

CHAPTER VI

EXPERIMENTAL STUDIES ON A BINARY LIQUID CRYSTAL SYSTEM EXHIBITING AN A_d - A_d TRANSITION

6.1 Introduction

The smectic A phase can be described as being composed of equi-spaced layers of molecules, the long axis of the molecules being on the average normal to the smectic planes but with no true long range translational order.' The Xray diffraction pattern reveals a sharp peak at low angles ($\theta \sim 1^\circ$) and a diffuse outer ring at large angles ($8-8^\circ$). The low angle scattering corresponds to the periodicity of the mass density wave² along the layer normal (fig. 6.1). The large angle diffuse ring, which corresponds to the mean intermolecular distance within a layer, is isotropic showing thereby that the in-plane correlations are indeed liquid like. Such being the case, one expects the layer spacing - the periodicity of the density wave - to be approximately equal to the molecular length. This is indeed the case in most of the non polar compounds and also some strongly polar compounds. However, as we saw in the preceding chapters, in a large number of strongly polar compounds, the layer spacing is found to be much larger than the molecular length. Madhusudana and Chandrasekhar³ argued that the neighbouring molecules in strongly polar systems should have antiparallel correlation. That the longitudinal components of the dipolar groups in the molecules play an important role in stabilizing or destabilizing the smectic A and nematic phases is a well known fact.⁴ Xray and

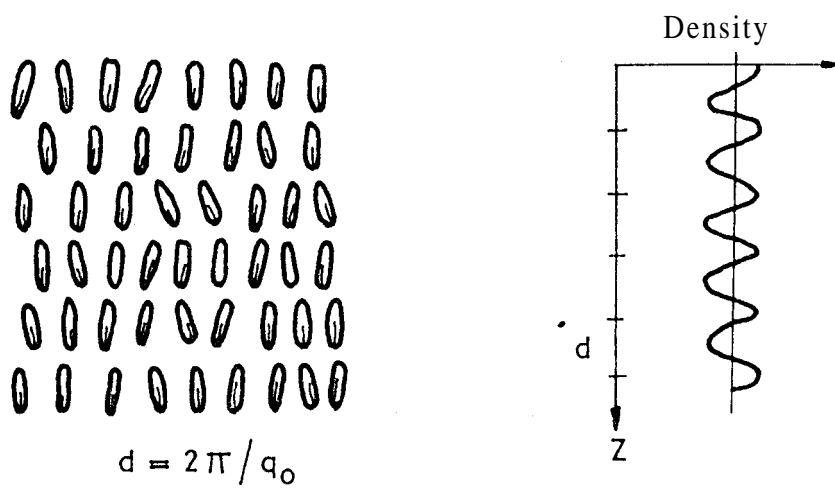


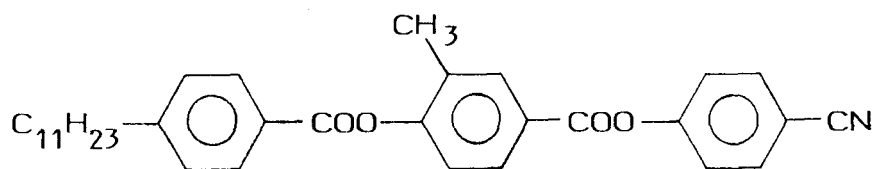
Figure 6.1 Schematic diagram of smectic A phase with its one dimensional density wave along the average direction of the molecular axis

neutron diffraction experiments^{5,6} on cyano biphenyls - typical strongly polar compounds - showed that the layer spacing is about 1.4 times molecular length.

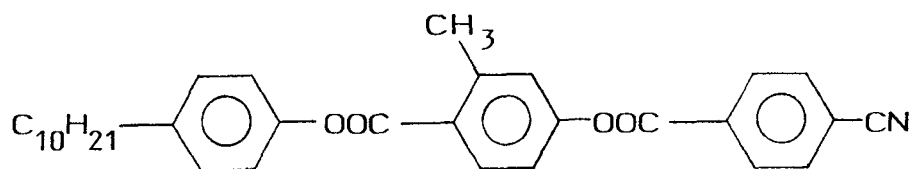
To account for these observations, Leadbetter et al⁵ proposed a bilayer structure where in the aromatic cores overlap in the middle of the layers, the alkyl chains extending outwards. Compounds having such a bilayer (more appropriately referred to as partially bilayer here onwards) structure have exhibited several interesting phenomena like reentrance^{7,8} and polymorphism of smectic A and smectic C phases.^{9,10}

As explained in chapter IV and V the structure of the bilayer depends on the chemical nature of the molecule. In particular, the mutual disposition of all the dipolar groups in the molecules plays a very dominant role, large bilayer spacing being, observed in molecules where the linkage group dipoles oppose that of the terminal polar group.^{11,12} For instance, two compounds 10 PMCBB and 11 CPMBB (whose chemical formulae are shown below)

4-cyanophenyl-3-methyl-4'-(4''-n-undecyl benzoyloxy)benzoate (11 CPMBB)



4-n-decylphenyl-3'-methyl-4'-(4''-cyanobenzoyloxy)benzoate (10 PMCBB)



which have identical cores, but for the fact that in the former the ester linkage dipoles are oriented antiparallel to the CN group dipole while in the latter they point towards the CN group, show different type of layer spacing behaviour. 10 PMCBB shows a large d/l ratio (about 1.6)¹² and 11 CPMBB comparatively a smaller ratio (about 1.3)¹³.

The mass density wave mentioned earlier can be mathematically represented by expanding the centre of mass density $\rho(r)$ in a Fourier Series¹⁴

$$\rho(r) = \rho_0 \left[1 + \frac{1}{\sqrt{2}} \{ |\psi| \cos(q_s z - \phi) \} \right]$$

Where ρ_0 is the average density, $|\psi|$ is the amplitude of the density wave and is a measure of the strength of the smectic order, $q_s = 2\pi/d$ is the wave vector of the density wave, d being the layer spacing.

ϕ is a phase factor which fixes the position of the layers.

Meyer and Lubensky¹⁵ have pointed out that the smectic symmetry does not necessarily correspond to the onset of just one Fourier component, the development of the mass density has to be periodic but may contain higher harmonics ρ_{2q_0} and so on. The first direct evidence for the coupling between the fundamental and the second harmonic of the Fourier series was obtained in a mixture of strongly polar 4-n-pentylphenyl-4'-cyanobenzoyloxy benzoate (DB5 CN) and non-polar terephthal-bis-4-n-butylaniline (TBBA). While studying the phase diagram of this binary system Sigaud et al¹⁶ found evidence of a transition between two optically identical smectic A phases (see fig. 6.2). Calorimetric measurements showed that there is an enthalpy change at the transition. Xray studies¹⁷

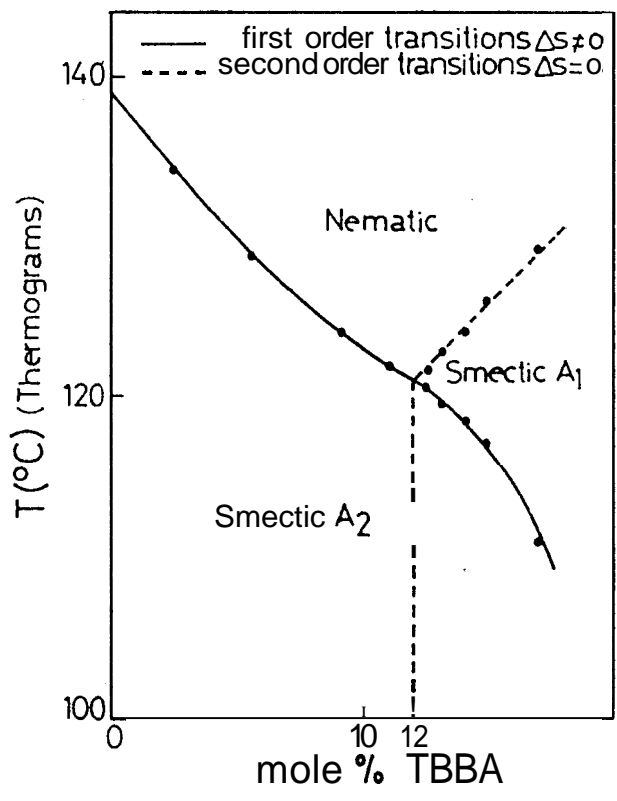


Figure 6.2 A section of DB5 CN/TBBA binary phase diagram showing the A_1 - A_2 transition (from ref. 16)

showed that the characteristic diffraction patterns in the two phases are different. These studies also showed that the transition is between a monolayer A phase (A_1) with $d = \frac{2\pi}{q_1} \sim 1$ and a bilayer A phase (A_2) whose layer spacing $d = \frac{2\pi}{q_2} \sim 2l, q_1 = 2q_2$ [It may be recalled that pure DB5 CN has a bilayer A phase (A_2)]. Fig. 63 shows the proposed molecular arrangement in the two phases. The next A-A transition to be observed was the A_d - A_2 transition¹⁸ which was seen in a pure compound DB7 CN, a higher homologue of DB5 CN. The observation of this A_d - A_2 transition was through X-ray studies only. No calorimetric or optical changes were reported at this transition. The A_d phase has a layer spacing $d = 1.6 l$ at the highest temperature and is strongly temperature dependent. In the A_2 phase both the first and second harmonics condense and thus it shows two sharp reflections corresponding to $d \approx l$ and $d \approx 2l$. Yet another type of smectic A phase was soon observed¹⁹ in a mixture of 4'-(4-n-pentylstyryl) phenyl-4"-cyanobenzoate (C5 Stilbene) and DB5 CN. This new phase, called the smectic antiphase \tilde{A} appeared between A_1 and A_2 phases. Barois et al²⁰ proposed a model for these A-A transitions according to which the antiphase appears out of 'frustration'. These two A-A transitions i.e., A_1 - \tilde{A} and \tilde{A} - A_2 were again found to be first order -'like. Optical observations did not show any change at these transitions when the sample was between two glass plates. But when observations were made with a free surface distinct changes could be seen at both the transitions. Then came the observation of this antiphase (\tilde{A}) in a pure compound.²¹ The compound DB7 NO_2 showed an A_1 - \tilde{A} transition. The transition was again found to be first order-like. More recently, accurate specific heat²² and high resolution X-ray studies²³ have been done on A-A transitions.

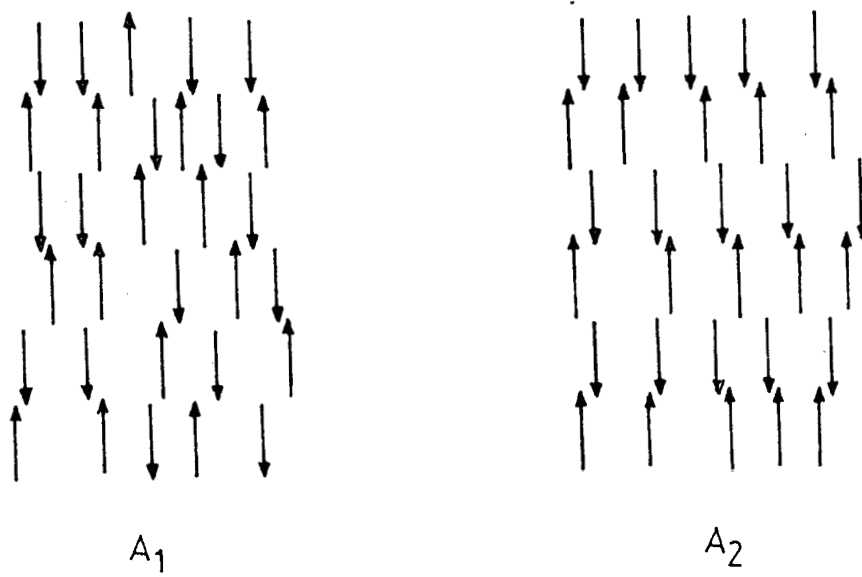


Figure 6.3 Molecular arrangement model for the A_1 and A_2 phases proposed by Hardouin et al (ref. 17)

Levelut et al²⁴ while summarising the different A phases observed in polar systems, noted remarkable sequence of transitions: $A_d-A_1-A_2$ & $A_d-A_1-\tilde{A}$, A_d-A_1 being observed for the first time here. The phase diagram obtained by them showing all these transitions in the DB5 CN and 4-n-octyloxybenzoyloxy-4'-cyano-stilbene (T8) binary system is shown in fig. 64. The A_d-A_1 transition, like other A-A transitions, was observed to be first order-like.

Madhusudana et al^{12,25} undertook studies on compounds similar to the dibenzoates (DBn CN) studied by the Bordeaux group - but with a lateral methyl or methoxy substituent. It was observed that these compounds have a large value of d (about 1.6 μ) and further, the bilayer spacing exhibits a very large expansion with decreasing temperature. These authors also found evidence of an A-A transition in one of the compounds.¹² This transition at which there is a jump (about 0.4 \AA) in the layer spacing was subsequently identified as the A_d-A_2 transition.

The most recent polar smectic system to show A-A transitions is a series having four phenyl rings and a terminal nitro group.²⁶ However, in these observations the identification and characterization of the A phases is not unambiguous as no Xray studies have been reported.

Thus, so far 4 types of A phases are known to exist in polar systems. These phases can be unambiguously characterised on the basis of their Xray diffraction patterns

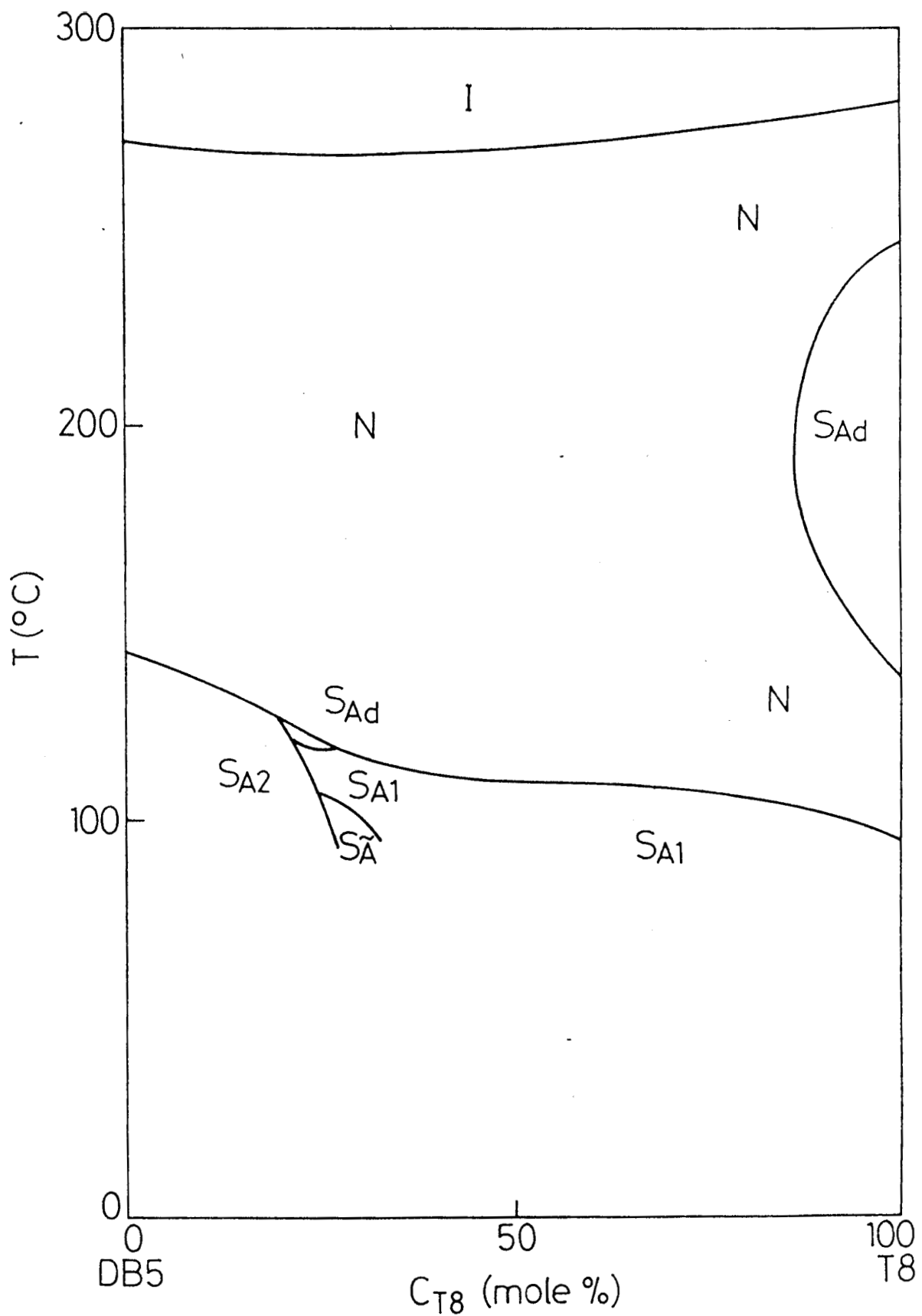


Figure 6.4 Binary phase diagram of DB5 CN and T8 (from ref. 24)

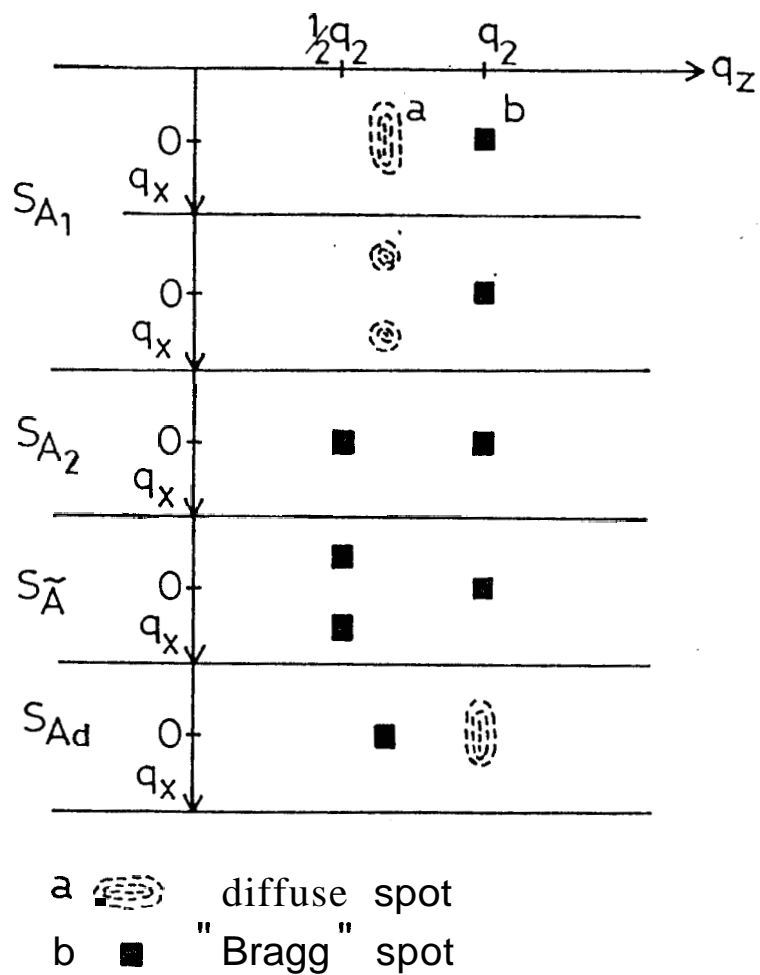
- a) The monolayer A_1 phase exhibits a peak at a wave vector $2q_0 = [2\pi/l]$ where l is approximately equal to the molecular length. In addition there may be diffuse scattering centred around a wave vector intermediate between q_0 and $2q_0$.
- b) The bilayer phase (A_2) is characterised by two reflections, the fundamental at q_0 and its second harmonic at $2q_0$.
- c) In the case of the partially bilayer A_d phase there is a reflection at $q_0' = [2\pi/l']$ where $1 < l' < 2l$ and, generally a diffuse maximum centred around $2q_0$.
- d) In the \tilde{A} antiphase, there is a condensed spot at $2q_0 = [2\pi/l]$ and, two condensed spots split out of the Z axis in a direction perpendicular to the Z axis and situated symmetrically about the q_0 position.

The Xray signatures for the different A phases obtained by detailed Xray scattering studies²⁴ are summarized in Table 6.1. The arrangement of the molecules in these A phases is schematically represented⁹ in fig. 6.5.

In the A_1 phase the molecules are stacked in a layer whose thickness $d = l$ and are randomly pointed up or down. In the A_2 phase the dipolar heads are preferentially pointed either up or down within a molecular layer. Consequently, the periodicity d , is equal to $2l$, twice the molecular length. In the partially bilayer A_d phase the layer thickness can be between l and $2l$. In the \tilde{A} phase the local order is the same as in the A_2 phase but there is in addition a modulation of the dipolar heads within the layer. The periodicity

TABLE 6.1

Schematic representation of the expected X-ray diffraction pattern from different modifications of smectic A phase (from ref. 24)



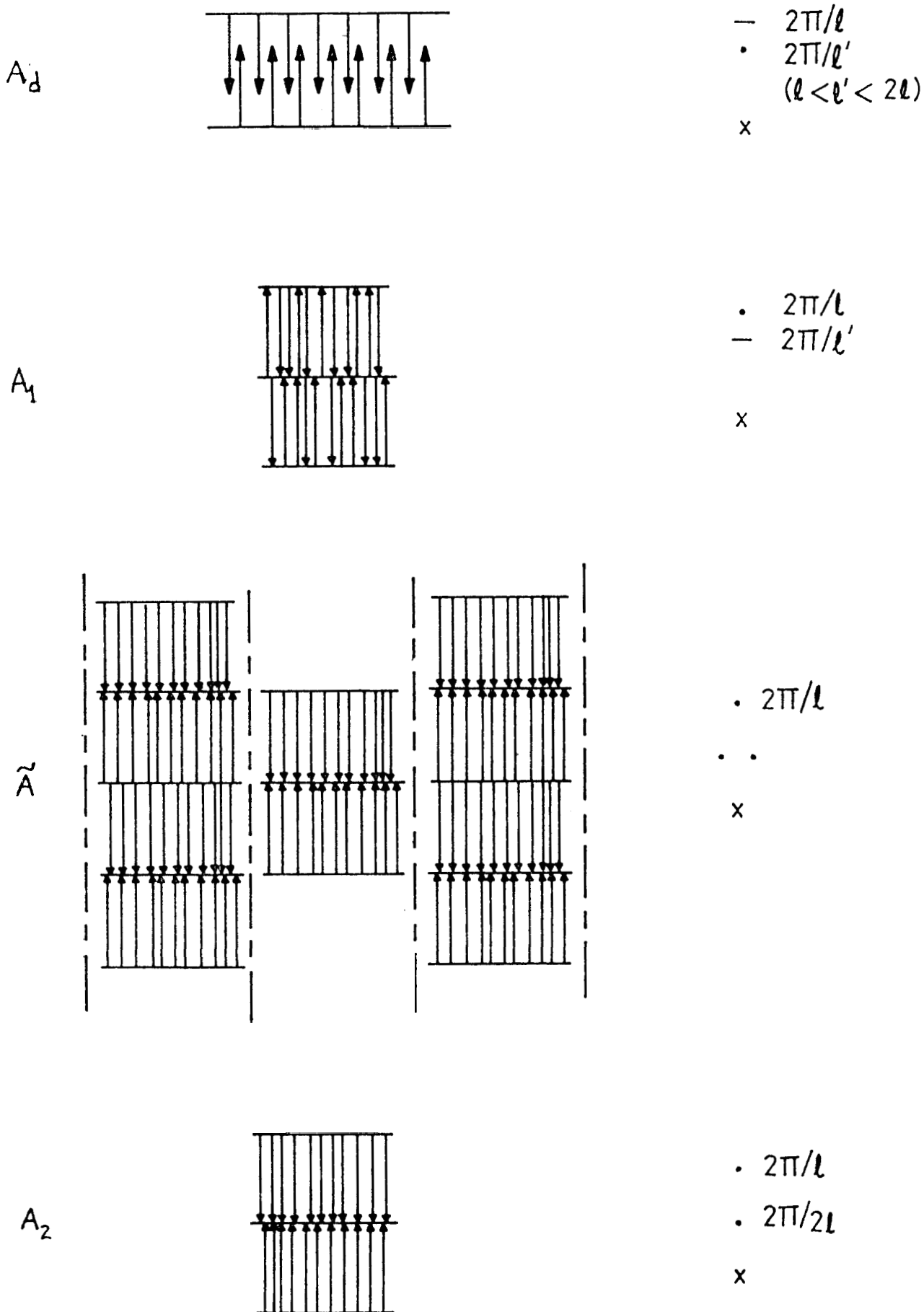


Figure 6.5 Schematic representation of the molecular arrangement in the different A phases (from ref. 9)

of this wave which gives a two dimensional rectangular symmetry to this \tilde{A} phase, is of the order of 130 \AA .

In all 5 types of A-A transitions have been observed in binary systems or single component systems consisting of strongly polar molecules. They are A_1-A_2 , A_d-A_2 , $A_1-\tilde{A}$, $\tilde{A}-A_2$ and $A_d-\tilde{A}$ (the $A_d-\tilde{A}$ transition is still to be confirmed by Xray experiments).

Two important features of these systems that exhibit the A-A transitions are the following:

1. For a single component system to exhibit the A-A transitions the disposition of the bridging group dipole closest to the end chain should be such that the longitudinal component of these dipoles opposes that of the strongly polar terminal group.
2. In the binary systems exhibiting A-A transitions it can' be generalised that at least one constituent compound should have a bridging dipole that satisfies condition (1) for e.g., DB5 CN and T8.

We shall now present the results of our high pressure, Xray and dielectric measurements on a binary system in which both the constituents have all the bridging groups disposed additive with respect to the end group. The behaviour of the constituent compounds themselves was discussed in chapters IV and V.

6.2 Compounds

The molecular structures of 6 ONPBB and 9 OBCAB are given in fig. 6.6. As seen in chapters IV and V, 9 OBCAB, a cyano compound, shows N, S_{Ad} , N_{re} and S_{A1} phases whereas 6 ONPBB, a nitro compound, exhibits S_{Ad} and N phases. The transition temperatures for the two compounds are listed in Table 6.2.

6.3 Experimental

High pressure studies have been done using the high pressure optical cell. Details of this setup as well as of the dielectric and Xray experiments are given in Chapter II.

6.4 Results and Discussion

The temperature concentration (T-X) diagram of binary mixtures of 6 ONPBB and 9 OBCAB is shown in fig. 6.7. It is seen that the reentrant nematic phase is completely bounded in the T-X plane and does not exist for 6 ONPBB concentrations $(X) > 0.29$. The two A_d phases as well as the A_1 phase appear to be isomorphous, no transitions between these phases being observable either optically or by DSC. A somewhat similar situation has been observed by Hardouin et al⁹ wherein the A_n and the A_d phases appeared to be continuously miscible without a phase transition. Since we know from our earlier pressure studies described in chapters IV and V, that the pressure behaviour of the A-N

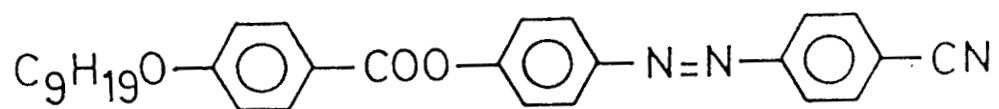
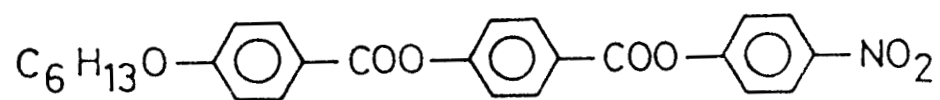


Figure 6.6 Chemical structures of 6 ONPBB (top) and 9 OBCAB (bottom)

TABLE 6.2

Transition temperatures (at 1 bar) of 6 ONPBB and 9 OBCAB

Compound	Transition	Short form	Temperature (°C)
6 ONPBB ,	Solid - Smectic A	K - A _d	124.0
	Smectic A - Nematic	A _d - N	151.5
	Nematic - Isotropic	N - I	238.4
9 OBCAB	Solid - Reentrant Nematic	K - N _{re}	91.0
	Reentrant Nematic - Smectic A _d	N _{re} - A _d	116.1
	Smectic A _d - Nematic	A _d - N	212.4
	Nematic - Isotropic	N - I	249.5
	Smectic A ₁ - Reentrant Nematic	A ₁ - N _{re}	(72.4)

() denotes that the transition is monotropic

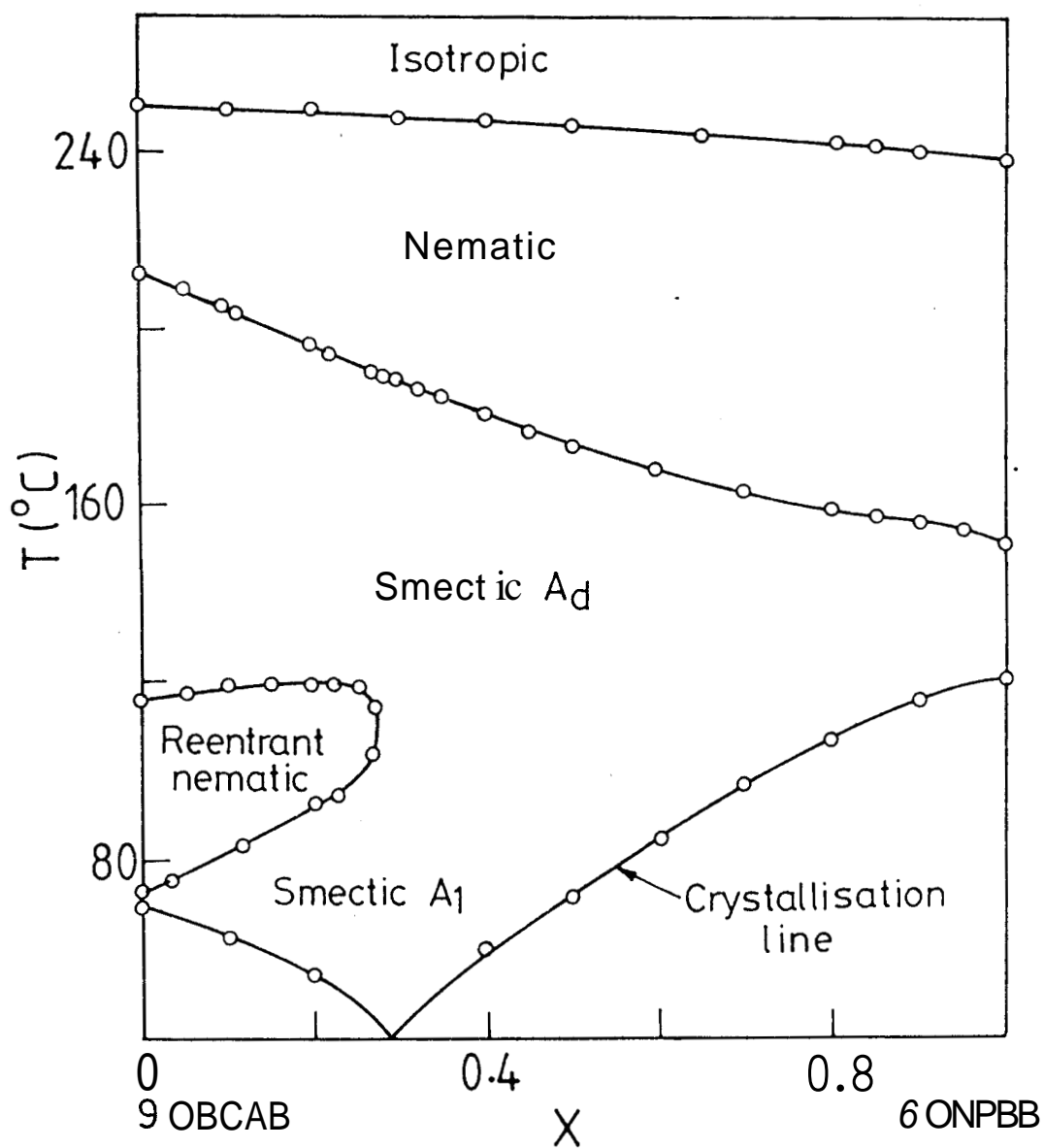


Figure 6.7 Binary phase diagram of 6 ONPBB and 9 OBCAB. X is the mole fraction of 6 ONPBB in the mixture

phase boundary is strongly related to the interdigitation of the molecules in the A phase, we took up a detailed high pressure study of the A-N transition in 6 ONPBB/ 9 OBCAB mixtures.

6.4.1 Pressure Studies

The pressure-temperature (P-T) diagrams of the two pure compounds and the mixtures with $X = 0.22, 0.45, 0.6, 0.7, 0.8$ and 0.9 are given in figs. 6.8 through 6.15. For 9 OBCAB (fig. 6.8) the A_1-N_{re} phase boundary is a straight line while the A_d phase is bounded. It is easy to see by extrapolating the A_1-N_{re} and $N_{re}-A_d$ phase boundaries to negative pressures that at a pressure of about -1.7 kbar the N_{re} phase should cease to exist resulting in a direct A_1-A_d transition. In the case of the $X = 0.22$ mixture (fig. 6.9) such a transition is expected to take place at nearly -0.2 kbar. We can therefore infer that the pressure at which the A_1-A_d transition occurs increases with X . For $X > 0.29$ (the concentration at which N_{re} phase ceases to exist at 1 bar) the transition should occur at atmospheric pressure itself. Indeed for $X = 0.45$ the presence of this transition is manifested dramatically on the A-N phase boundary in the P-T plane (fig. 6.10) as an abrupt change in slope at about 0.3 kbar. Thus one can see that even though the A_1-A_d phase boundary itself is not observed (by optical transmission technique) in the P-T plane, it leaves its signature on the A-N phase boundary. In fig. 6.11 we have shown the P-T diagram for $X = 0.6$. Here again we observe a kink at about 0.4 kbar which we associate with the ending of the A_1-A_d transition. In addition we see a second kink at a lower pressure (about 0.08 kbar) which we associate with the

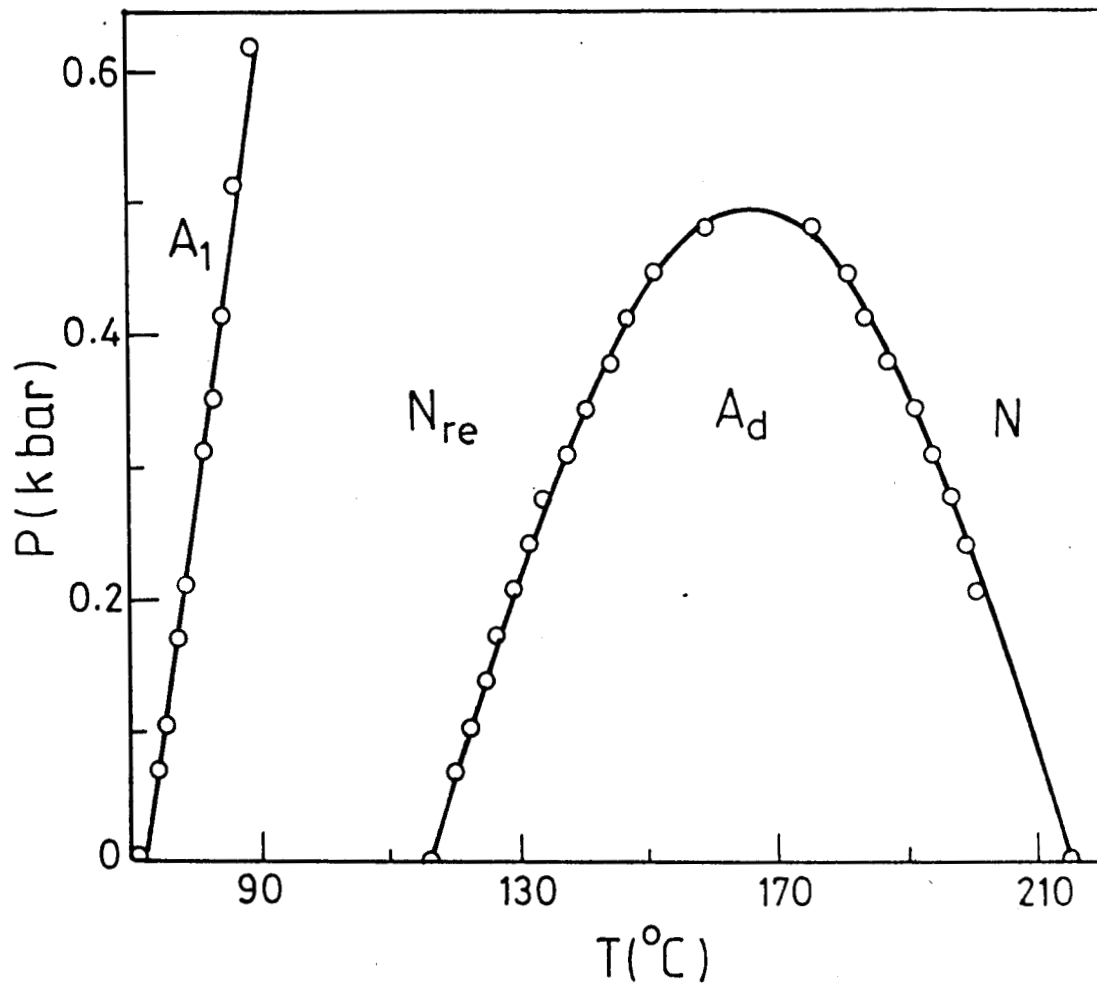


Figure 6.8 P-T diagram of 9 OBCAB

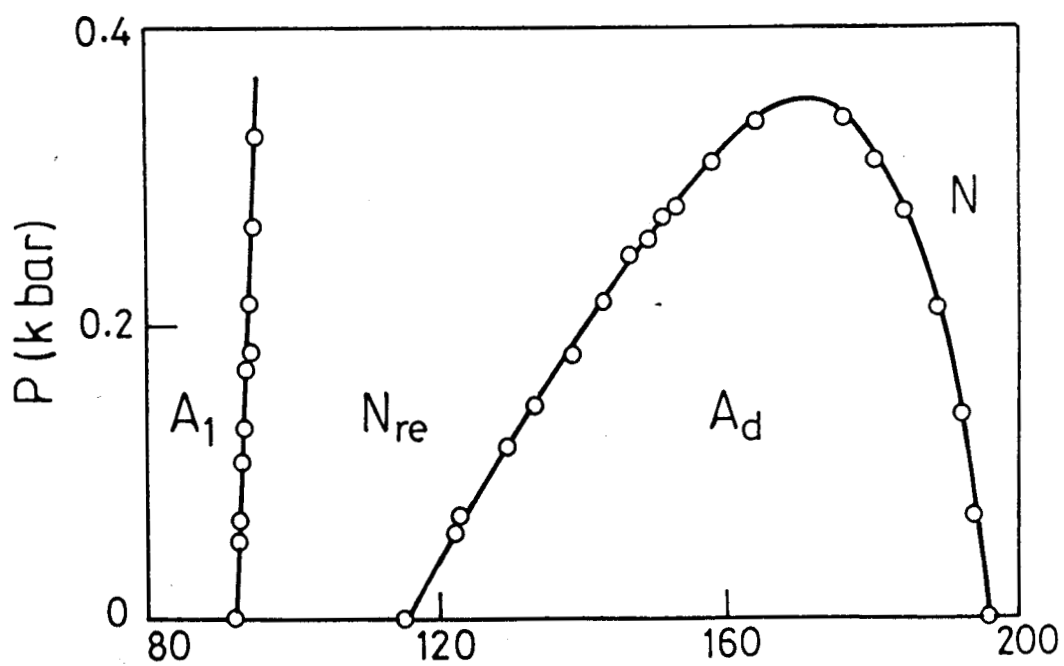


Figure 6.9 P-T diagram of the binary mixture $x = 0.22$

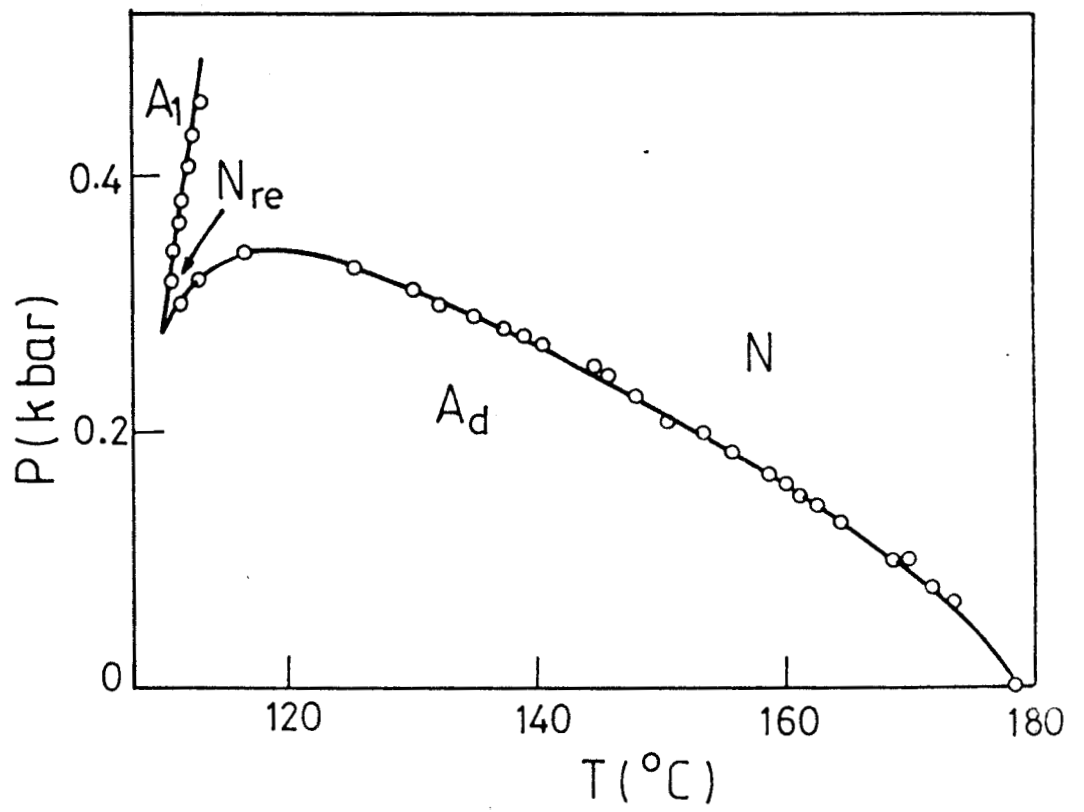


Figure 6.10 P-T diagram of the binary mixture X = 0.45

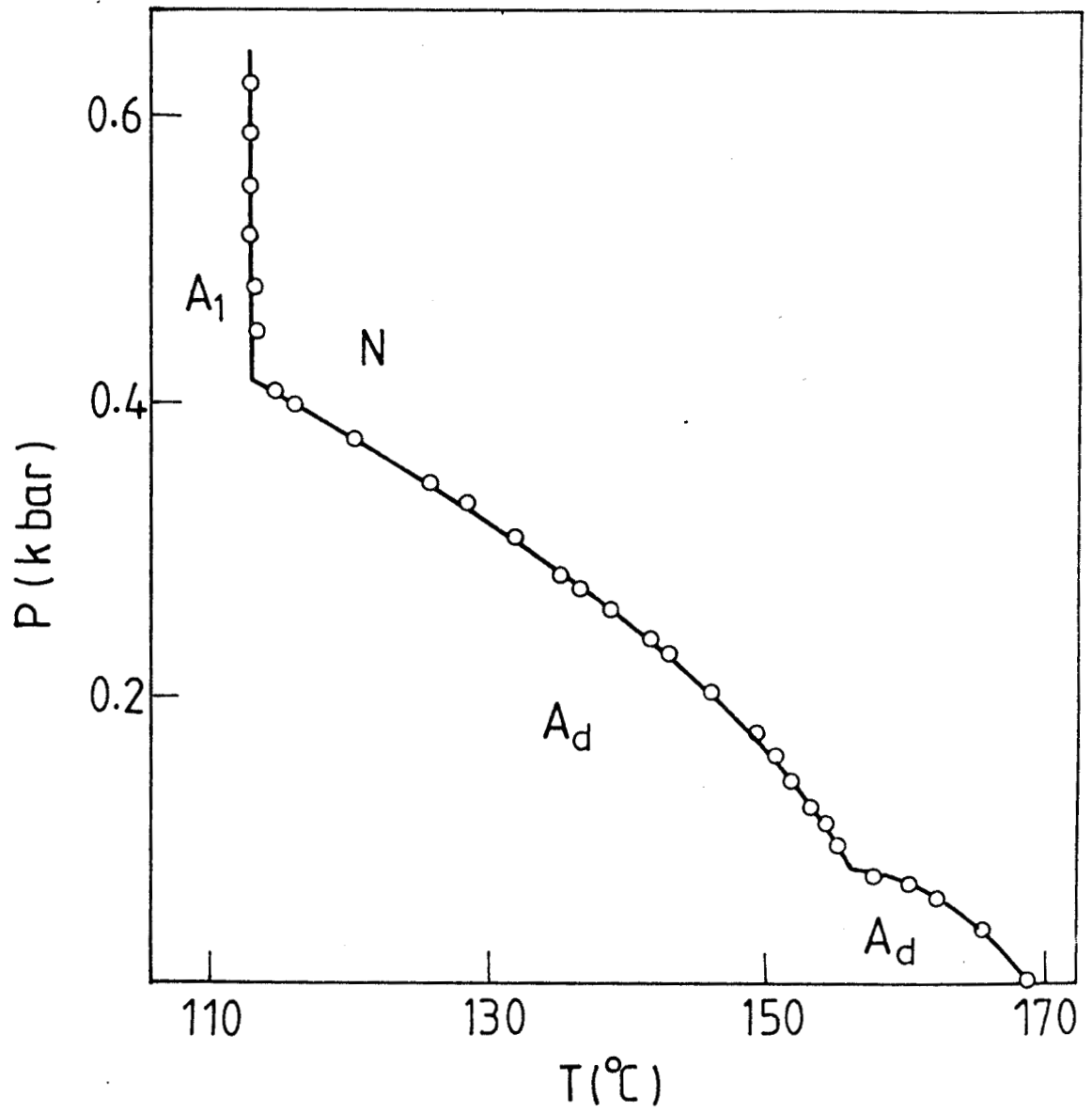


Figure 6.11 P-T diagram of the binary mixture X = 0.6

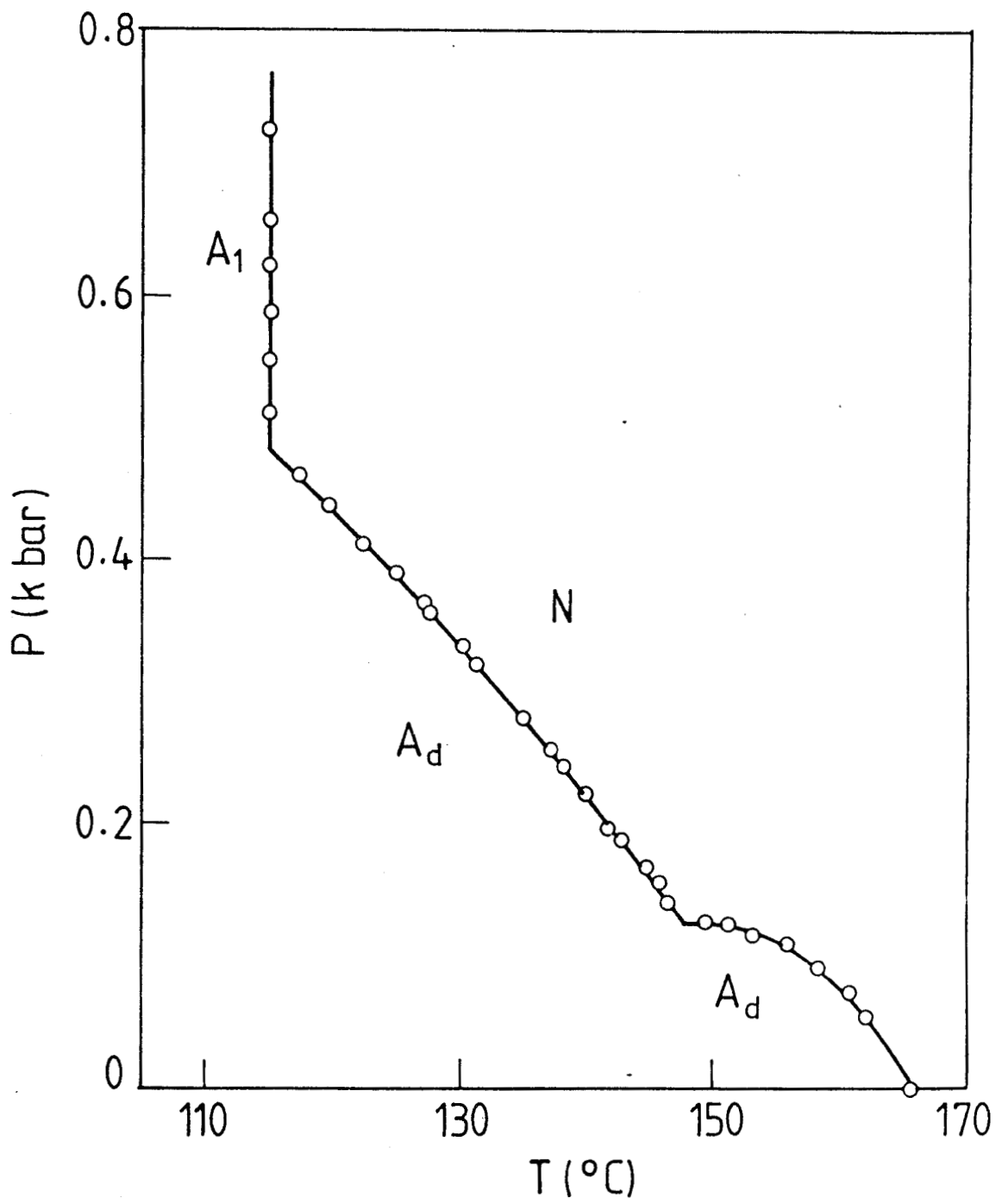


Figure 6.12 P-T diagram of the binary mixture X = 0.7

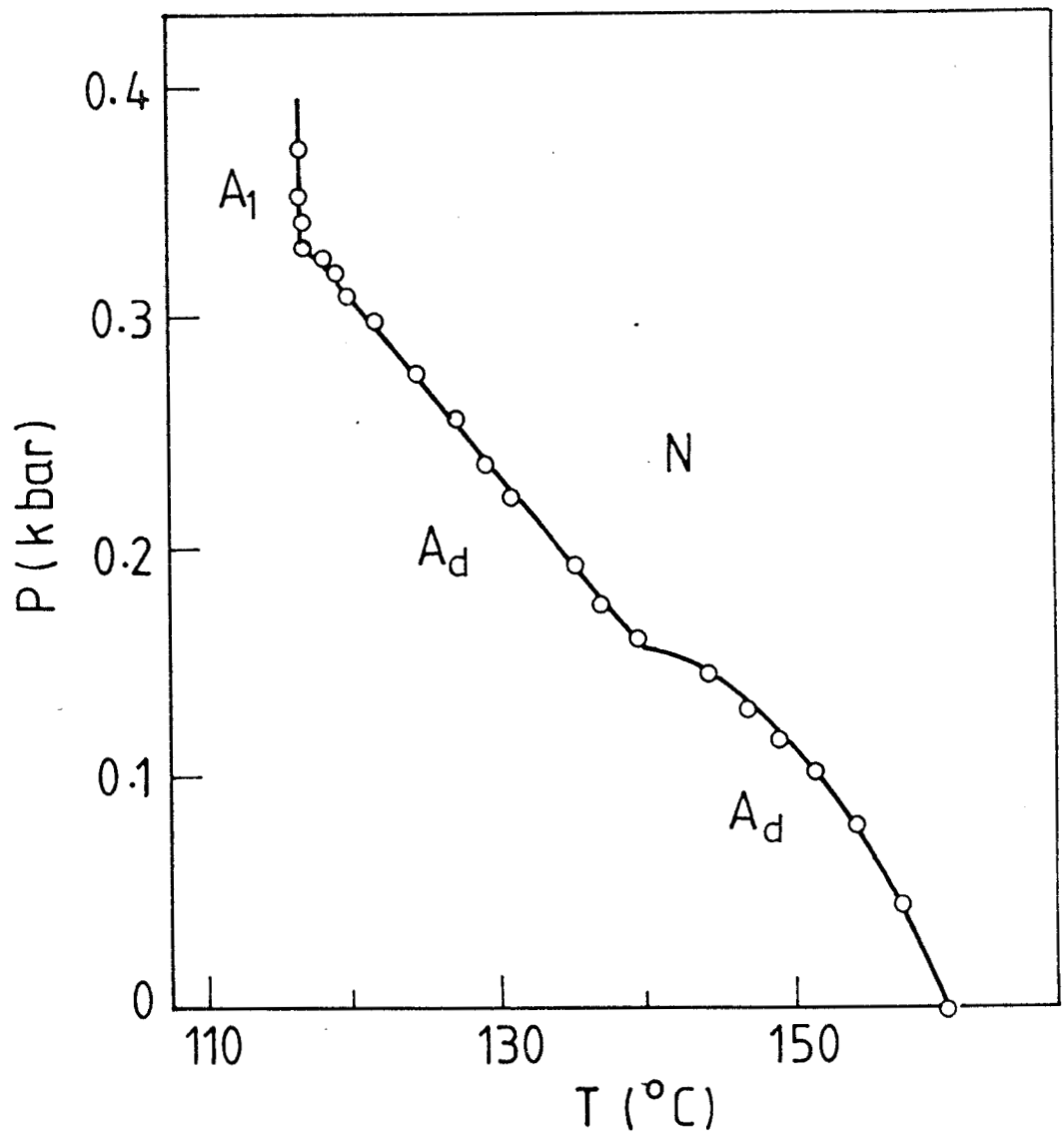


Figure 6.13 Pressure-temperature diagram of the binary mixture X = 0.8

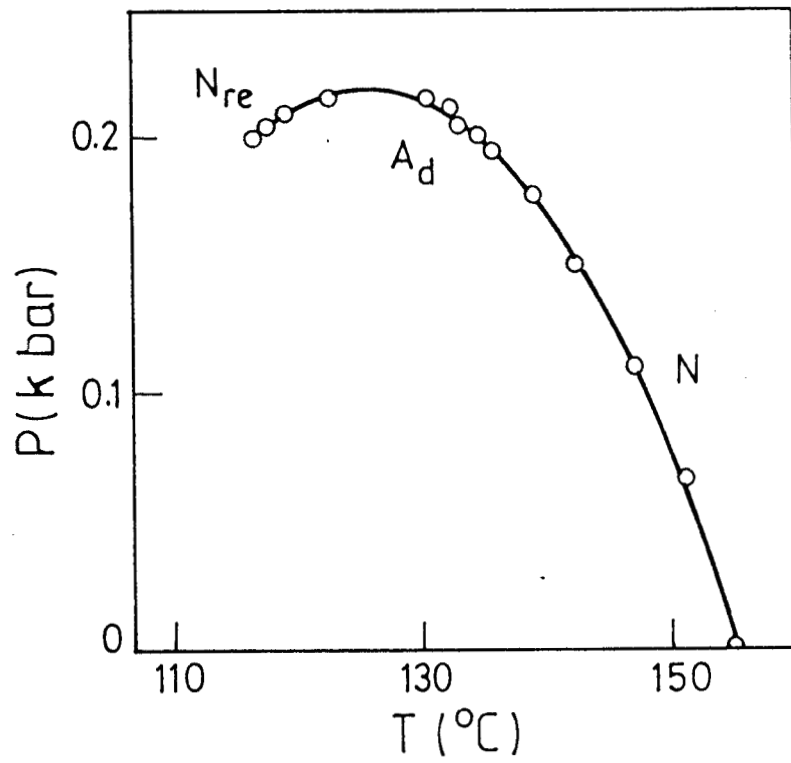


Figure 6.14 P-T diagram of the binary mixture $X = 0.9$

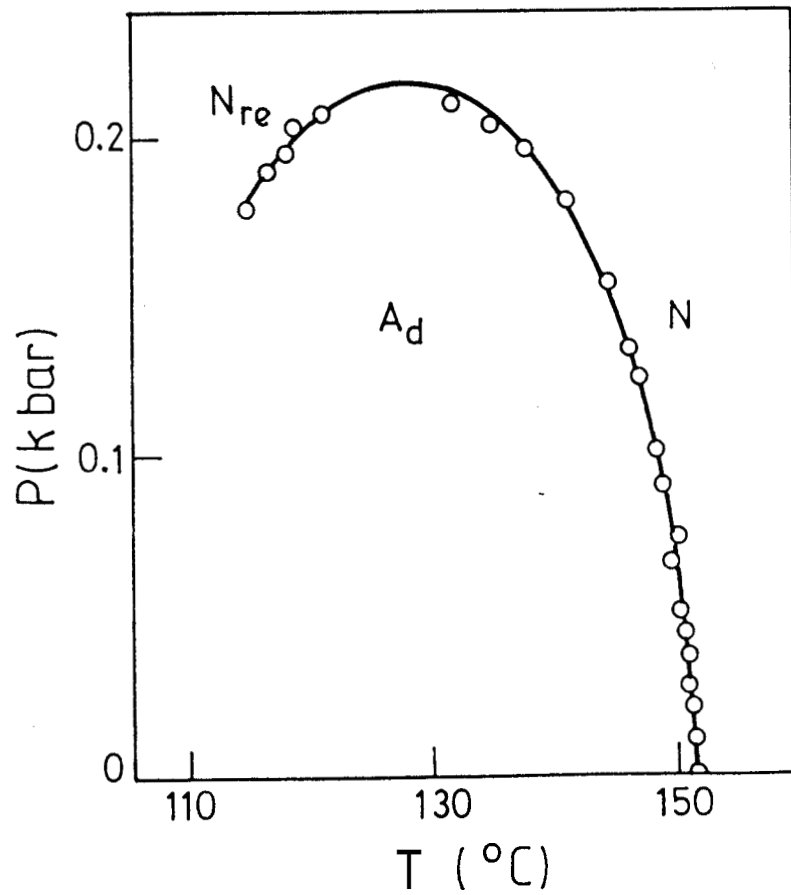


Figure 6.15 P-T diagram of 6 ONPBB

existence of an A_d-A_d line below that pressure. Similar features are observed for $X = 0.7$ and $X = 0.8$ (figs. 6.12 and 6.13) mixtures also, the range of the high temperature A_d phase increasing at the expense of that of the low temperature one. For $X = 0.9$ (fig. 6.14) both kinks are absent showing thereby that the A_d-A_d and A_d-A_1 transitions do not exist for this concentration. In fact this P-T diagram resembles that of pure 6 ONPBB (fig. 6.15).

We shall now examine in slightly greater detail the topology of the P-T diagrams in figs. 6.10-6.15 near the points at which the A_1-A_d and A_d-A_d lines meet the A-N phase boundary. For the sake of comparison we have shown in fig. 6.16 the T-X diagram of binary mixtures of DB7NO₂ and DB8NO₂.²⁷ The point at which the A_d-N_{re} , $N_{re}-A_1$ and A_d-A_1 phase boundaries intersect has been pointed out²⁸ to be a bicritical point for two reasons:

1. By symmetry considerations the transition between the A_d and A_1 phases is expected to be at least weakly first order while $N_{re}-A_d$ and $N_{re}-A_1$ are nearly second order transitions.
2. The topology of the phase diagram in the vicinity of the $A_d-N_{re}-A_1$ point resembles closely the topology of bicritical point observed in other systems.

We can therefore conclude from the topology of our P-T diagrams (figs. 6.10-6.15) that the points at which the A_1-A_d and A_d-A_d lines meet the A-N phase boundary, should also be bicritical points.

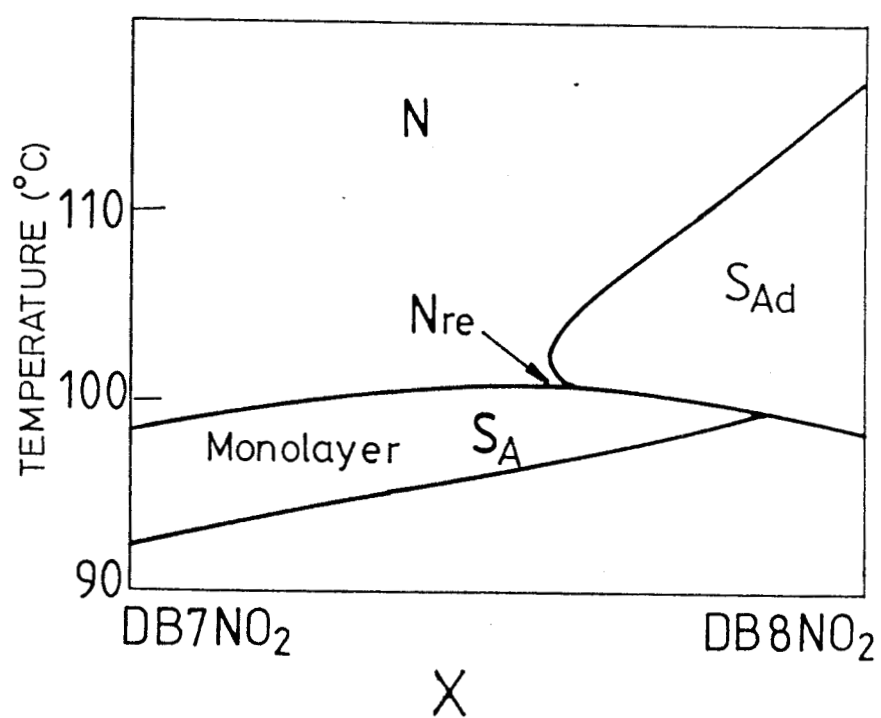


Figure 6.16 Temperature-concentration-(T-X) phase diagram of 4-n-heptylphenyl-4'-nitrobenzoyloxybenzoate (DB7 NO₂) and 4-n-octylphenyl-4'-nitrobenzoyloxybenzoate (DB8 NO₂)

X denotes the concentration of DB8 NO₂ in the mixture (from ref. 27)

6.42 Xray Studies

Precise determination of the thermal evolution of the smectic A layer spacing is of great importance in locating transitions between two types of A phases. In fact recently Hardouin et al²⁹ observed in several members of the DBnO Cl series that the A_d - A_2 transition was not seen either as a textural change or in DSC traces, the only hint in favour of its existence being the change of slope observed in the temperature variation of the layer spacing.

We have carried out a precise layer spacing (d) determination as a function of temperature for $X = 0.4, 0.55, 0.59, 0.72$ and 0.79 mixtures with a view to locate the A_1 - A_d and A_d - A_d transitions at atmospheric pressure.

The temperature variation of d in the A phases of the pure compounds 9 OBCAB and 6 ONPBB is known from our previous Xray experiments (these results have already been discussed in chapters IV and V). For 9 OBCAB, d is independent of temperature in the A_1 phase while it varies quite appreciably in the A_d phase.³⁰ In the case of 6 ONPBB, d is practically independent of temperature in the entire A_d phase.³¹ With these facts in mind we shall now examine the d versus temperature curves for the mixtures. For $X = 0.4$ (fig. 6.17) the layer spacing is constant with respect to temperature upto 105°C after which it suddenly starts increasing linearly right upto the A-N transition temperature. The point at which d develops the temperature dependence is identified as the A_1 - A_d transition. For the $X = 0.55$ mixture (fig. 6.18) d versus temperature curve exhibits a change of slope at two points. Initially d is temperature independent, but starts increasing with increasing temperature at 114°C . The

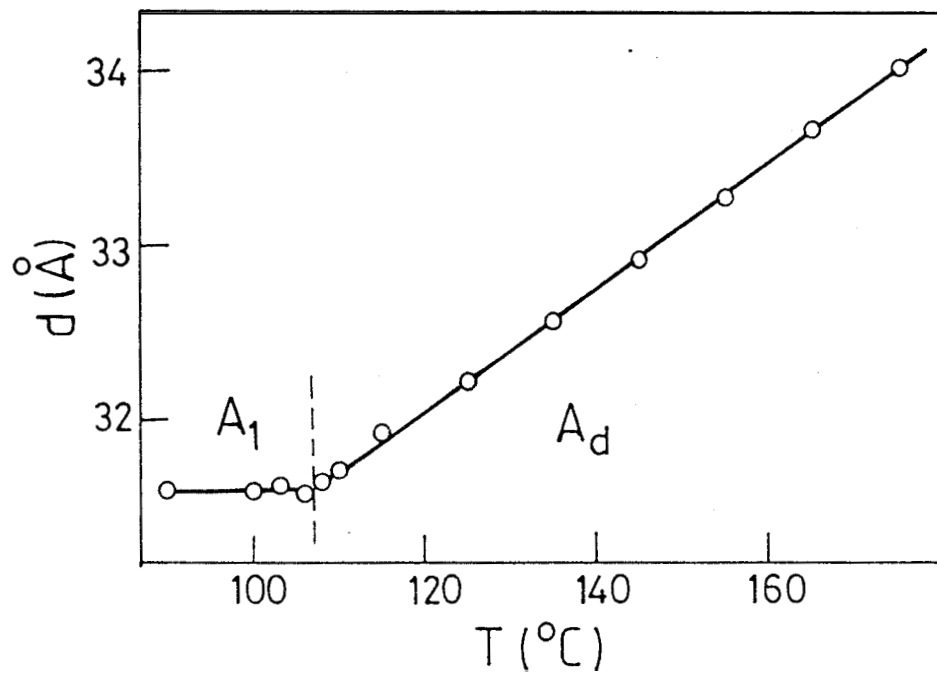


Figure 6.17 Temperature variation of the layer spacing for the binary mixture $X = 0.4$

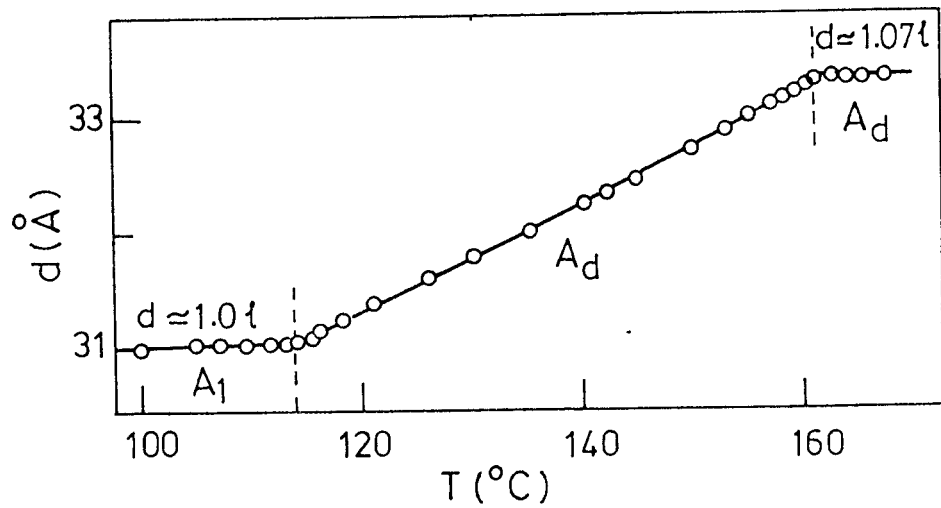


Figure 6.18 Temperature variation of the layer spacing for the binary mixture $X = 0.55$

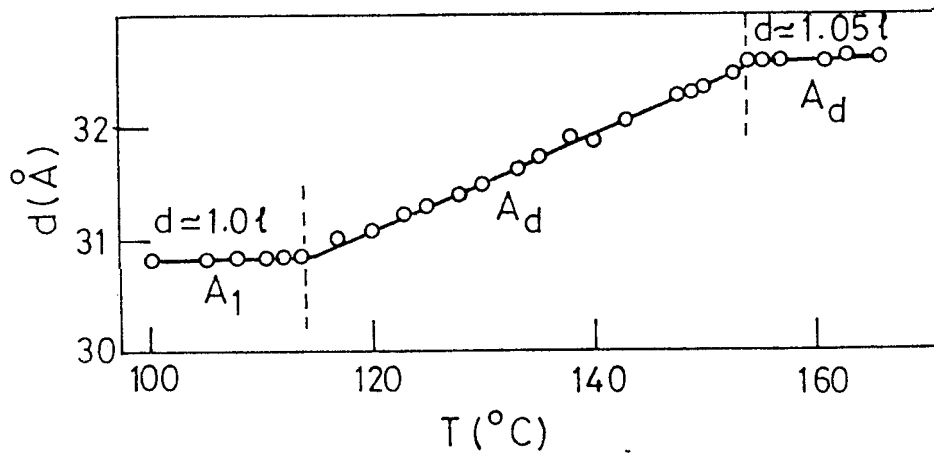


Figure 6.19 Temperature variation of the layer spacing for the binary mixture $X = 0.59$

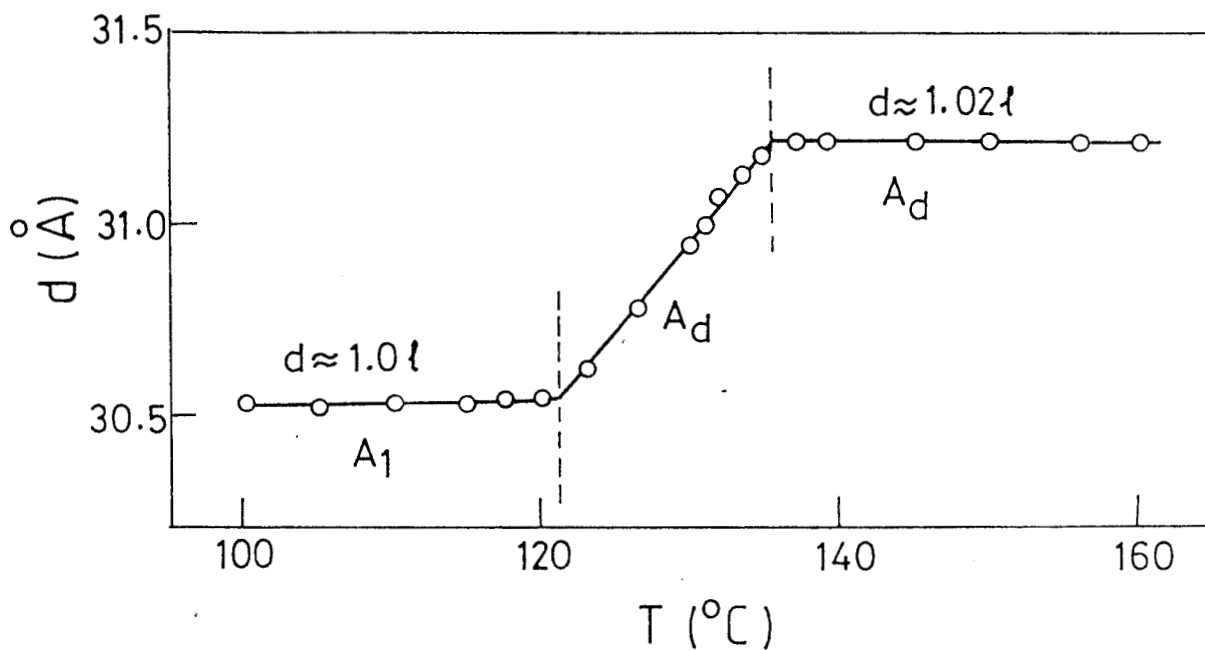


Figure 6.20 Temperature variation of the layer spacing for the binary mixture $X = 0.72$

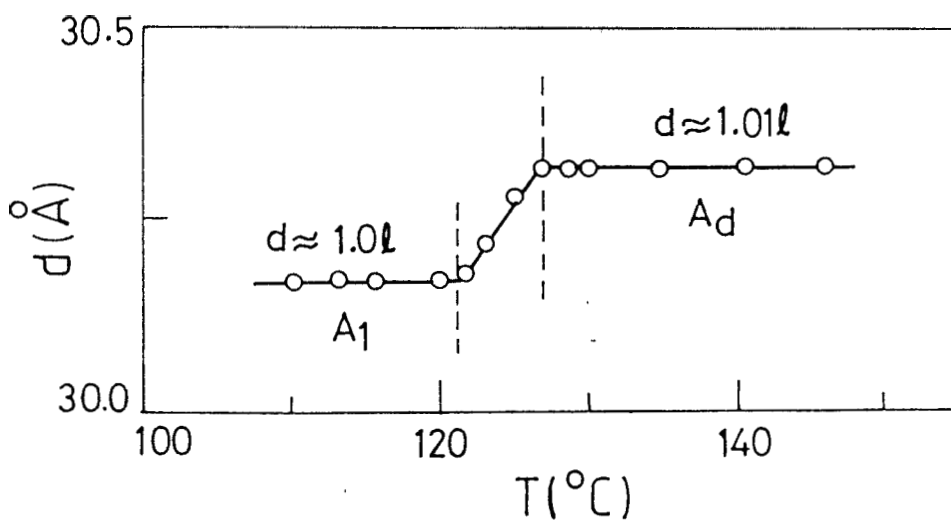


Figure 6.21 Temperature variation of the layer spacing for the binary mixture $X = 0.79$

increase in d continues till 161°C after which d again becomes independent of temperature. Essentially the same behaviour is seen for $X = 0.59, 0.72$ and 0.79 (figs. 6.19-6.21 respectively) also. From these curves we can therefore identify three kinds of A phases:

1. the A_1 phase ($d \approx 1.0 l$) at low temperatures with a temperature independent layer spacing.
2. the A_d phase with a temperature dependent layer spacing.
3. another A_d phase at higher temperatures characterised by a temperature independent layer spacing.

Thus we have identified the A_1-A_d and A_d-A_d transitions in these mixtures. The transition temperatures were used to map the A_1-A_d and A_d-A_d boundaries in the T-X plane. The resultant phase diagram is given in fig. 6.22. It is seen that the range of the intermediate A_d phase decreases with X while that of the higher temperature phase increases, a fact which is borne out by the results of both high pressure and Xray studies.

It may be recalled that Prost and Barois³² have discussed the theoretical aspects of polymorphism in polar mesogens by considering a free energy expansion with the mass density and the molecular dipolar potential as the basic order parameters. They have considered the possibility that when $l' \approx l$ (l' is the length of the molecular pair and l the length of the molecule), the system can go continuously from A_d to A_1 . However, in our case we believe that

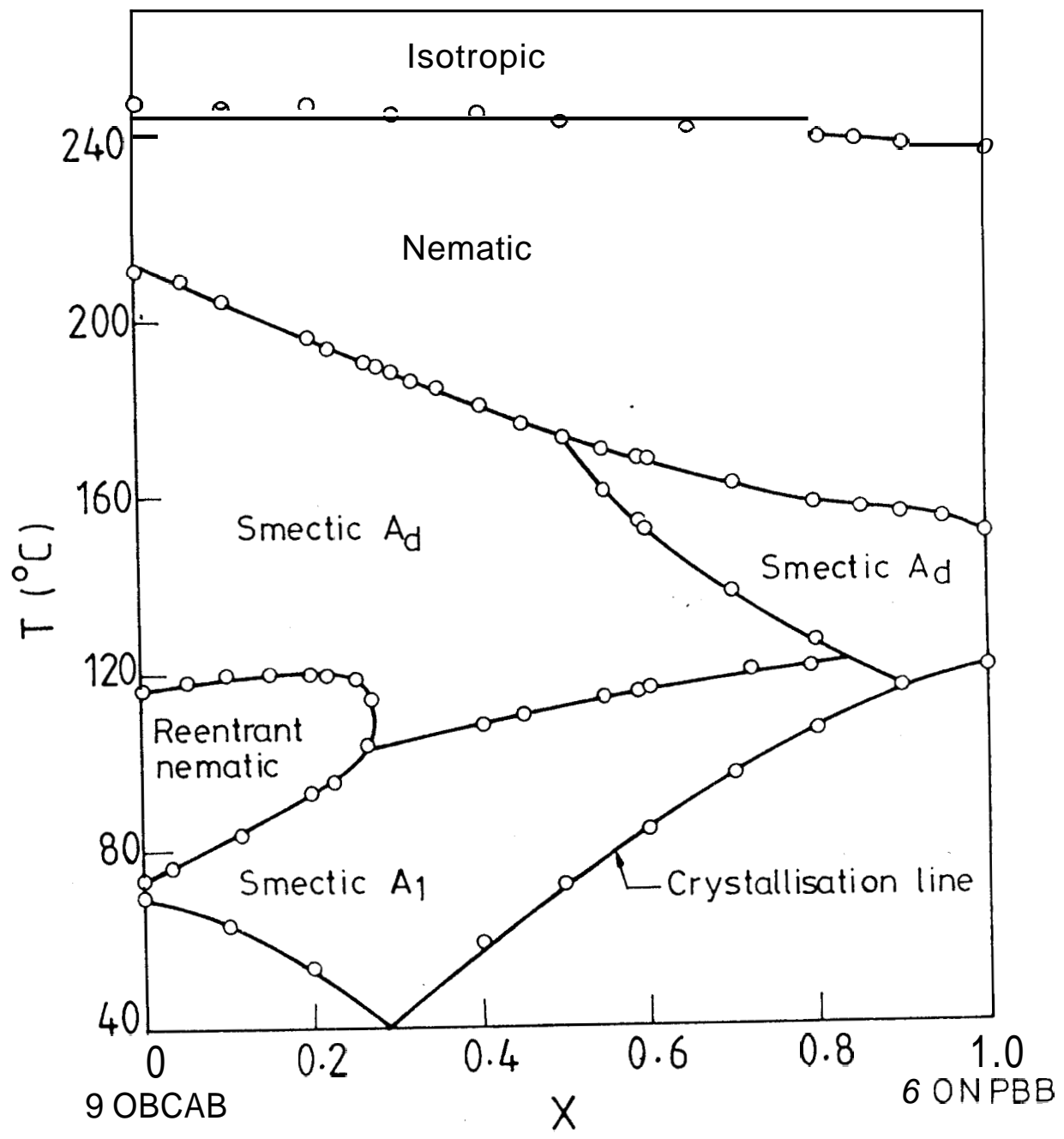


Figure 6.22 T-X diagram of 6 ONPBB/9 OBCAB mixtures showing the A_1 - A_d and A_d - A_d phase boundaries

the two important observations, viz., (i) the abrupt changes in the layer spacing versus temperature curves and (ii) the occurrence of two kinks in the A-N phase boundaries in the P-T plane, clearly reveal the existence of the A_1 - A_d and A_d - A_d transitions in this binary system. It must also be remarked that as far as we are aware this appears to be the only instance of the A-A transition being observed in a binary system wherein both the constituent compounds have the longitudinal components of the linkage dipoles oriented additive with respect to that of the end group dipole.

6.4.3 Dielectric Relaxation Studies

It is well known that the dielectric constants of liquid crystals are frequency dependent (for a recent review see Kresse³³). Because of the orientational order in the medium, ϵ_{\parallel} and ϵ_{\perp} (the principal dielectric constants along and perpendicular to the director respectively) have different frequency dependencies. While ϵ_{\perp} exhibits only the normal Debye relaxation which usually occurs in the GHz region, ϵ_{\parallel} shows an additional dispersion in the MHz region or even in the KHz region. The low frequency relaxation was first observed by Maier and Meier³⁴ in alkoxy aroxybenzenes. Ratna and Shashidhar³⁵ have extensively studied the low frequency dispersion of ϵ_{\parallel} for a number of strongly polar compounds.

As mentioned earlier it is now well established that there exists in polar compounds strong antiparallel correlation between neighbouring molecules. It is also known that subtle changes in such correlations can give rise to such

exotic behaviours as reentrance and polymorphism in A phases. The low frequency dispersion of ϵ_{\parallel} is therefore a useful tool to probe the molecular associations in these phases.

In fact, Ratna et al³⁶ who have studied the low frequency ϵ_{\parallel} dispersion in several reentrant compounds, have shown that the activation energy (W) in the N_{re} phase is much higher than that in the normal nematic phase.

Recently, Druon and Wacrenier³⁷ have conducted low frequency dispersion studies of compounds exhibiting polymorphic A phases. They have demonstrated that the dielectric relaxation can be used as a potential tool to show the existence of different polymorphic forms of the A phase.

We shall now present the results of our low frequency dielectric relaxation studies of ϵ_{\parallel} for two representative mixtures of 6 ONPBB/9 OBCAB system, viz., $X = 0.6$ and $X = 0.8$. Fig. 6.23 gives the plot of ϵ_{\parallel}'' against frequency at different temperatures for $X = 0.6$ mixture. It was observed that the maximum of the dielectric loss i.e., $\epsilon_{\parallel}''_{max} = \epsilon_{\parallel}''$ at f_R , the frequency of relaxation, increases continuously in the nematic and the two A_d phases but gets saturated in the A_1 phase. The same behaviour is seen for the $X = 0.8$ mixture also.

A plot of ϵ_{\parallel}' versus ϵ_{\parallel}'' is a semicircle with the centre lying on the ϵ_{\parallel}' axis, denoting a single relaxation time. These cole-cole arcs for representative temperatures (2 in each phase) are plotted in figs. 6.24 and 6.25. The

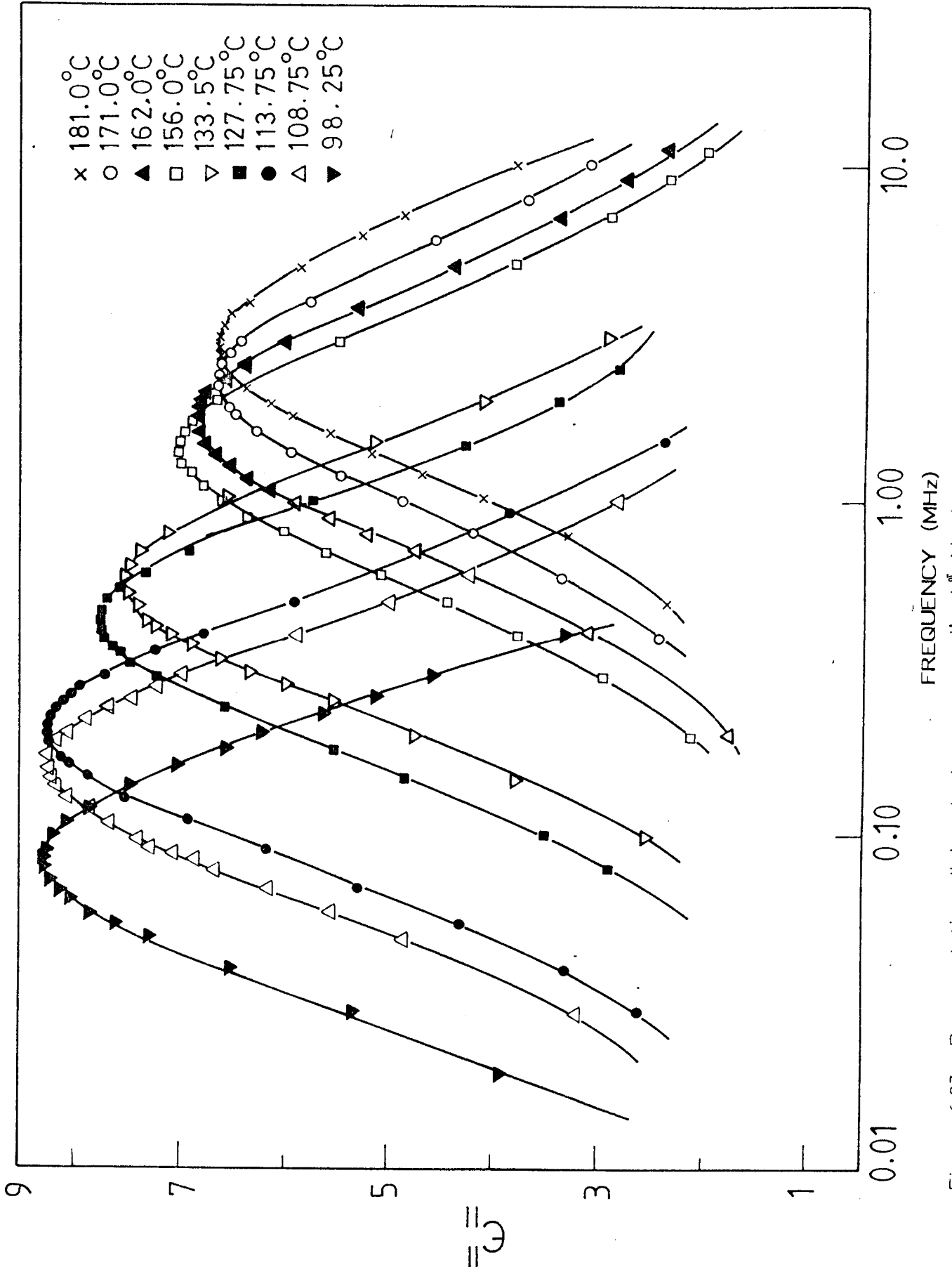


Figure 6.23 Representative dielectric large curves in the A_D and the A_1 phase for the binary mixture X = 0.6

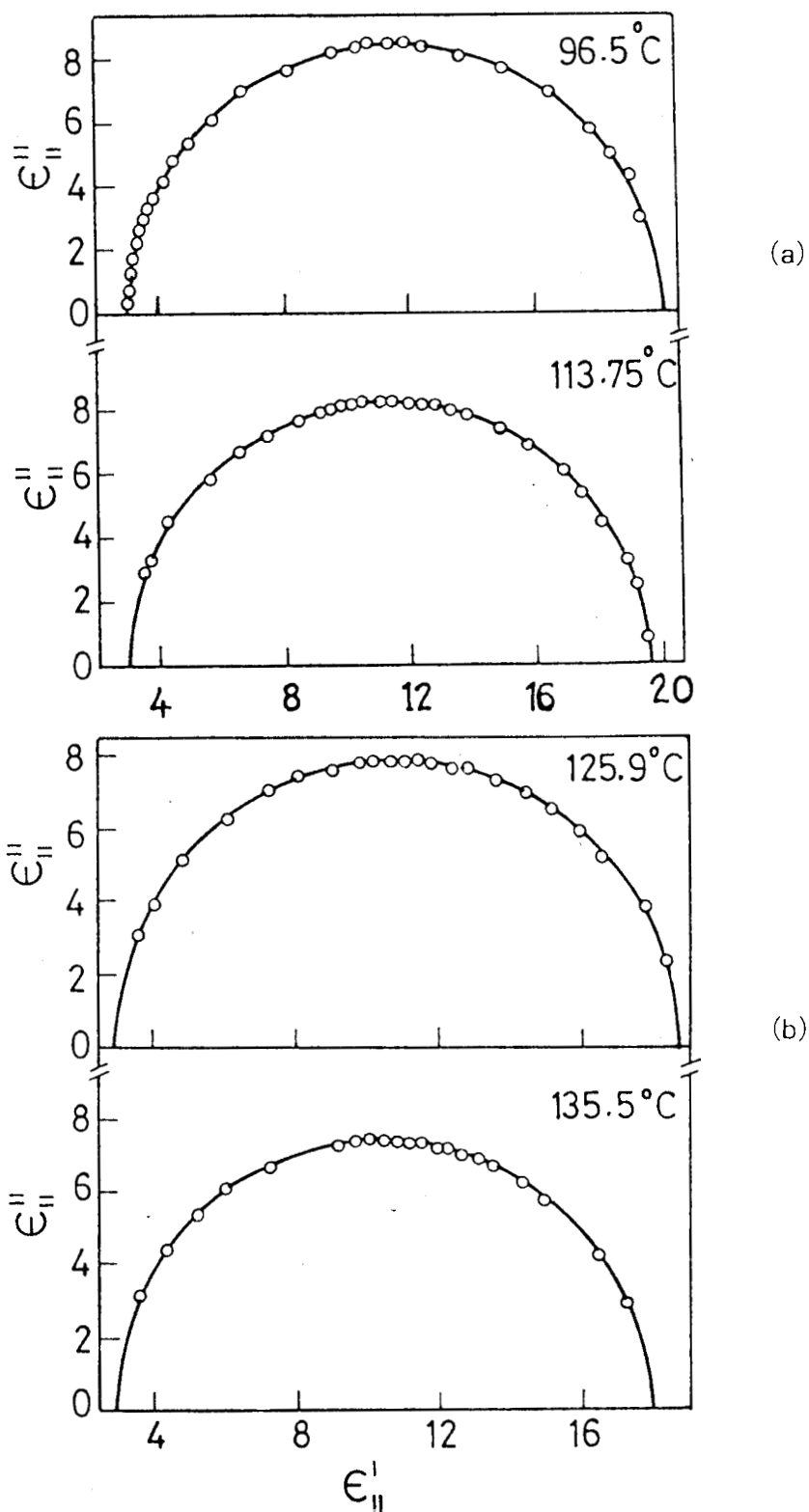


Figure 6.24 Representative cole-cole plots in the A_1 (a) and the low temperature A_d phase (b) for the binary mixture $X = 0.6$

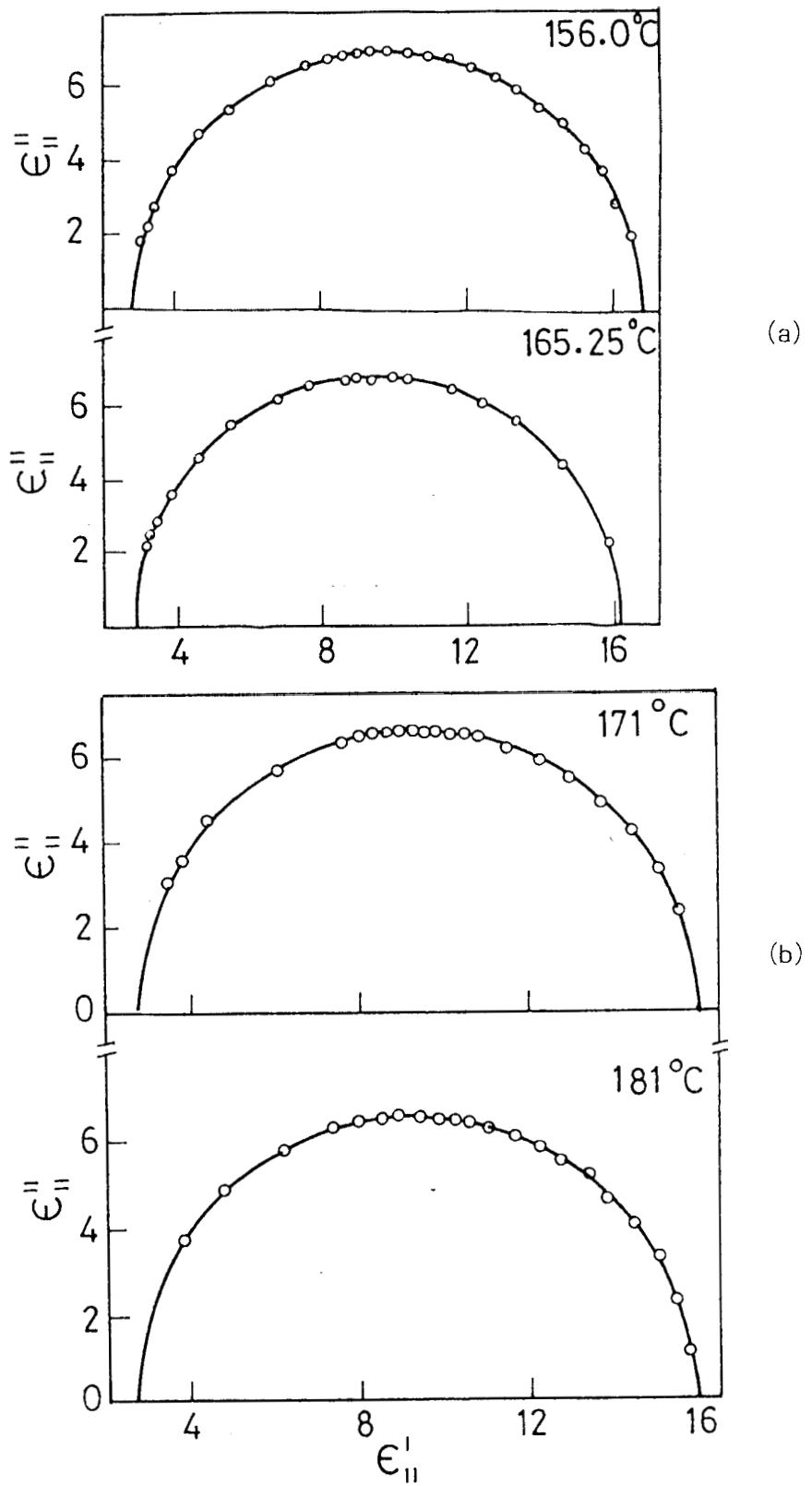


Figure 6.25 Representative cole-cole plots in the high temperature A_D (a) and the N phase (b) for the binary mixture $X = 0.6$

temperature behaviour of ϵ''_{\max} is reflected in the value of the radius of these semicircles also, i.e., a monotonic increase in the nematic and the A_d phases followed by a saturation in the A_1 phase.

The frequency of relaxation f_R is related to the activation energy W by the following expression

$$f_R \propto \exp(-W/kT)$$

where k is the Boltzmann constant and T is the temperature in absolute units.

Hence by determining f_R at various temperatures one can get the value for the activation energy W . The values of f_R obtained from both loss curves and cole-cole plots for $X = 0.6$ and $X = 0.8$ mixtures are tabulated in Tables 6.3 and 6.4. It is seen that the agreement between the values obtained from loss curves & cole-cole arcs is very good.

According to the above mentioned expression, a plot of f_R versus $1/T$ on a log-linear scale gives a straight line, the slope of which is the activation energy W . The plots obtained for $X = 0.6$ and 0.8 mixtures are shown in figs. 6.26 and 6.27 respectively. The value of W obtained in the different phases for the two mixtures are given in Table 6.5. In both the cases it is found that W is distinctly different in the nematic, A_1 and the two A_d phases. Also it is seen that the value of W is lowest in the nematic while it is highest in the A_1 phase.

Thus our high pressure, Xray and dielectric studies have shown the exist-

TABLE 6.3

Relaxation frequency as a function of temperature for X = 0.6 mixture

T(°C)	f _R from Loss Curve MHz	f _R from Cole-Cole MHz
	<u>N Phase</u>	
181.0	3.00	3.00
174.65	2.55	2.54
171.0	2.32	2.34
	<u>S_{Ad1} Phase</u>	
165.25	1.95	1.96
162.0	1.75	1.76
159.10	1.60	1.58
156.0	1.44	1.44
	<u>S_{Ad2} Phase</u>	
147.75	1.050	1.054
144.75	0.940	0.944
143.50	0.890	0.886
142.0	0.830	0.840
139.25	0.740	0.750
137.40	0.680	0.690
135.50	0.640	0.643
133.50	0.575	0.580
131.75	0.530	0.530
129.79	0.475	0.475
127.75	0.430	0.435
125.9	0.390	0.391
124.25	0.380	0.381
123.0	0.346	0.345
121.0	0.325	0.323
	<u>S_{A1} Phase</u>	
110.75	0.183	0.181
108.75	0.165	0.165
106.75	0.145	0.143
102.6	0.112	0.111
99.5	0.093	0.091
98.25	0.085	0.084
96.5	0.078	0.079
95.3	0.072	0.071
92.4	0.059	0.059
88.5	0.047	0.047

Smectic A_{d1} is the A_d phase which has a temperature independent layer spacing

Smectic A_{d2} is the A_d phase which has a temperature dependent layer spacing

TABLE 6.4

Relaxation frequency as a function of temperature for X = 0.8 mixture

T (°C)	f_R from Loss Curve MHz	f_R from Cole-Cole MHz
	<u>N Phase</u>	
170.85	1.99	1.99
168.10	1.85	1.83
166.0	1.75	1.77
164.0	1.65	1.66
162.2	1.55	1.55
160.3	1.45	1.46
	<u>S_{Ad1} Phase</u>	
155.80	1.30	1.30
153.10	1.18	1.19
151.30	1.10	1.09
149.10	1.00	1.00
145.40	0.950	0.948
145.0	0.900	0.891
142.60	0.810	0.814
141.10	0.750	0.755
136.20	0.625	0.620
134.0	0.575	0.570
133.50	0.560	0.553
131.70	0.510	0.504
130.80	0.500	0.500
129.40	0.480	0.483
128.10	0.460	0.453
	<u>S_{Ad2} Phase</u>	
126.20	0.410	0.409
124.90	0.390	0.385
124.10	0.370	0.370
123.20	0.360	0.356
121.90	0.340	0.339
121.30	0.330	0.329
	<u>S_{A1} Phase</u>	
118.50	0.290	0.287
116.70	0.260	0.262
114.45	0.230	0.230
113.40	0.220	0.218
111.60	0.195	0.195
110.0	0.185	0.184
109.0	0.175	0.174

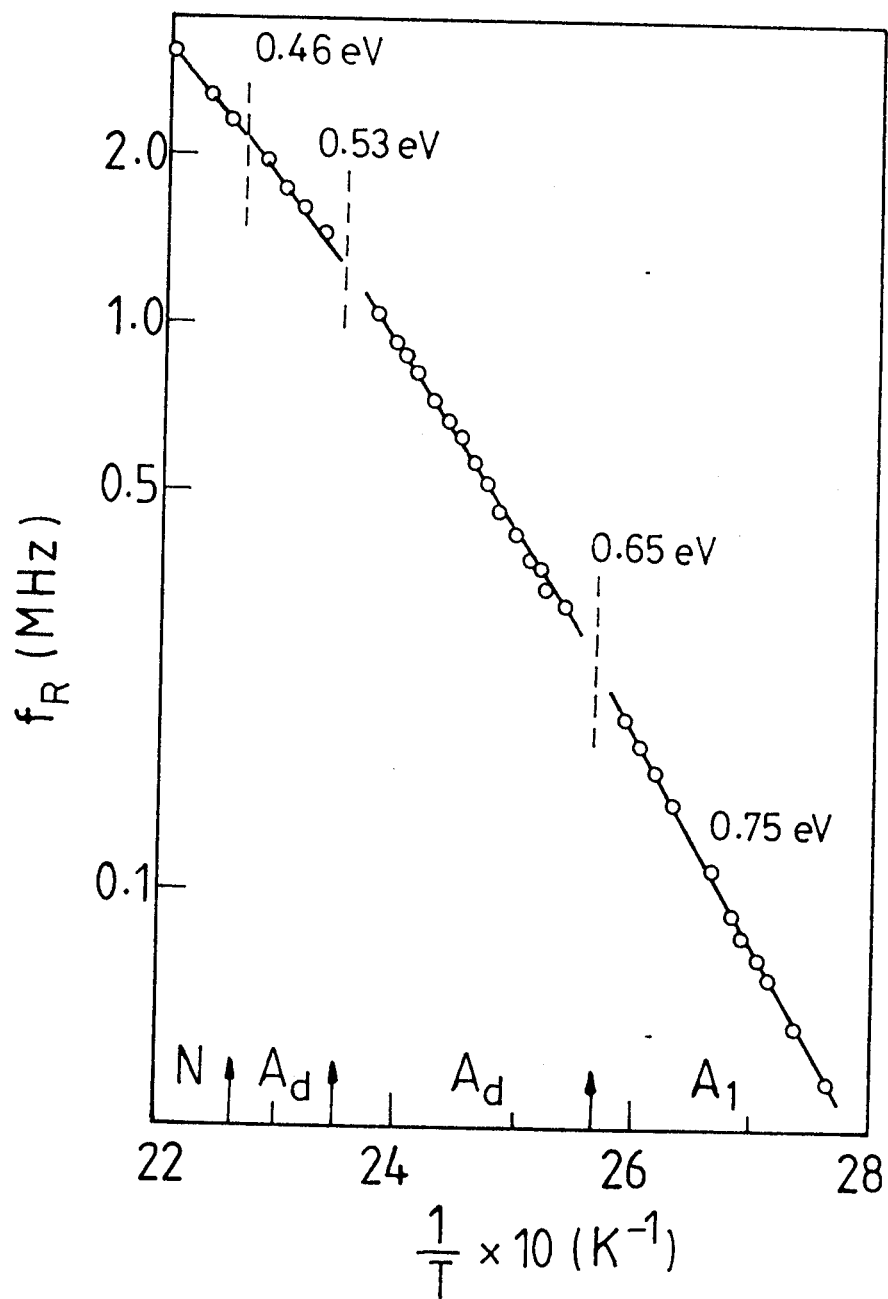


Figure 6.26 Relaxation frequency (f_R) versus $1/T$ for the binary mixture $X = 0.6$

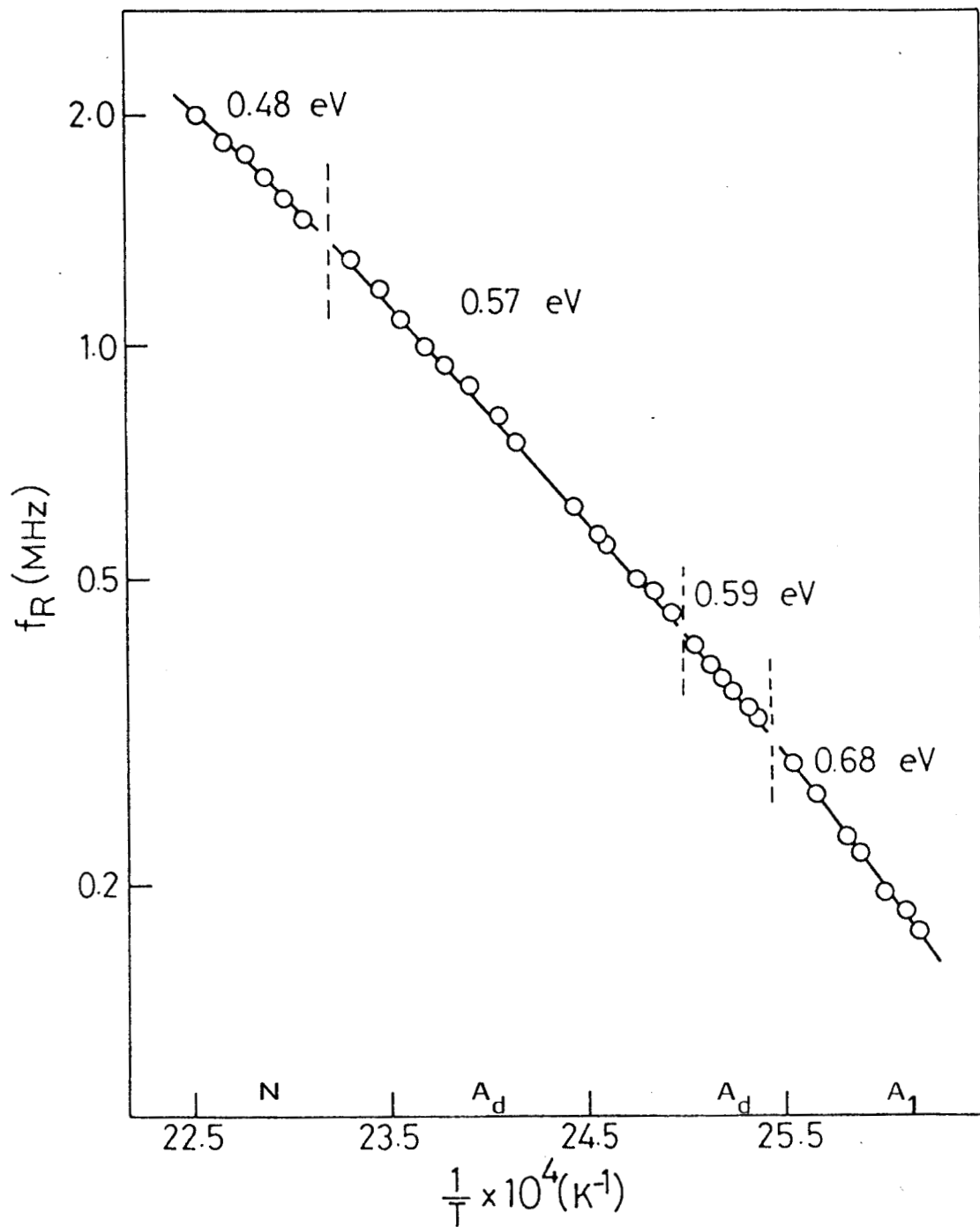


TABLE 65

Activation energy (W) corresponding to the low frequency dispersion of
in $X = 0.6$ and $X = 0.8$ mixtures obtained by linear least square fit of the
data

Phase	Activation Energy (W) eV	
	X = 0.6	X = 0.8
Nematic	0.46	0.48
Smectic A _{d1}	0.53	0.57
Smectic A _{d2}	0.65	0.59
Smectic A ₁	0.75	0.68

ence of the A_1 - A_d and A_d - A_d transitions in binary mixtures of 6 ONPBB and 9 OBCAB. The reason for the occurrence of such transitions could perhaps be due to the structural incompatibility of nitro and cyano compounds which constitute the binary system. In fact, several phase diagrams are known wherein two A_d phases are separated in the T-X plane.^{24,38,39}

It may be recalled that the problem of A_d - A_1 transition has been discussed by Prost⁴⁰ and more recently by Prost and Barois³² who have argued that since the A_1 and A_d phases have the same symmetry, any phase transition between them has to be first order except possibly at a critical point like the gas-liquid system. One would therefore expect a discontinuity in the layer spacing at this transition. But within our experimental accuracies, we do not see such a discontinuity in the layer spacing at either the A_1 - A_d or the A_d - A_d transition, although we do observe a break in the thermal expansion at these transitions. To this extent these transitions are somewhat unusual. This also leads us to conclude that the differences between the A_1 and the two A_d phases should be quite subtle. Clearly, more experiments are needed to understand these differences.

References

1. R.Schaetzing and J.D.Litster, "Advances in Liquid Crystals", Vol. 4, Ed. G.H.Brown (Academic Press, 1979) p. 147; J.D.Litster, C.W.Garland, K.J.Lushington and R.Schaetzing, Mol. Cryst. Liq. Cryst., 68, 145 (1981).
2. P.G. de Gennes, "The Physics of Liquid Crystals", Oxford University Press, Oxford 1974.
3. N.V.Madhusudana and S.Chandrasekhar, Proc. Int. Liq. Cryst. Conf., Bangalore 1973, Pramana Suppl. 1, 57 (1973).
4. P.E.Cladis, D.Guillon, F.R.Bouchet and P.L.Finn, Phys. Rev., A23, 2594 (1981).
5. A.J.Leadbetter, R.M.Richardson & C.N.Colling, J.Physique, 36, C1-37 (1975).
6. A.J.Leadbetter, J.C.Frost, J.P.Gaughan, G.W.Gray and A. Mosley, J.Physique, 40, 375 (1979).
7. P.E.Cladis, Phys. Rev. Lett. 35, 48 (1975); P.E.Cladis, R.K.Bogardus, W.B.Daniels and G.N.Taylor, Phys. Rev. Lett., 39, 720 (1977).
8. F.Hardouin, G.Sigaud, M.F.Achard and H.Gasparoux, Phys. Lett., 71A, 347 (1979); N.V.Madhusudana, B.K.Sadashiva and K.P.L.Moodidithaya, Curr. Sci., 48, 613 (1979).
9. F.Hardouin, A.M.Levelut, M.F.Achard and G.Sigaud, J.Chim. Phys., 80, 53 (1983). Also see N.V.Madhusudana, B.S.Srikanta and M.Subramanya Raj Urs, Mol. Cryst. Liq. Cryst., 97, 49 (1983).

10. Nguyen Huu Tinh, J.Chim. Phys., 80, 83 (1983); Nguyen Huu Tinh, H.Gasparoux and C.Destrade, Mol. Cryst. Liq. Cryst., 123, 271 (1985).
11. A.M.Levelut, B.Zaghloul and F.Hardouin, J.Physique Lett., 43, L-83 (1982).
12. N.V.Madhusudhana, B.S.Srikanta and M.Subramanya Raj Urs, Mol. Cryst. Liq. Cryst. Lett., 82, 317 (1982).
13. S.Chandrasekhar, K.A.Suresh and K.V.Rao, Proc. Int. Liq. Cryst. Conf., Bangalore, December 1979, Ed. S.Chandrasekhar, (Heyden, London) 1980 p.131.
14. P.G. de Gennes, Solid State Commun., 10, 753 (1972).
15. R.B.Meyer and T.C.Lubensky, Phys. Rev., A14, 2307 (1976).
16. G.Sigaud, F.Hardouin, M.F.Achard and H.Gasparoux, J.Physique, 40, C3-356 (1979).
17. F.Hardouin, A.M.Levelut, J.J.Benattar and G.Sigaud, Solid State Commun., 33, 337 (1980).
18. F.Hardouin, A.M.Levelut and G.Sigaud, J.Physique, 42, 71 (1981).
19. G.Sigaud, F.Hardouin, M.F.Achard and A.M.Levelut, J.Physique, 42, 107 (1981).
20. P.Barois, C.Coulon and J.Prost, J.Physique Lett., 42, L-107 (1981).
21. F.Hardouin, G.Sigaud, Nguyen Huu Tinh and M.F.Achard J. Physique Lett., 42, L-63 (1981).

22. C.C.Huang, S.C.Lien, S.Dumrongrattana and L.Y.Chiang, Phys. Rev. A30, 965 (1984); C.Chiang and C.W.Garland, Mol. Cryst. Liq. Cryst., 122, 25 (1985).
23. K.K.Chan, "Xray Scattering Study of Nematic and Smectic A Critical Behaviour in Liquid Crystals", Ph.D.Thesis, Harvard University, 1984.
24. A.M.Levelut, R.J.Tarento, F.Hardouin, M.F.Achard and G.Sigaud, Phys. Rev., A24, 2180 (1981).
25. N.V.Madhusudana, B.S.Srikanta and M.Subramanya Raj Urs, Mol. Cryst. Liq. Cryst. Lett., 82, 25 (1982).
26. S.Takenaka, S.Hayashi and S.Kusabayashi, Mol. Cryst. Liq. Cryst., 111, 255 (1984).
27. F.Hardouin, Nguyen Huu Tinh, M.F.Achard and A.M.Levelut, J. Physique Lett., 43, L-327 (1982).
28. J.Prost, Advances in Physics, 33, 1 (1984).
29. F.Hardouin, M.F.Achard, C.Destrade and Nguyen Huu Tinh, J.Physique, 45, 765 (1984).
30. See fig. 4.13 of Chapter IV.
31. See fig. 5.5 of Chapter V.
32. J.Prost and P.Barois, J.Chim. Phys., 80, 65 (1983).

33. H.Kresse, "Advances in Liquid Crystals", Vol. 6, Ed. G.H.Brown (Academic Press, 1983) p. 109.
34. W.Maier and G.Meier, Z. Naturforsch., 16a, 262 (1961).
35. B.R.Ratna and R.Shashidhar, Mol. Cryst. Liq. Cryst., 42, 113 (1977).
36. 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.
37. C.Druon and J.M.Wacrenier, Mol. Cryst. Liq. Cryst., 98, 201 (1983).
38. See fig. 5.7 of Chapter V.
39. B.R.Ratna, R.Shashidhar and S.Somasekhar (unpublished).
40. J.Prost, "Liquid Crystals of one- and two dimensional order", Eds. W.Helfrich and G.Heppke, (springer-verlag), 1980, p. 125.