

CHAPTER II

RE-ENTRANT NEMATIC PHASE IN SOME PURE COMPOUNDS AND MIXTURES AT ATMOSPHERIC PRESSURE

2.1 Introduction

As described in chapter I mesogens exhibiting both nematic and smectic A phases usually have the following sequence of phase transitions on cooling from the isotropic phase.

Isotropic — Nematic — Smectic A — Crystal

For example

1. 4'-n-octyloxy-4-cyanobiphenyl (8 OCB)

Isotropic $\xrightarrow{79.7^{\circ}\text{C}}$ Nematic $\xrightarrow{66.9^{\circ}\text{C}}$ Smectic A — Crystal

2. N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA)

Isotropic $\xrightarrow{108^{\circ}\text{C}}$ Nematic $\xrightarrow{82.6^{\circ}\text{C}}$ Smectic A — Crystal .

Indeed, this sequence of phase transitions is what one would expect, since the nematic phase has a higher symmetry than the smectic A phase. The nematic phase is characterised by only an orientational ordering of molecules whereas the smectic A phase has a one-dimensional translational order in addition to the orientational order.

Gladis (1975) discovered that mixtures of CBOOA and p-[(p-hexyloxybenzylidene)-amino]benzonitrile (HBAB) having about 7-11 mole per cent of HBAB show the following interesting sequence of phase transitions:

Isotropic — Nematic — Smectic A — Nematic — Crystal .

The nematic phase obtained on cooling the smectic A phase is called the re-entrant nematic phase. Gladis has pointed out that the occurrence of re-entrant nematic phase in liquid crystals is analogous to the re-entrant phenomena in superconducting materials doped with magnetic materials and in Helium-3.

We may recall here the analogy given by de Gennes (1972) between the normal metal-superconductor transition and nematic-smectic A transition. The smectic order parameter

$$\psi = |\psi| \exp(i\phi)$$

is a two component function. Analogously, the order parameter of superconductors is also a two component function. The analogy is further supported by the following facts.

In the smectic A medium, $\text{curl } \vec{n} = 0$ since the line integral $\int \vec{n} \cdot d\vec{r}$ around a closed loop is zero in a dislocation free sample (de Gennes, 1969). From the Oseen-Frank expression for elastic energy density we see that the twist and bend deformations involve $\text{curl } \vec{n}$. Since $\text{curl } \vec{n}$ is zero, the

twist and bend deformations are forbidden in the smectic A phase. Similarly, in a superconductor, magnetic flux is excluded from the medium and $\text{curl } \vec{A}$ is zero where $\vec{A}$ is the vector potential. Further, the occurrence of the re-entrant nematic phase below smectic A phase is analogous to the occurrence of normal metal below the superconductor.

Gladis et al (1977, 1978) showed that the re-entrant nematic phase can be induced in some pure cyano compounds like 8 OCB and CBOOA and in some mixtures by subjecting them to high pressures. In all these cases, the re-entrant nematic phase is obtained only on supercooling the sample from the smectic A phase.

From x-ray diffraction studies of a mixture of 6 OCB (4'-n-hexyloxy-4-cyanobiphenyl) and 8 OCB in the nematic and the re-entrant nematic phases, Guillon et al (1978) have concluded that the re-entrant phase is similar to the normal nematic phase with practically no difference in the observed x-ray spacings.

Recent high pressure x-ray investigations (Chandrasekhar et al 1979, Shashidhar and Rao 1980) on 8 OCB have shown that the re-entrant behaviour of this compound which occurs at higher pressures is associated with an expansion of smectic A layer spacing with increasing pressure as was predicted by Gladis et al (1978).

Engelen et al (1979) have reported the presence of re-entrant nematic phase in a number of binary mixtures. They have observed that mixtures of 8 OCB and CBOOA show the re-entrant nematic phase in certain range of compositions and by extrapolation they have estimated the virtual smectic *h*-nematic transition temperatures in 8 OCB and CBOOA. They have also observed re-entrant nematic phase in binary mixtures of some terminal non-polar compounds with 8 OCB or CBOOA. In these mixtures, the re-entrant phase is observed when they are rich in the terminal polar compound. These mixtures also exhibit the phenomenon of induced smectic mesomorphism in some range of compositions (see chapter V).

It is clear from the description given above that all the pure compounds and at least one component of the mixtures which exhibit the re-entrant nematic phase consist of molecules having the strongly polar cyano end group. From energy considerations, it has been concluded that in such compounds, the neighbouring molecules should have strong antiparallel correlations (Madhusudana and Chandrasekhar, 1973). Measurements of dielectric constants of cyano-compounds (Schadt 1972, Ratna et al 1973) have shown that the average dielectric constant increases on passing from the nematic to the isotropic phase. This has been interpreted as arising from a discontinuous decrease in the antiparallel short range order between neighbouring molecules in such cases (Madhusudana and Chandrasekhar 1973).

More recently, x-ray studies have provided a direct evidence for the existence of such antiparallel correlations between neighbouring molecules in the cyano-compounds. In the smectic A phase of compounds whose molecules do not possess strongly polar end-groups, the layer spacing is found to be almost equal to the molecular length (see for example, Doucet et al 1973). But in compounds having the cyano end-group, the layer spacing is found to be about 1.4 times the molecular length as indicated by the x-ray observations of McMillan (1973) in CBOOA and of Gray and Lydon (1974) in 8CB (4'-n-octyl-4-cyanobiphenyl). In order to account for the observed values of layer spacing, some kind of interdigitation of molecules was postulated (Leadbetter et al 1975, Lydon and Coakley 1975). Such an interdigitation arises due to antiparallel correlations between neighbouring molecules. The strongly polar cyano end-group polarises the aromatic core of the molecule. The polarised aromatic segments of neighbouring molecules overlap on each other as shown in figure 2.1. Leadbetter et al (1977) and Cladis et al (1977) have also suggested such an overlap, with the aliphatic chains hanging out at the ends. Recently, Leadbetter et al (1979) have confirmed that this is indeed the right picture by x-ray diffraction and neutron diffraction studies of deuterated samples of 8 OCB.

From the above description, it is quite clear that the occurrence of re-entrant nematic phase is closely linked with

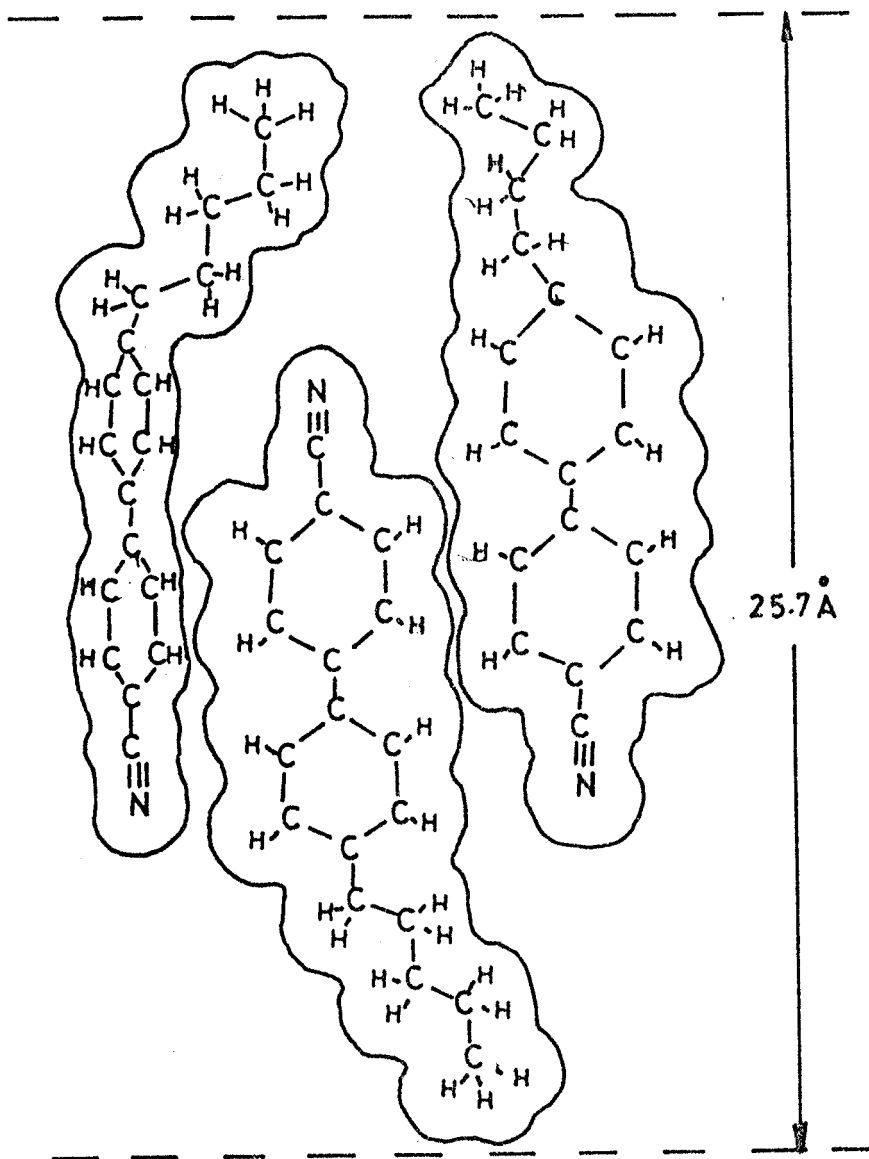


FIGURE 2.1

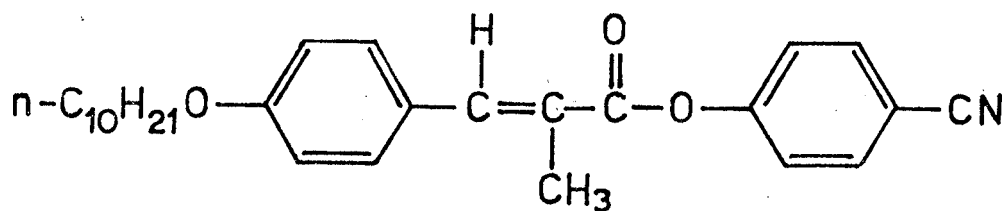
Schematic diagram of the bilayer structure in 5CB.
(Reproduced from Leadbetter et al 1975).

the bilayer structure of the compounds. In a recent paper, Gladis (1980) has suggested a possible (qualitative) mechanism of occurrence of the re-entrant nematic phase. A nematic phase can be stabilised by the anisotropic steric repulsive forces existing between neighbouring molecules. On the other hand to stabilise the layered structure of smectic A phase some kind of weak, lateral attractive interaction between molecules is essential. Gladis presumed that the origin of these attractive forces is electrostatic and is related to the molecular polarisability. According to this scheme, the highly polar molecules stabilise the layers better. In cyano-compounds, the neighbouring molecules which are interdigitated can be assumed to form associated pairs. Quite obviously these associated pairs are very much less polar than *the* individual molecules. As the temperature is decreased or as the pressure is increased, the number of such associated pairs as well as their stability increase. Consequently, the attractive interactions between the pairs decrease. Thus as that density increases, the enhanced repulsive interactions appear to favour the formation of the re-entrant nematic phase. Pershan and Prost (1979) have developed this idea in terms of a Landau theory of the re-entrant nematic-smectic A phase transition. By assuming the existence of an optimum density ⁱⁿ the smectic A phase they could explain the P-T phase diagrams of compounds showing the re-entrant nematic phase.

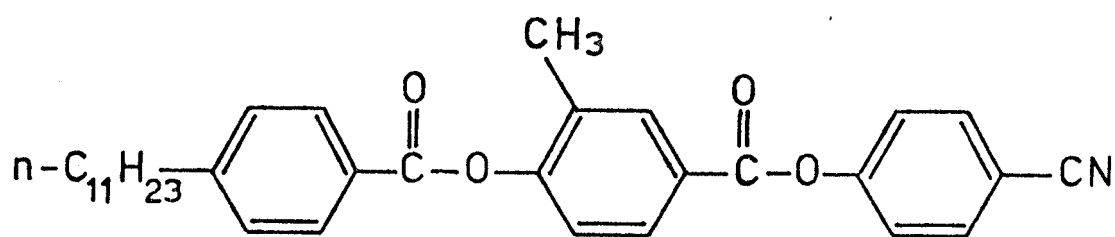
Clark (1979) and Klug and Whalley (1979) have also given thermodynamic theories to explain the elliptic phase boundaries occurring in such phase diagrams. A thermodynamic theory explaining the isobaric phase diagrams of binary mixtures showing re-entrant nematic phase has been developed by Heppke et al (1980) and also by Billard (1980). We will have occasion to refer to the latter theory later in this chapter.

2.2 Re-entrant nematic phase in pure compounds at atmospheric pressure

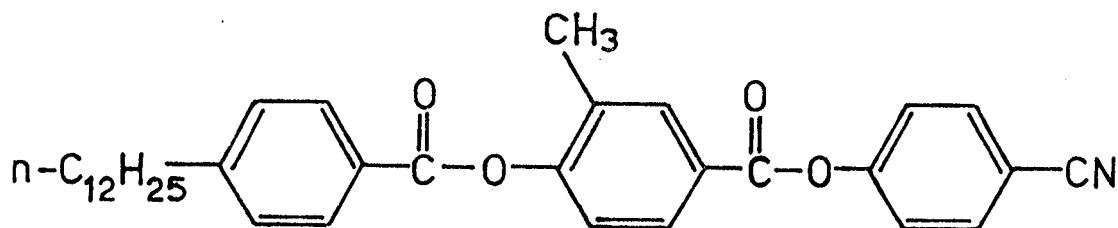
Until the beginning of 1979, the re-entrant nematic phase was seen either in mixtures or in single component systems only at high pressures. In early 1979, we discovered the existence of the re-entrant nematic phase in three pure compounds at atmospheric pressure. These compounds were prepared in our chemistry laboratory by Sadashiva (1976, 1979). The compounds are (i) trans-p-n-decyloxy- α -methyl-p'-cyanophenyl cinnamate (10 OMCPG); (ii) 4-cyanophenyl-3-methyl-4-(4-n-undecylbenzoyloxy)benzoate (11 CPMBB) and (iii) 4-cyanophenyl-3-methyl-4-(4-n-dodecylbenzoyloxy)benzoate (12 CPMBB). The molecular structures of these compounds are given in figure 2.2. All these compounds show the re-entrant nematic phase only in the cooling cycle. In other words, the re-entrant nematic phase is monotropic. In the case of 30 OMCPG the crystal, on heating, melts directly to the normal nematic phase. In the



I



II,



III

FIG.
FIGURE 2.2

Structural formulae of (I) 10 OMCPG, (II) 11 CPMBB, and
(III) 12 CPMBB

other two compounds, the crystal melts to the smectic A phase which then goes over to the nematic phase at a higher temperature. On cooling, the normal nematic phase transforms first to the smectic A phase which on supercooling gives the re-entrant nematic phase, metastable with respect to the crystalline phase. The transition temperatures of these compounds are listed in table 2.1.

The transition temperatures were determined using a Mettler hot-stage (Mettler FP-52) in conjunction with a polarising microscope and also using a differential scanning calorimeter (Perkin-Elmer DSC Model-2). Through the polarising microscope, we could see the schlieren texture as well as many threads in the re-entrant nematic phase. On displacement of the cover slip, brilliant flashes could be seen just as in the case of normal nematic phase.

In 10 OMCPG, the re-entrant phase appears only on ^{cooling} the sample rapidly from the smectic A phase, just before solidification starts. If the cooling is slow, the smectic A phase transforms directly into the crystalline phase. The observable range of the re-entrant phase is very small ($\sim 0.5^{\circ}\text{C}$). On the other hand, in 11 CPMBB and 12 CPMBB, the re-entrant nematic phase is formed more readily and the crystallisation begins to occur well below the smectic A-re-entrant nematic transition point even when the compound is cooled at a relatively

TABLE 2.1

Transition temperatures of compounds exhibiting re-entrant nematic phase at atmospheric pressure

Compound	Transition temperatures on heating	Transition temperatures on cooling
10 OMCPG	solid-nematic	isotropic-nematic 73.4°C
	nematic-isotropic	nematic-smectic A 56.8°C
		smectic A-nematic 32.5°C
		nematic-solid ~ 32.0°C
11 CPMBB	solid-smectic A	isotropic-nematic 152.5°C
	smectic A-nematic	nematic-smectic A 127.0°C
	nematic-isotropic	smectic A-nematic 78.0°C
		nematic-solid ~ 65.0°C
12 CPMBB	solid-smectic A	isotropic-nematic 148.5°C
	smectic A-nematic	nematic-smectic A 138.0°C
	nematic-isotropic	smectic A-nematic 59.8°C
		nematic-solid ~ 56.0°C

slow rate ($\sim 1^\circ/\text{minute}$). The observable range of the re-entrant phase is much smaller in the higher homologue (12 CPMBB) compared to that in the lower homologue (11 CPMBB). The thermal range of the smectic A phase is wider in the case of the higher homologue (12 CPMBB) as compared with that; of 11 CPMBB. None of the lower homologues of 11 CPMBB exhibit the smectic A phase.

Using the thermograms obtained in the DSC studies, the heats of some of the transitions in 11 CPMBB and 12 CPMBB were calculated. In these calculations, the heat of the melting transition of Indium was taken as the standard for the purpose of calibration. The data are given in table 2.2.

Table 2.2

Heats of transitions of compounds exhibiting re-entrant nematic phase at atmospheric pressure

Compound	Transition	Heat of transition in joules/mole
11 CPMBB	nematic-smectic A	14.7
	smectic A - re-entrant nematic	15.4
12 CPMBB	nematic-smectic A	255.0
	smectic A - re-entrant nematic	46.4

In 11 CPMBB, both the nematic-smectic A and smectic A - re-entrant nematic transitions are nearly second-order transitions

whereas in 12 CPMBB the two transitions are relatively stronger. Further, it is interesting to note that heat is liberated at both the nematic-smectic A and smectic A - re-entrant nematic phase transitions, even though the latter phase transition is accompanied by a loss of translational order. Any theory of the smectic A - re-entrant nematic phase transition will have to account for this observation.

The compounds listed in table 2.1 can also be expected to have a bilayer structure by virtue of the strongly polar cyano-group present at one end of the molecule. This has been confirmed by the x-ray diffraction studies of 11 CPMBB and 12 CPMBB (Chandrasekhar et al 1980) which showed that the layer spacing is about 1.4 times the molecular length in these compounds.

Almost simultaneous with our observation of re-entrant nematic phase in pure compounds at atmospheric pressure, Hardouin et al (1979a, 1979b, 1980) and Tinh and Gasparoux (1979) have made similar observations in some other compounds. For the sake of comparison, these compounds and their transition temperatures are given in table 2.3.

Interestingly, two of the compounds listed in the table show not only a re-entrant nematic phase but also a re-entrant smectic A phase which is observed on cooling the compound from the re-entrant nematic phase. Again, invoking the analogy with

TABLE 2.3

Name of the compound	Transition temperatures in °C					Reference
	K	S _A	N	S _A	I	
4-octyloxy-benzoyloxy-4'-cyanostilbene	94.5	96.0	138.9	247.0	283.0	Hardouin et al (1979)
4-nonyloxy-benzoyloxy-4'-cyanotolane	90.0	(75.7)	141.0	183.0	239.0	Tinh and Gasparoux (1979)
4-decyloxy-benzoyloxy-4'-cyanotolane	84.0	-	102.0	208.0	233.5	Tinh and Gasparoux (1979)
4-cyanobiphenyl-4'-n-octyloxybenzoate	97.0	-	120.0	201.0	240.0	Hardouin et al (1980)
4-cyanobiphenyl-4'-n-nonyloxybenzoate	96.0	-	(71.0)	217.0	232.0	Hardouin et al (1980)

[Note: Brackets denote monotropic transition. K - crystal, S_A - smectic A, N - nematic, I - isotropic]

superconductors, it may be mentioned that in the case of superconductors with Kondo impurities not only the vanishing of superconductivity was predicted to occur below a second critical temperature, but also the reappearance of superconductivity at some third critical temperature (see Gladis 1980).

Levelut et al (1980) have measured the x-ray spacing of 4-n-octyloxybenzoxyloxy-4'-cyanostilbene in both the normal and the re-entrant smectic A phases. They found that the spacing of the high temperature smectic A phase corresponds to a bilayer structure, whereas that of the re-entrant smectic A corresponds to a monolayer structure. In the high temperature smectic A phase of this compound the spacing was found to decrease continually as the temperature was lowered from AN transition point to the AN_x transition point.

Chandrasekhar et al (1980) have measured the x-ray spacing of 11 CPMBB and 12 CPMBB and have found that it decreases initially as the temperature is lowered from AN transition point, attains a minimum value and then shows an increasing trend as the AN_x transition point is approached. This may indicate that some change in the smectic bilayer is occurring as a precursor to the formation of the re-entrant nematic phase. The dielectric measurements carried out on these systems by Ratna et al (1980) provide further evidence for this. They found from dielectric relaxation studies that

in the smectic A phase of these compounds a plot of relaxation frequency versus $1/T$ consists of two distinct straight lines with different slopes (i.e., corresponding to different activation energies). The activation energy is higher in the low temperature range compared to that in the high temperature range. The change in slope occurs at a temperature roughly corresponding to the minimum x-ray spacing of the bilayer smectic A.

All the compounds listed on table 2.3 have three phenyl rings in the central core and the strongly polar cyano group at one end of the molecule. Two of the compounds listed in table 2.9 viz., 11 CPMBB and 12 CPMBB also have three phenyl rings at the core of the molecule. However, the other compound in table 2.1, viz., 10 OMCPG consists of only two phenyl rings. To date, this appears to be the only compound with two phenyl rings exhibiting the re-entrant phase at atmospheric pressure.

Very recently, Sadashiva (1980) has reported the observation of re-entrant nematic phase at atmospheric pressure in one more pure compound, viz., 4-cyanophenyl-4'-(4"-n-decyloxybenzoyloxy)benzoate.

In order to confirm that the phase obtained on cooling the smectic A phase of 11 CPMBB, 12 CPMBB and 10 OMCPG is truly nematic, we have carried out miscibility studies. It was found that the re-entrant phase exhibits continuous

miscibility with the nematic phase of compounds like 4-n-pentyl-4'-cyanobiphenyl (5CB) and 4-n-heptyl-4'-cyanobiphenyl (7CB).

23 Study of binary mixtures

The observable thermal ranges of the re-entrant nematic phase in the three compounds mentioned above (see table 2.1) are fairly small. It is desirable to enhance the range to facilitate quantitative measurements. With this in mind we studied the isobaric phase diagrams of the following mixtures:

- a) 10 OMCPG and 8 OCB
- b) 10 OMCPG and 11 CPMBB.

Preparation of mixtures. The two components were weighed into a cup provided with a lid using a sensitive balance (SAHM 68 Labor Kustner, East Germany). The cup was heated until the mixture passed on to the nematic phase. Then the contents of the cup were mechanically stirred so that the two components form a homogeneous mixture. The mixture was maintained in the nematic phase for about 24 hours. While preparing the sample, the mixture was always taken out in the isotropic phase to avoid the possibility of any concentration gradient.

Measurement of transition temperature. The transition temperatures of the mixtures were determined using a Mettler

hot stage as well as a differential scanning calorimeter. In many cases, the heats of transition involved in the nematic-smectic A and smectic A - re-entrant nematic transitions are very small. In such cases the transitions could be detected only by the visual observation of textures. Most of these mixtures as well as the pure compounds have a strong tendency to align homeotropically. Consequently, the detection of phase transitions by observations of textures is very difficult. In such cases homogeneously aligned samples were prepared (by coating the slides and cover slips with silicon monoxide at oblique angles) to facilitate the detection of phase transitions.

24 Results and discussion

The phase diagrams of the two binary mixtures are shown in figures 2.3 and 2.4.

In all the mixtures we studied, the re-entrant nematic phase was monotropic: it was observed only on supercooling the smectic A phase. Hence we have shown only the transition temperatures observed in the cooling cycle. The nematic-isotropic transition points of the mixtures were not sharp, (in some cases the transitions took place over a range of 1-2°) though this has not been indicated in the diagrams. The re-entrant nematic-solid transition temperatures are represented by dotted lines in the diagrams since those temperatures depend very much on the rate of cooling.

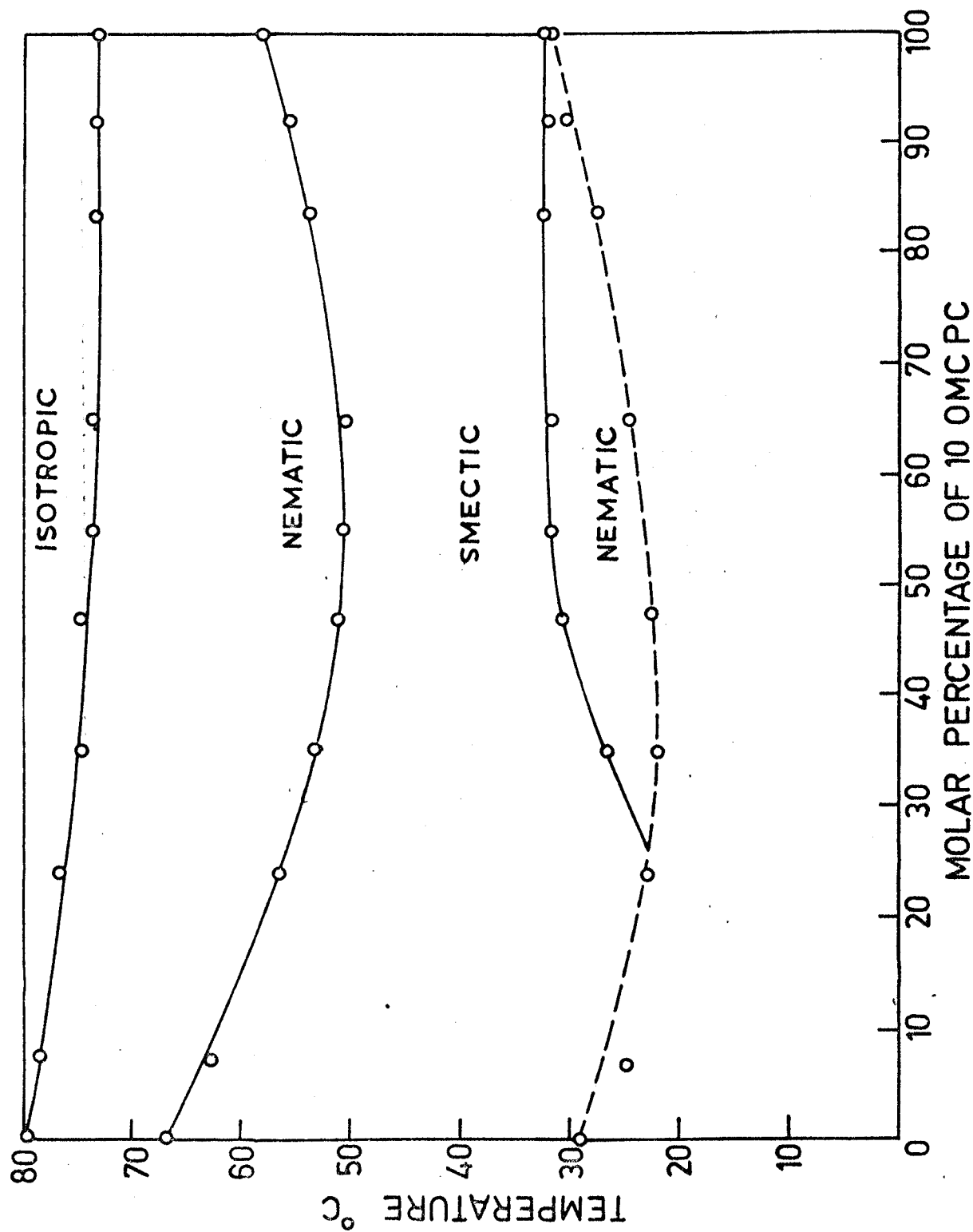


FIGURE 2.3: Phase diagram of the binary mixtures of 8 OCB and 10 OMCP.

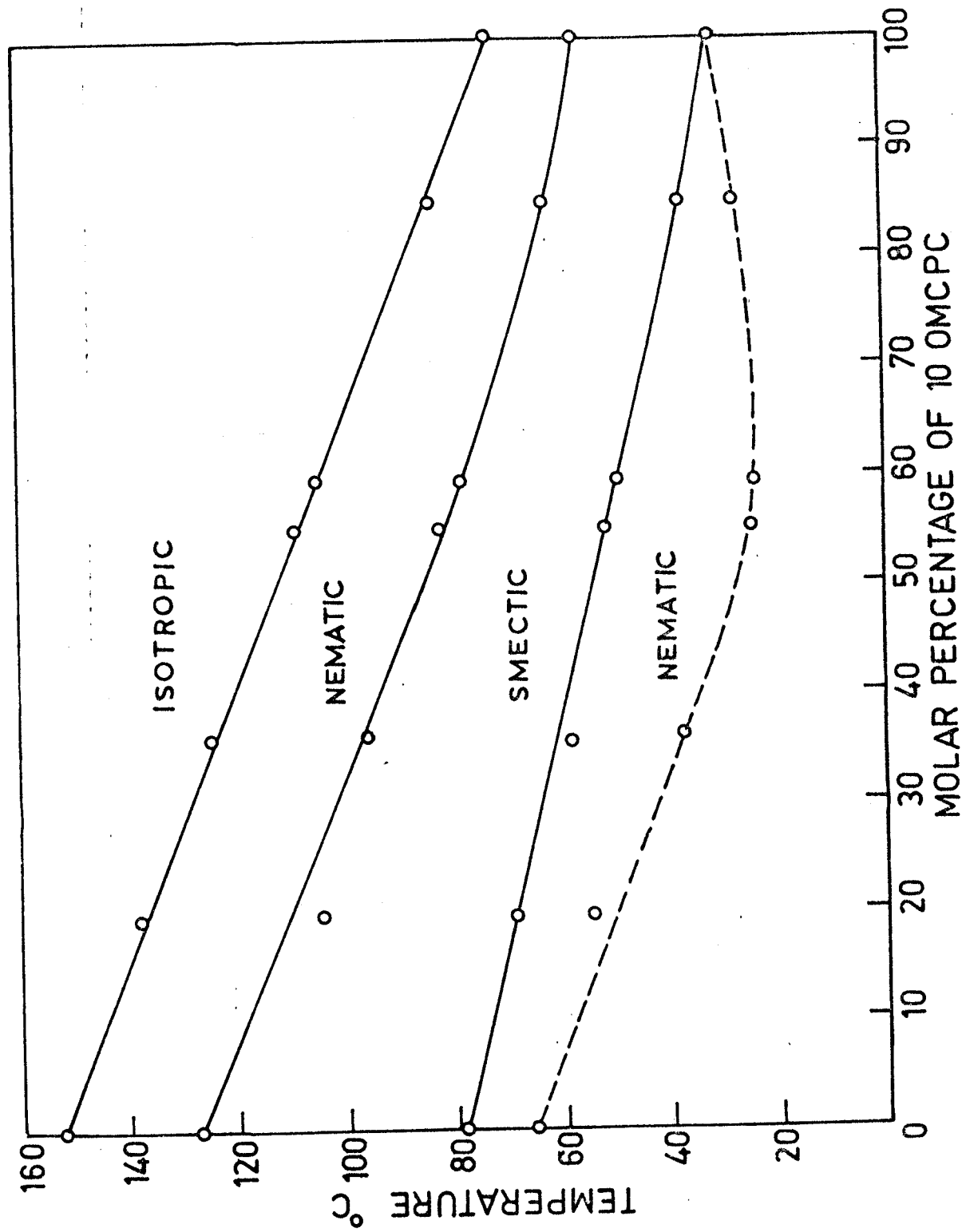


FIGURE 2.4: Phase diagram of the binary mixtures of 10 OMPC and 11 CPMBB.

(a) Binary mixtures of 10 OMCPG and 8 OCB. Pure 8 OCB does not show the re-entrant phase at atmospheric pressure though it does so at elevated pressures (Gladis et al 1978). Pure 10 OMCPG shows a monotropic re-entrant nematic phase (see table 2.1). As the molar percentage of 10 OMCPG is increased in the mixture, the nematic-isotropic transition (NI) point falls off gradually from 80.1°C to 73.4°C . The nematic-smectic A transition temperature curve has a decreasing trend initially. It reaches a minimum corresponding to a composition of ~ 60 per cent of 10 OMCPG. With further addition of 10 OMCPG, the transition temperature shows an increasing trend. The re-entrant nematic phase can be observed only in those mixtures having more than ~ 26 per cent of 10 OMCPG. The smectic A - re-entrant nematic transition temperature increases initially as the percentage of 10 OMCPG is increased, but beyond a composition of ~ 60 mole per cent of 10 OMCPG, it almost levels off.

The smectic A-nematic (AN) transition points lie on a smooth curve which is convex towards the concentration axis whereas the smectic A - re-entrant nematic (AN_r) transition points lie on another smooth curve which is concave. The range of the smectic A phase is smaller for mixtures having 40-60 mole per cent of 10 OMCPG, compared to that of either of the pure compound. The observable range of the re-entrant phase is wider in this composition range compared to other

compositions. In some of these compositions, the re-entrant phase can be observed in the mixtures even at room temperature.

When the smectic A - re-entrant nematic transition curve is extrapolated, it is found to meet the 100 per cent concentration axis of 8 OCB at a temperature of $\sim 8^{\circ}\text{C}$. This corresponds to the virtual smectic A - re-entrant nematic transition temperature of pure 8 OCB (at atmospheric pressure). This value is in agreement with the value obtained by Engelen et al (1979) by using their data on mixtures of 8 OCB and CBOOA.

(b) Binary mixtures of 10 OMCP and 11 OPMBB. The phase diagram for binary mixtures of 10 OMCP and 11 OPMBB is given in figure 2.4. As we have already seen both these compounds show the re-entrant nematic phase at atmospheric pressure. As the molar percentage of 10 OMCP in the mixture is increased, the N_I , N_N as well as N_{I-N} transition temperatures decrease almost linearly. The observable range of the re-entrant nematic phase initially increases as the concentration of 10 OMCP is increased. It attains a maximum value of $\sim 25^{\circ}$ for the composition of ~ 55 mole per cent of 10 OMCP. With further increase in the percentage of 10 OMCP this range decreases. Almost similar phase diagrams have been studied by Tinh et al (1979) using some other compounds.

As already pointed out, very recently, Heppke and Schneider (1980) as well as Billard (1980) have given thermodynamic

theories of mixtures exhibiting re-entrant nematic phase. We shall summarise below the results of this theory.

If μ_1^H is the chemical potential in the nematic phase of a pure compound (labelled 1) and μ_1^S is the chemical potential in the smectic phase,

$$\Delta\mu_1 = \mu_1^H - \mu_1^S \quad (2.1)$$

must be positive within the temperature range of the smectic phase and must be negative above T_1^+ (nematic-smectic transition temperature) as well as below T_1^- (smectic-re-entrant nematic transition temperature). The temperature dependence of $\Delta\mu_1$ is given by the relation,

$$\frac{\partial}{\partial T} \left(\frac{\Delta\mu_1}{T} \right) = - \frac{\Delta H_1(T)}{T^2} = - \frac{\Delta C_{p1}}{T^2} (T - \tilde{T}_1) \quad (2.2)$$

where the specific heat difference ΔC_{p1} is assumed to be constant and positive and $\tilde{T}_1$ is the temperature where $\Delta\mu_1/T$ has the maximum value (figure 2.5). The temperature dependence of $\Delta\mu_1/T$ is obtained by integrating equation (2.2)

$$\frac{\Delta\mu_1}{T} = \frac{\Delta\tilde{\mu}_1}{\tilde{T}_1} - C_{p1} \left[\ln \frac{T}{\tilde{T}_1} + \frac{\tilde{T}_1}{T} - 1 \right] \quad (2.3)$$

For a thermodynamically stable system, the constant of integration $\Delta\tilde{\mu}_1/\tilde{T}_1$ will be positive. $\Delta\tilde{\mu}_1/\tilde{T}_1$ is the maximum value of $\Delta\mu_1/T$ at $T = \tilde{T}_1$ as shown in figure 2.5.

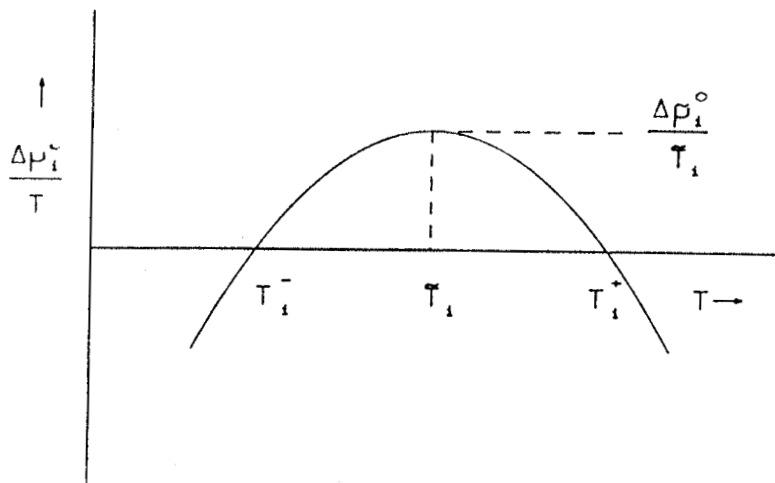


FIGURE 2.5

Schematic representation of *the* temperature dependence of the chemical potential difference. (Reproduced from Heppke and Schneider 1980).

The three independent parameters involved in equation (2.3) are related to the transition temperatures T_1^+ by

$$\tilde{T}_1 = \frac{T_1^+ T_1^-}{T_1^+ - T_1^-} \ln \frac{T_1^+}{T_1^-} \quad (2.4)$$

$$\frac{\Delta \tilde{\mu}_1}{\tilde{T}_1 \Delta \phi_{p1}} = \ln \frac{T_1^+}{\tilde{T}_1} + \frac{\tilde{T}_1}{T_1^+} - 1 \quad (2.5)$$

Equation (2.5) holds good when T_1^+ is replaced by T_1^- .

For mixtures exhibiting the re-entrant nematic phase, assuming ideal behaviour the chemical potential will be of the form

$$\mu_1' = \mu_1 + RT \ln x_1 \quad (2.6)$$

where μ_1' is the chemical potential of the component 1 in the mixture and x_1 is its mole fraction. Equation (2.6) holds good separately for nematic and smectic phases. At the phase boundary the chemical potentials of each of the components in the two phases must be equal,

$$\text{i.e., } \Delta \mu_1' = 0$$

$$\text{or } \Delta \mu_1 = -RT \ln \frac{x_1^N}{x_1^S} \quad (2.7)$$

where x_1^N and x_1^S are the mole fractions of the component 1 in the nematic and smectic phases respectively.

Applying the condition that $\sum x_i = 1$ in both the nematic and smectic phases, we get,

$$x_2^S(T) = \frac{1 - \exp\left(-\frac{\Delta\mu_1}{RT}\right)}{\exp\left(-\frac{\Delta\mu_2}{RT}\right) - \exp\left(-\frac{\Delta\mu_1}{RT}\right)} \quad (2.8)$$

where the suffix 1 stands for component 1 and suffix 2 stands for the other component of the binary mixture.

Generally, A . Then expanding the exponential terms, we get

$$x_2^S(T) = 1 - \frac{\Delta G_{p2}}{\Delta G_{p1}} \cdot \left[\frac{\frac{\Delta\mu_2}{\tilde{T}_2 \Delta G_{p2}} - \ln \frac{T}{\tilde{T}_2} - \frac{\tilde{T}_2}{T} + 1}{\frac{\Delta\mu_1}{\tilde{T}_1 \Delta G_{p1}} - \ln \frac{T}{\tilde{T}_1} - \frac{\tilde{T}_1}{T} + 1} \right]^{-1} \quad (2.9)$$

Equation (2.9) shows that the phase boundary can be found out if five parameters are known. If both the components exhibit the re-entrant nematic phase four parameters are determined by the transition temperatures T_1^+ and T_2^+ . Then knowing the ratio $\Delta G_{p2}/\Delta G_{p1}$ one can obtain the phase diagram. If T_2 of the two components are comparable the values of T_1^+ and T_1^- of the mixture calculated using equation (2.9) lie in between those of the pure components. And for reasonable values of the ratio $\Delta G_{p2}/\Delta G_{p1}$, straight lines connecting the transition temperatures of the pure components are obtained

in the phase diagram.

Indeed, this trend is seen in the phase diagram of the binary mixtures of 10 OMCPG and 11 CPMBB. However, in the other phase diagram (of mixtures of 10 OMCPG and 8 OCB) there are marked deviations from the results of the above theory. In some range of compositions, the nematic-smectic transition temperatures of the mixtures are less than the corresponding temperatures of either of the two pure compounds.

The compounds 10 OMCPG and 11 CPMBB are structurally similar to some extent as both of them are esters. On the other hand, the chemical structures of 10 OMCPG and 8 OCB differ considerably. Probably, the assumption made in the above theory that the mixtures are ideal is *NOT* true in the latter case, and this may be responsible for the deviations from the predicted behaviour.

References

- Billard, J. 1980 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London, p. 155.
- Chandrasekhar, S., Shashidhar, R. and Rao, K.V. 1979 III Liquid Crystal Conference of Socialist Countries, Budapest, August 1979.
- Chandrasekhar, S., Suresh, K.A. and Rao, K.V., 1980 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London, p. 131.
- Cladis, P.E. 1975 Phys. Rev. Letts., 35, 48.
- Cladis, P.E., Bogardus, R.K., Daniels, W.B. and Taylor, G.N. 1977 Phys. Rev. Letts., 39, 720.
- Cladis, P.E., Bogardus, R.K. and Aadsen, D. 1978 Phys. Rev. A18, 2292.
- Cladis, P.E. 1980 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London, p. 105.
- Clark, N.A. 1979 J. de Physique, 40, C3-345.
- de Gennes, P.G. 1969 J. de Physique, 30, C4-65.
- de Gennes, P.G. 1972 Solid State Commun. 10, 753.
- Doucet, J., Levelut, A.M. and Lambert, M. 1973 Mol. Cryst. Liq. Cryst. 24, 317.
- Engelen, B., Heppke, G., Hopf, R. and Schneider, F. 1979 Mol. Cryst. Liq. Cryst. Letts. 49, 193.

- Gray, G.W. and Lydon, J.E. 1974 *Nature*, 252, 221.
- Guillon, D., Gladis, P.E. and Stamatoff, J. 1978 *Phys. Rev. Letts.*, 41, 1598.
- Hardouin, F., Sigaud, G., Achard, M.F. and Gasparoux, H. 1979a *Phys. Letts.*, 71A, 347.
- Hardouin, F., Sigaud, G., Achard, M.F. and Gasparoux, H. 1979b *Solid State Commun.*, 30, 265.
- Hardouin, F., Levelut, A.M., Tinh, N.H. and Sigaud, G. 1980 *Mol. Cryst. Liq. Cryst. Letts.*, 56, 35
- Heppke, G. and Schneider, F. 1980 *Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979*, Ed. S. Chandrasekhar, Heyden, London, p. 147.
- Klug, D.D. and Whalley, E. 1979 *J. Chem. Phys.*, 71(4), 74.
- Leadbetter, A.J., Richardson, R.M. and Colling, C.N. 1975 *J. de Physique*, 36, C1-37.
- Leadbetter, A.J., Durrant, L.A. and Rugman, M. 1977 *Mol. Cryst. Liq. Cryst.*, 34, 231
- Leadbetter, A.J., Frost, J.C., Gaughan, J.P., Gray, G.S. and Mosley, A. 1979 *J. de Physique*, 40, 375.
- Levelut, A.M., Hardouin, F. and Sigaud, G. 1980 *International Liquid Crystals Conference, Bangalore, December 1979*, Ed. S. Chandrasekhar, Heyden, London, p. 143.
- Lydon, J.E. and Coakley, C.J. 1975 *J. de Physique*, 36, C1-45.
- Madhusudana, N.V. and Chandrasekhar, S. 1973 *Proc. International Liquid Crystals Conference, December 1973*, Ed. S. Chandrasekhar, *Pramana Supplement 1*, p. 57.

- McMillan, W.L. 1973 Phys. Rev. A7, 1419.
- Perhnsn, P.S. and Prost, J. 1979 J.Physique, 40, L-27.
- Ratna, B.R., Vijaya, M.S., Shashidhar, R. and Sadashiva, B.K.
1973 Proceedings of the International Liquid Crystals
Conference, Bangalore, December 1973, Ed. S.Chandrasekhar,
Pramana Supplement, 1, p.69.
- Ratna, B.R., Shashidhar, R. and Rao, K.V. 1980 Proceedings
of the International Liquid Crystals Conference, Bangalore,
December 1979, Ed. S.Chandrasekhar, Heyden, London, p. 135.
- Sadashiva, B.K. 1976 Mol. Cryst. Liq. Cryst., 35, 205.
- Sadashiva, B.K. 1979 Mol. Cryst. Liq. Cryst., 53, 253.
- Sadashiva, B.K. 1980 Proceedings of the International
Liquid Crystals Conference, Bangalore, December 1979,
Ed. S.Chandrasekhar, Heyden, London, p. 165.
- Schadt, M. 1972 J. Chem. Phys. 56, 1494.
- Shashidhar, R. and Rao, K.V. 1980 Proceedings of the
International Liquid Crystals Conference, Bangalore,
December 1979, Ed. S. Chandrasekhar, Heyden, London, p. 131.
- Tinh, N.H. and Gasparoux, H. 1979 Mol. Cryst. Liq. Cryst.
Lett., 49, 287.