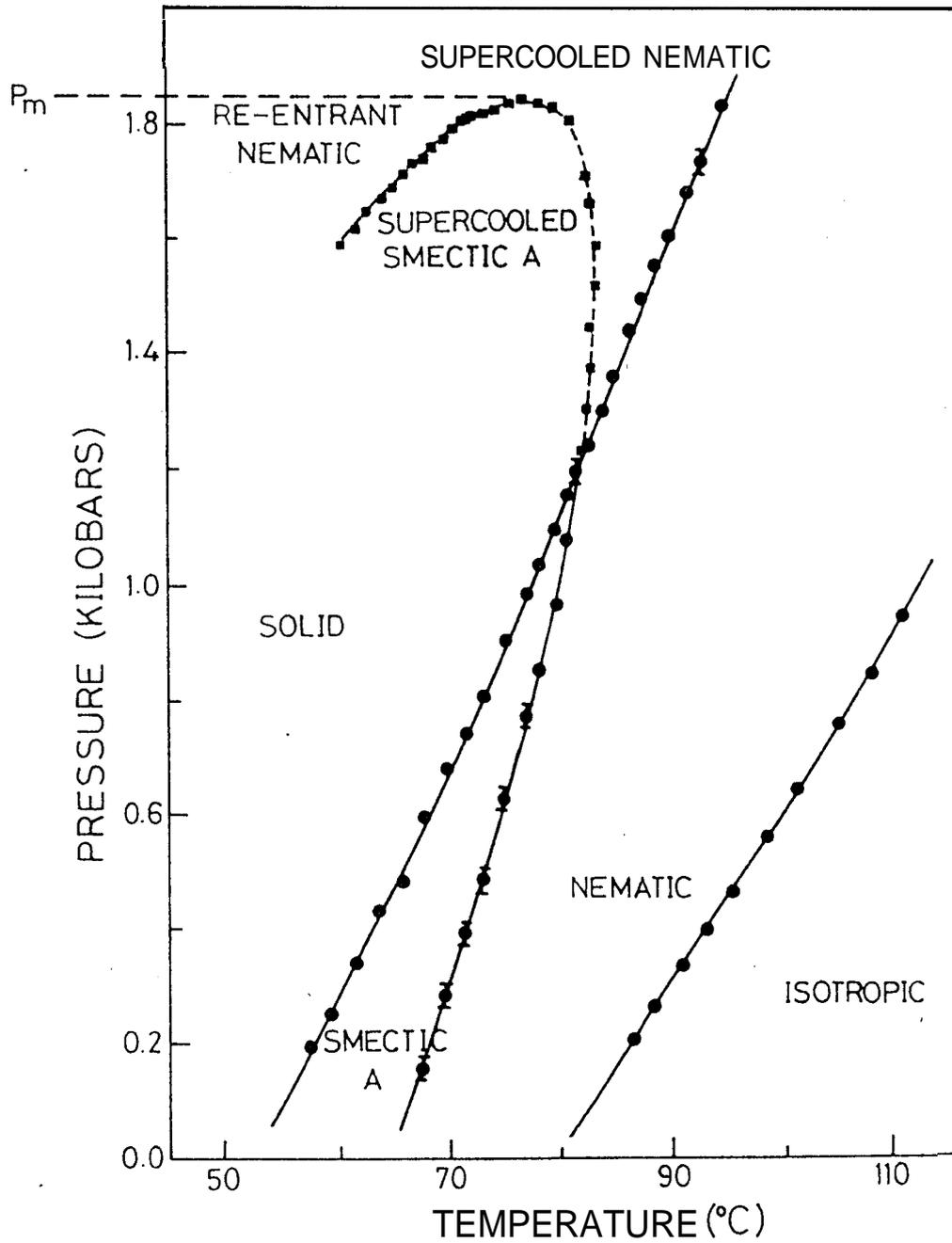


Figure 5.7 P-T diagram of 8OCB obtained by Cladis13

Here ΔS and ΔV represent the difference in the molar entropy and molar volume between the nematic and smectic A phases respectively. In fig. 5.7 it is seen that $[\delta P/\delta T]_{\Delta G=0}$ is positive at $P = 1$ bar. Hence $\Delta V > 0$ (as $\Delta S > 0$) at atmospheric pressure. As the pressure is increased, $[\frac{\delta P}{\delta T}]_{\Delta G=0}^{-1}$ approaches zero and changes sign, thereby implying that $\Delta V = 0$ at 1.6 kbar & 83°C and becomes negative at higher pressures. Defining the compressibility of a phase as $\beta = [\partial V/\partial P]_T$ one can conclude from the above that $\Delta\beta = \beta_N - \beta_A$ is negative. Since, both β_N and β_A are negative we have $|\beta_N| > |\beta_A|$. If we continue around the phase boundary $(\frac{\delta P}{\delta T})_{\Delta G=0}$ approaches zero and changes sign. This implies that ΔS goes through zero ($\Delta S = 0$ at $P = P_m = 1.84$ kbar, $T = 77^\circ\text{C}$) and becomes negative. Therefore both ΔS and ΔV are negative in the reentrant portion of the phase boundary. Since the specific heat $C_p = T(\frac{\partial S}{\partial T})_p$, the fact that ΔS decreases with decreasing temperature implies that the difference in the specific heat between the nematic and smectic A phases at the phase boundary, i.e., $\Delta C_p = C_{pN} - C_{pA}$ is positive, hence one has $C_{pN} > C_{pA}$.

The shape of the phase boundary may be quantitatively related to the thermodynamic parameters of the two phases by obtaining an expression for the pressure and temperature dependence of the difference in the Gibbs free energy between the nematic and smectic A phases, i.e., expressing ΔG in terms of P and T . In the vicinity of some reference point (P_0, T_0) , ΔG may be expressed in a Taylor's series as

$$\begin{aligned} \Delta G = & \Delta G_0 + \Delta V_0 (P - P_0) - \Delta S_0 (T - T_0) + \frac{\Delta\beta}{2} (P - P_0)^2 \\ & + \Delta\alpha (P - P_0) (T - T_0) - \frac{\Delta C_p}{2T_0} (T - T_0)^2 + \dots \end{aligned} \quad [2]$$

where the following notations are used:

$$\begin{aligned}
 \Delta G &= G_N - G_A \\
 \Delta S &= S_N - S_A = -(\partial \Delta G / \partial T)_P \\
 \Delta V &= V_N - V_A = (\partial \Delta G / \partial P)_T \\
 \Delta G_o &= \Delta G(P_o, T_o) \\
 \Delta S_o &= \Delta S(P_o, T_o) \\
 \Delta V_o &= \Delta V(P_o, T_o) \\
 \Delta \beta &= (\partial \Delta V / \partial P)_T = (\partial V_N / \partial P)_T - (\partial V_A / \partial P)_T \\
 \Delta \alpha &= (\partial \Delta V / \partial T)_P = -(\partial \Delta S / \partial P)_T \\
 \Delta C_p &= T (\partial \Delta S / \partial T)_P
 \end{aligned} \tag{3}$$

The neglect of higher order terms in applying equation [2] is equivalent to assuming that $\Delta \alpha$, $\Delta \beta$ and ΔC_p are sufficiently independent of P and T over the range of pressure and temperature considered here. The $N-S_A$ phase boundary in the P - T plane is obtained from equation [2] by setting ΔG to zero and solving for $P(T)$. Expanding and rearranging equation [2], we have

$$aP^2 + bT^2 + cPT + dP + eT + f = 0 \tag{4}$$

where

$$\begin{aligned}
 a &= \Delta \beta / 2 \Delta G_o \\
 b &= -\Delta C_p / 2 T_o \Delta G_o \\
 c &= \Delta \alpha / \Delta G_o \\
 d &= -(\Delta \beta / \Delta G_o) P_o - (\Delta \alpha / \Delta G_o) T_o = -2aP_o - cT_o \\
 e &= (\Delta C_p / \Delta G_o) - (\Delta \alpha / \Delta G_o) P_o = -2bT_o - cP_o \\
 f &= 1 + (\Delta \beta / 2 \Delta G_o) P_o^2 + (\Delta \alpha / \Delta G_o) P_o T_o - (\Delta C_p / 2 \Delta G_o) T_o^2 \\
 &= 1 + aP_o^2 + cP_o T_o + bT_o^2
 \end{aligned}$$

Equation (4) is the general equation of a conic section. Thus elliptical phase boundaries can be obtained from equation (4) if

i) $C^2 - 4ab < 0$

ii) both a and b are either positive or negative.

The reference point (P_o, T_o) turns out to be the centre of the ellipse.

The fit of the data of Cladis et al¹³ to an ellipse was therefore attempted by Clark.¹⁴ The solid line in fig. 5.7 shows this fit and it is seen that the fit is extremely good. Kalkura¹⁶ has carried out a similar fit using the P-T data for 8 single component systems exhibiting the N_{re} phase at 1 bar. The fit of the data to an ellipse seem to be good for all these cases.

We shall now carry out a similar fit using our data of 6ONPBB. For the sake of ease of computation, we have reduced the number of constants in equation (4) by dividing throughout by f, so that equation (4) now reduces to the form

$$a'P^2 + b'T^2 + c'PT + d'P + e'T + 1 = 0 \quad [5]$$

where $a' = a/f$, $b' = b/f$ and so on.

The computations have been done using the ELLIPSE MATMUL Program on a LSI computer.¹⁷ The constants evaluated for the P,T data of 6 ONPBB is shown in Table 5.4. The curve drawn using these constants is shown in fig. 5.8. From Table 5.4 and fig. 5.8, it is clear that the shape of the A-N boundary of 6 ONPBB

TABLE 5.4

Computed values for the coefficients in equation (4)
(for details see the text)

P_o kbar	T_o °C	$a' \times 10^2$	$b' \times 10^5$	$c' \times 10^4$	$d' \times 10^2$	$e' \times 10^3$
-0.25	126.95	65.873	6.430	5.503	10.537	16.344

is an ellipse. The fit of the data points to the equation of an ellipse is indeed very good. An extrapolation of this fitted phase boundary to atmospheric pressure gives a virtual N_{re} - A_d transition temperature of 103°C .

c) Miscibility Studies

In order to confirm the results of pressure studies, miscibility studies of 6 ONPBB have been done with a compound (9 OCPBB) which has a N_{re} phase at 1 bar. As the smectic A phase of the latter compound i.e., 9 OCPBB is also a partially bilayered one," one would expect the smectic A phases of the two compounds to be miscible. The temperature-concentration phase diagram obtained for this system is shown in fig. 59. Rather surprisingly, the A phases get separated in the concentration range $0.3 < X < 0.44$, where X is the mole fraction of 9 OCPBB in the mixture. It may be recalled here that a similar instance of the A_d phases of the cyano and nitro compounds getting separated led to the observation of an A_d - A_d transition." Going back to fig. 5.9, we see that the N_{re} is observed even for mixtures which are rich in 6 ONPBB. The crystallization line, which cuts the A- N_{re} portion of the phase boundary for $X \approx 0.1$ prevents the occurrence of the N_{re} phase for concentration below $X = 0.1$. An extrapolation of the A- N_{re} phase boundary to $X = 0$ gives the virtual A- N_{re} transition temperature of 105°C for 6 ONPBB which is in reasonably good agreement with the value obtained (103°C) from the pressure studies. This emphasises the fact that the possibility of getting the reentrant nematic phase at 1 bar in terminally substituted nitro compounds in which the longitudinal components of the bridging group dipoles are additive with respect to the nitro end dipole is a distinct possibility.

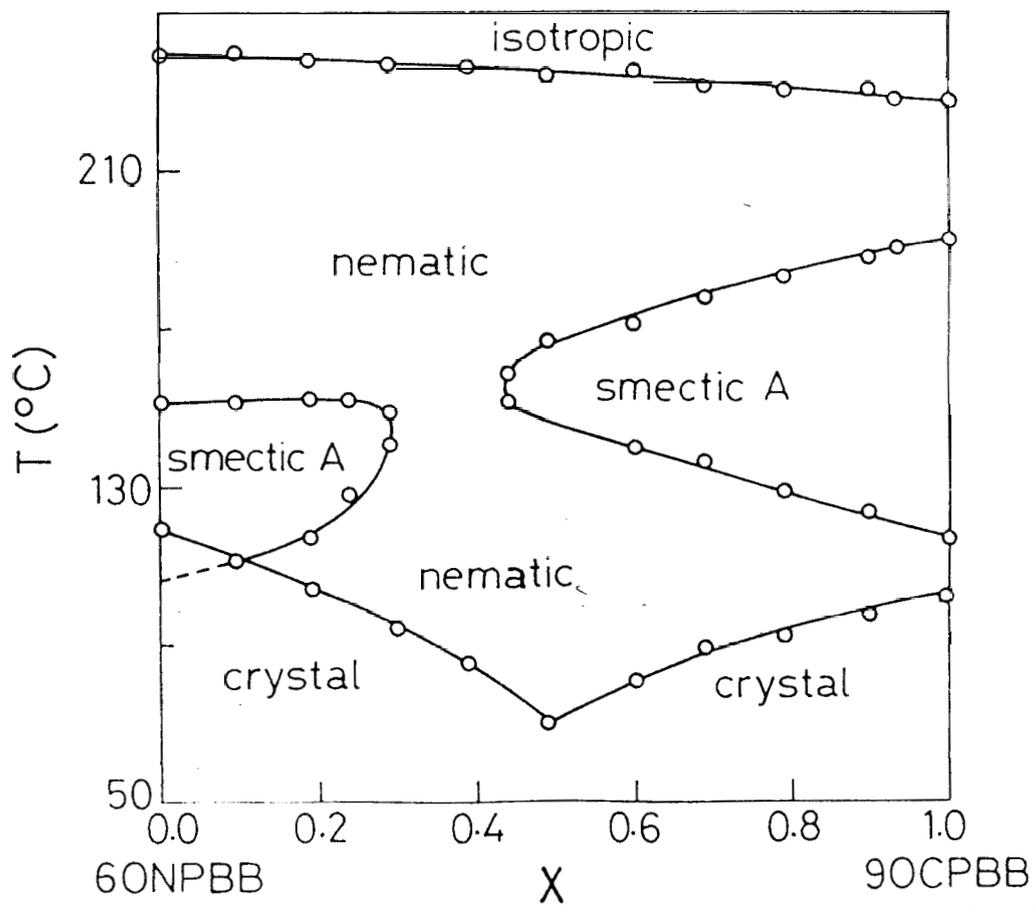


Figure 5.9 Temperature-concentration diagram (at 1 bar) for binary mixture of 6 ONPBB and 9 OCPBB. X is the mole fraction of 9 OCPBB in the mixture

d) Dielectric Studies

Since the first systematic measurements on dialkoxy substituted azo and azoxybenzenes by Maier and Meier,¹⁸ there have been a number of studies on the dielectric properties of liquid crystals (for the latest review see ref 19).

In strongly polar compounds, as mentioned earlier, the correlation between neighbouring molecules is antiparallel. An important consequence of such associations of the molecule is that the mean dielectric constant $\bar{\epsilon}$ in the mesophase becomes less than the isotropic value (ϵ_{is}), because of the decrease in antiparallel ordering in the isotropic phase. Here $\bar{\epsilon}$ is the average dielectric constant defined as $\bar{\epsilon} = [\epsilon_{\parallel} + 2\epsilon_{\perp}] / 3$, ϵ_{\parallel} and ϵ_{\perp} being the principal dielectric constants parallel and perpendicular to the director. Ratna and Shashidhar^{20,21} have experimentally verified that $\bar{\epsilon}$ is less than the extrapolated isotropic value in a number of cyano compounds. The experimental curves also showed that $\bar{\epsilon}$ as well as ϵ_{is} (extrapolated value) decrease with decrease in temperature, which again may be attributed to the increase of antiparallel ordering at lower temperatures.

Apart from the static values, the frequency dependence of the dielectric permittivity is important in understanding the dynamics of the system. ϵ_{\parallel} and ϵ_{\perp} exhibit different frequency dependencies. ϵ_{\perp} has a relaxation in the microwave region only where as ϵ_{\parallel} shows a relaxation in the low frequency region also. The relaxation frequency f_R is proportional to $\exp(-W/k_B T)$, where W is the total activation energy for dielectric relaxation, k_B is the Boltzmann constant

and T is the absolute temperature. A plot of $\ln f_R$ versus T should hence be a straight line, the slope of which gives the activation energy W . Thus, the total activation energy can be calculated by measuring the temperature variation of f_R of $\epsilon_{||}$

The dielectric constant ϵ is actually a complex quantity given by $\epsilon = \epsilon' + i\epsilon''$. The real part ϵ' describes the static dielectric constant whereas the imaginary part (ϵ'') describes the dielectric losses associated with the relaxation process.

K.S.Cole and R.H.Cole²² suggested a graphical representation (now known as the cole-cole plot) of ϵ' versus ϵ'' to indicate the nature of relaxation. The points (ϵ', ϵ'') lie on a semicircle with the centre on the ϵ' axis. Deviations from the semicircle plot indicate a distribution of relaxation times.

As our interest in this chapter is about reentrant nematogens, we shall summarise some of the salient features concerning the dielectric results of such compounds available in the literature.^{23,24}

1. The average dielectric constant $\bar{\epsilon}$ in the nematic phase is less than the extrapolated isotropic value (ϵ_{is}). The difference between $\bar{\epsilon}$ and ϵ_{is} increases as the temperature is lowered indicating an increase in the antiparallel associations.
2. There is a continuous increase of anisotropy $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$ with decrease of temperature throughout the nematic, smectic A and reentrant nematic

phases.

3. The activation energy W in the nematic and reentrant nematic phases are quite different; the latter being higher in all the cases. This was in fact the first experimental evidence that the molecular associations in the two nematic phases are different

With this in the background, we now present the results of the dielectric studies of 6 ONPBB which we have shown to have a latent reentrant nematic.

Fig. 5.10 shows the plot of the static dielectric constants along (ϵ_{\parallel}) and perpendicular (ϵ_{\perp}) to the director against temperature. Also plotted in the same diagram are the calculated anisotropy $\Delta \epsilon (= \epsilon_{\parallel} - \epsilon_{\perp})$ and the average dielectric permittivity $\bar{\epsilon} [= (\epsilon_{\parallel} + 2\epsilon_{\perp})/3]$. It is evident from the structural formula shown in fig. 5.4 that the bridging group dipoles are oriented additively with respect to the nitro end dipole and hence a large value of the dielectric constant is seen along the director. As seen in fig. 5.10 ϵ_{\parallel} exhibits a smooth variation right through the A-N transition and increases monotonically with decreasing temperature. The value of ϵ_{\perp} also increases with decreasing temperature but unlike ϵ_{\parallel} , shows a small decrease (about 2%) at the A-N transition. This effect of ϵ_{\perp} is reflected in $\Delta \epsilon$ and $\bar{\epsilon}$ also. It may be noted that $\Delta \epsilon$ shows a continuous increase and does not get saturated in the A_D phase.

Dielectric Relaxation Results

Representative cole-cole diagrams in the smectic A and nematic phases

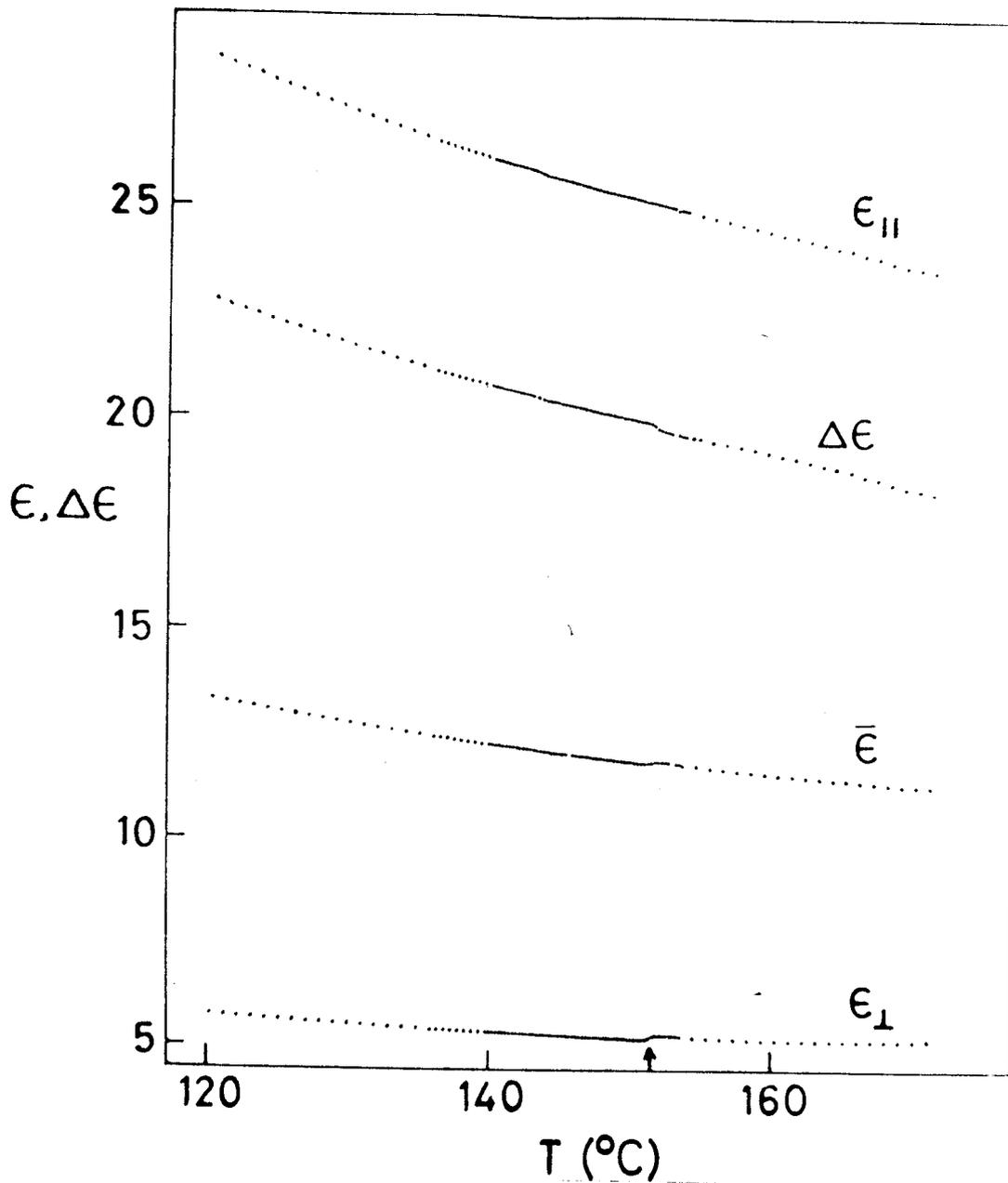


Figure 5.10 Temperature variation of static dielectric constant $\epsilon_{||}$ and ϵ_{\perp} and the dielectric anisotropy $\Delta\epsilon (= \epsilon_{||} - \epsilon_{\perp})$ in the A and N phases of 6 ONPBB. The diagram also shows the variation of $\bar{\epsilon} (= \frac{\epsilon_{||} + 2\epsilon_{\perp}}{3})$

are shown in fig. 5.11. It is seen that the points (ϵ', ϵ'') lie on a semicircle, with the centre on the ϵ' axis, which indicates that there is only a single relaxation of ϵ_{11} in the low frequency region.

A plot of relaxation frequency f_R versus $1/T$ is shown in fig. 5.12. Linear least square fits of the data points in the nematic and smectic phases yield the values of activation energy of 0.50 eV and 0.55 eV for the two phases respectively.

This result ($W_N < W_{Ad}$) is at variance with the data available in the literature ($W_N \gg W_{Ad}$). The reason for this unusual behaviour is not clear.

5.3.2 NBOOA

This compound is the nitro analogue of CBOOA, whose properties have been extensively studied. The compound exhibits smectic A and nematic phases at 1 bar (see Table 5.3). The layer spacing in the A phase is 31.6 \AA . The length of the molecule in its most extended conformation measured using a model came out to be 25.3 \AA . Thus, the d/l ratio, which we have ascertained to be temperature independent, is 1.25. Hence the A phase can be characterised as a partially bilayer $A(A_d)$ phase.

CBOOA, as we saw in the last chapter, exhibits a N_{re} phase at high pressure. Hence it was natural to expect a similar behaviour for NBOOA. Also, in NBOOA the bridging group dipoles oppose that of the nitro end group and as we mentioned in the introductory part of the chapter it is a strong candidate to show a reentrant behaviour. With this in view we performed high pressure

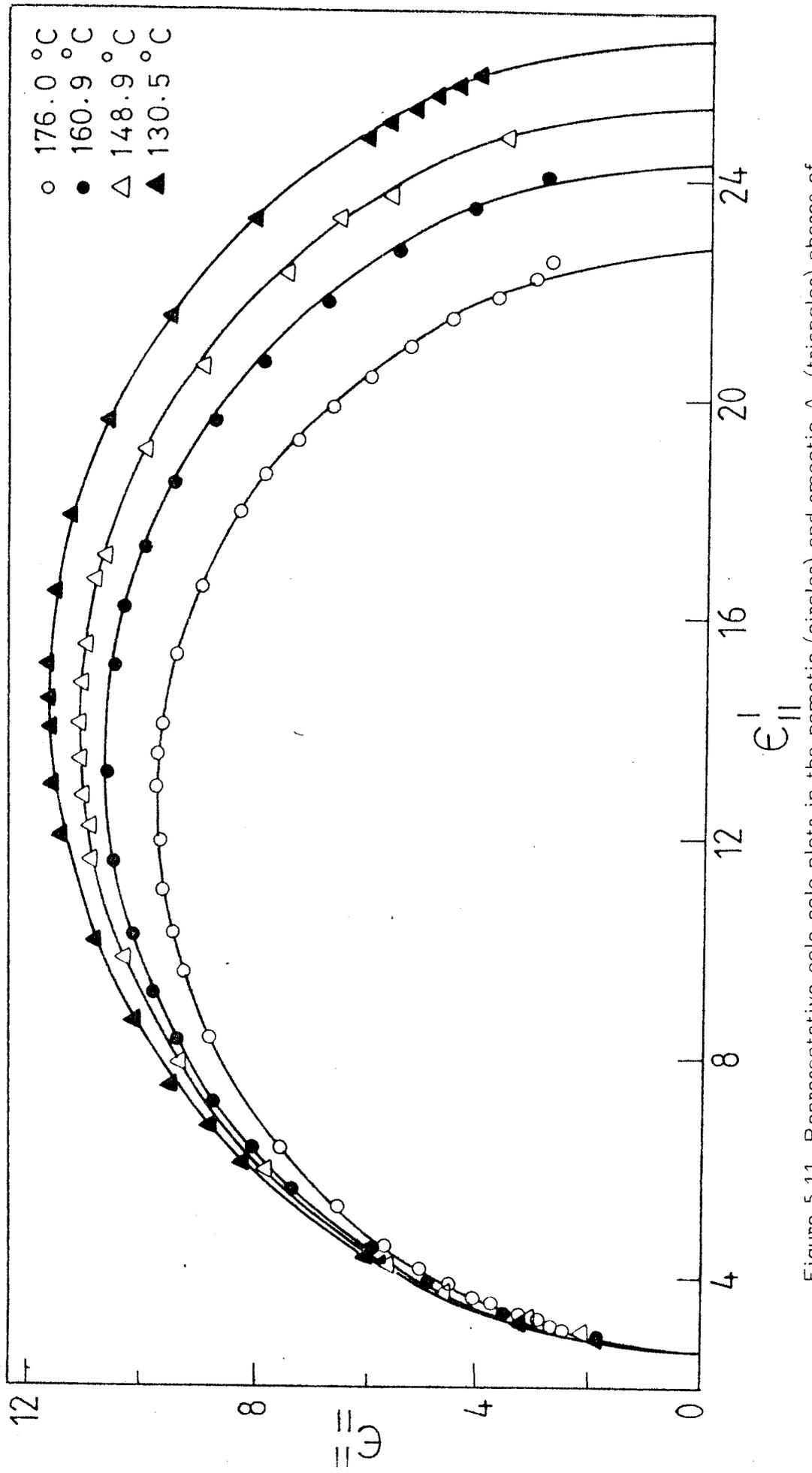


Figure 5.11 Representative cole-cole plots in the nematic (circles) and smectic A (triangles) phases of 6 ONPBB

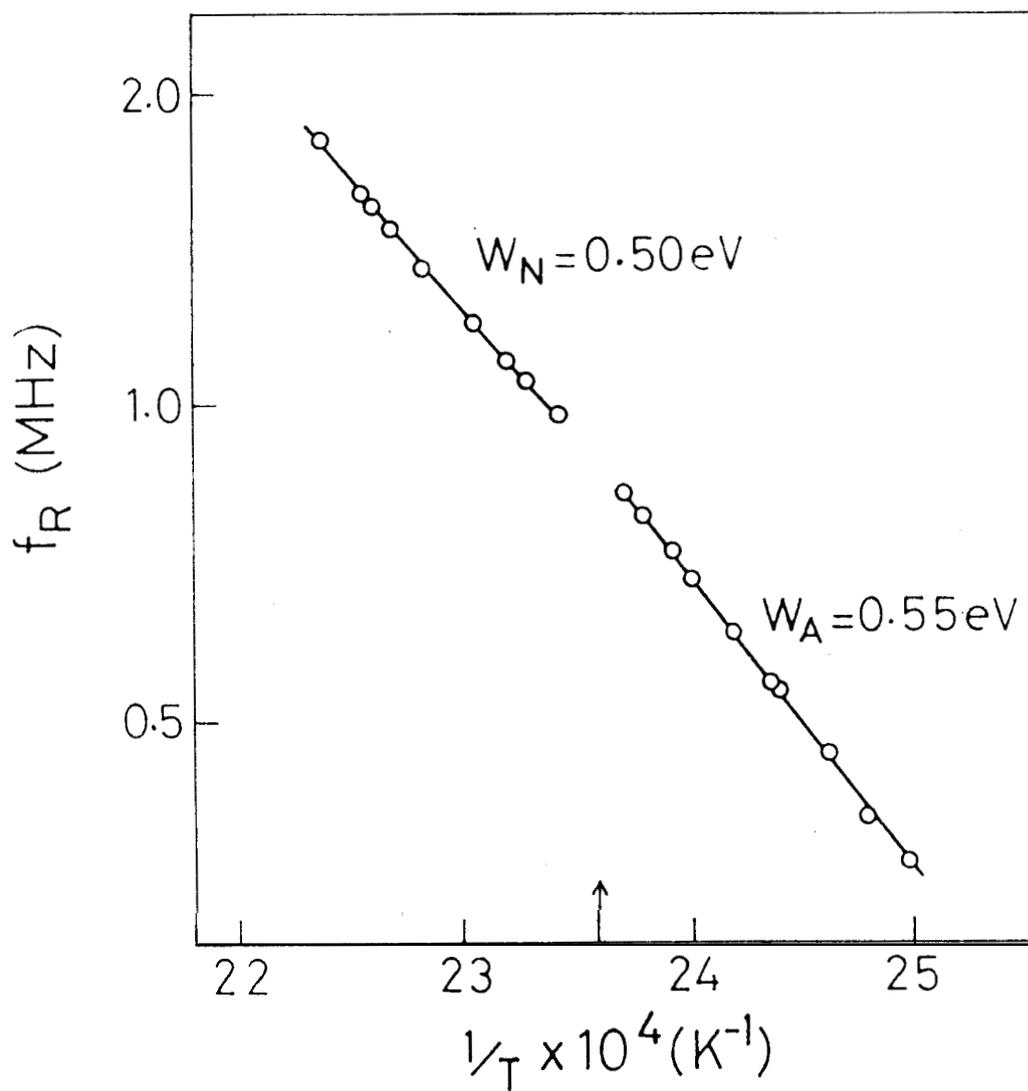


Figure 5.12 Plot of frequency of relaxation (f_R) versus $1/T$ in the A and N phases of 6 ONPBB

studies on this compound. The pressure-temperature phase diagram is shown in fig. 5.13. It can be seen that the A-N transition which is enantiotropic at lower pressures, becomes monotropic beyond about 1.8 kbar. Finally at about 2 kbar, the crystallization line cuts A-N line and thereby the A phase ceases to exist for pressures beyond 2 kbar. Also the A-N transition boundary is practically linear throughout and the absence of any curvature of the boundary precludes the possibility of observing the N_{re} phase. This result shows that the occurrence of the reentrant nematic phase is clearly less favoured in two phenyl ring systems than in three phenyl ring ones even in terminally nitro substituted compounds.

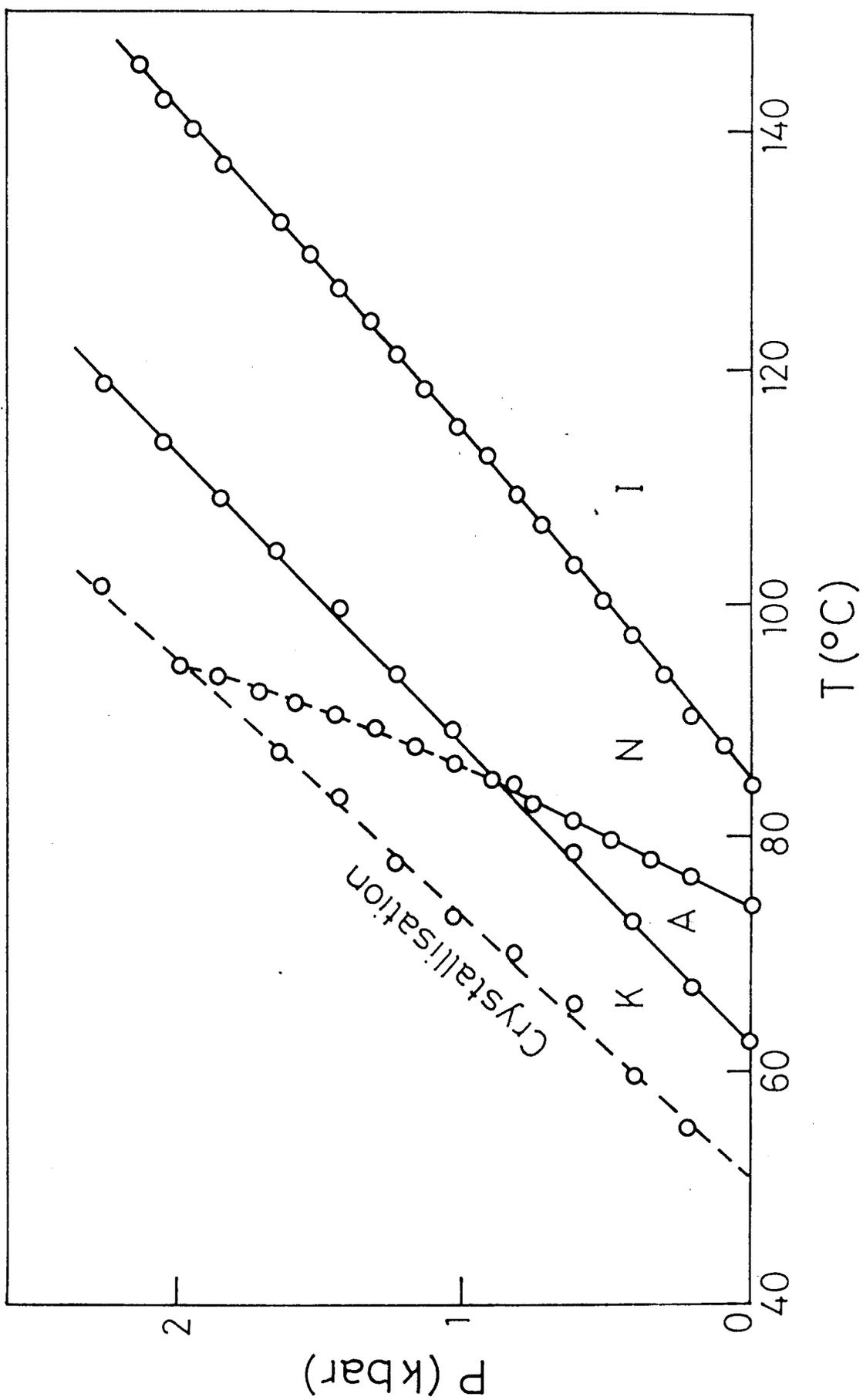


Figure 5.13 Pressure-temperature phase diagram of NBOOA

References

1. A.J.Leadbetter, J.C.Frost; J.P.Gaughan, G.W.Gray and A.Mosley, *J.Physique*, 40, 375 (1979).
2. A.C.Griffin and J.F.Johnson, *J. Am. Chem. Soc.*, 99, 4859 (1977).
3. P.E.Cladis, D.Guillon, W.B.Daniels and A.C.Griffin, *Mol. Cryst. Liq. Cryst. Lett.*, 56, 89 (1979).
4. V.I.Minkin, O.A.Osipov and V.A.Zhdanov, "Dipole Moments in organic Chemistry", (Plenum) 1970.
5. G.Sigaud, Nguyen Huu Tinh, F.Hardouin and H.Gasparoux, *Mol. Cryst. Liq. Cryst.*, 69, 81 (1981).
6. G.Pelzl, V.Bottger, S.Kallweit, D.Demus and H.Sackmann, *Cryst. Res. Technol.* 16, 119 (1981).
7. Nguyen Huu Tinh, F. Hardouin and C.Destrade, *J. Physique*, 43, 1127 (1982).
8. Nguyen Huu Tinh, *J.Chim. Phys.*, 80, 83 (1983).
9. Nguyen Huu Tinh, H.Gasparoux, J. Malthete and C. Destrade, *Mol Cryst. Liq. Cryst.*, 114, 19 (1984).
10. Nguyen Huu Tinh, H.Gasparoux and C.Destrade, *Mol. Cryst. Liq. Cryst.*, 123, 271 (1985).
11. See section 4.4 of chapter IV
12. For a detailed study see chapter VI.
13. P.E.Cladis, R.KBogardus, W.B.Daniels and G.N.Taylor, *Phys. Rev. Lett.*, 39, 720 (1977).

14. N.A.Clark, J. Physique, 40, C3-345 (1979).
15. D.D.Klug and E.Whalley, J.Chem. Phys., 71, 1874 (1979).
16. A.N.Kalkura, "High Pressure Optical Studies of Liquid Crystals", Ph.D. Thesis, University of Mysore, 1982.
17. The author thanks Ms. Jayanthi Ramachandran and Mr. B.Nataraj for their help in carrying out the computations.
18. W.Maier and G.Meier, Z.Naturforsch., 16a, 262 (1961).
19. H.Kresse, "Advances in Liquid Crystals", Vol. 6, Ed. G.H.Brown (Academic Press, 1983) p.109.
20. B.R.Ratna and R.Shashidhar, Pramana, 6, 278 (1976).
21. B.R.Ratna and R. Shashidhar, Mol. Cryst. Liq. Cryst., 42, 113 (1977).
22. K.S.Cole and R.H.Cole, J. Chem. Phys. 9, 341 (1941).
23. B.R.Ratna, R.Shashidhar and K.V.Rao, Proc. Int. Liq. Cryst. Conf., Bangalore, December. 1979, Ed. S.Chandrasekhar (Heyden, London) 1980, p.135.
24. C.Legrand, J.P.Parneix, A.Chapoton, Nguyen Huu Tinh and C.Destrade, J.Physique Lett., 45, L-283 (1984).