

EXPERIMENTAL STUDIES OF PHASE DIAGRAMS OF LIQUID CRYSTALS

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By

S. SOMASEKHARA

Liquid Crystals Laboratory
RAMAN RESEARCH INSTITUTE
BANGALORE-560 080, INDIA

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DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.


S. SOMASEKHARA

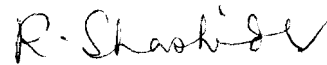
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Professor S. CHANDRASEKHAR
Liquid Crystal Laboratory
Raman Research Institute
BANGALORE 560 080

C E R T I F I C A T E

I certify that this thesis has been composed by Mr. S.Somasekhara, based on investigations carried out by him at the Liquid Crystal Laboratory, Raman Research Institute, under my supervision. The subject matter of this thesis has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar title.



Dr. R. SHASHIDHAR
Liquid Crystal Laboratory
Raman Research Institute
BANGALORE 560 080

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CHAPTER I

INTRODUCTION

Liquid crystals¹ constitute states of matter in which the degree of molecular ordering is intermediate between that of a three-dimensionally ordered crystal and that of a completely disordered isotropic liquid. Liquid crystals (also referred to as mesophases) exhibit anisotropic behaviour in their optical, magnetic and electrical properties while they also possess some of the mechanical properties of a fluid, like, inability to support shear. Liquid crystallinity can be brought about either by varying temperature or by the addition of a solvent. In the former case, the substances are referred to as thermotropic liquid crystals, while in the latter they are called lyotropic liquid crystals. Since all the work described in this thesis deals with thermotropic liquid crystals only, we shall give in the following a very brief description of thermotropic liquid crystals and their broad structural characteristics.

1.1 CLASSIFICATION OF THERMOTROPIC LIQUID CRYSTALS

Following the scheme of classification of Friedel,² the thermotropic liquid crystals composed of rod-like molecules can be categorised briefly into three types: nematic, cholesteric and smectic.

Nematic

A simplified picture of the arrangement of the molecules in the nematic phase is shown in Fig.1.1a. This phase is characterised by a long range orientational order of the molecules without any long range positional order. The molecules are spontaneously oriented with their long axes parallel to some preferred direction referred to as the **director** denoted by a unit vector n . The preferred direction usually varies from point to point in the medium, but a homogeneously aligned sample is optically uniaxial (positive) and strongly birefringent. (Recently biaxial nematics have been discovered in lyotropic systems.³) The director n is apolar, i.e., n and $-n$ are indistinguishable and thus the mesophase is non-ferroelectric.

Cholesteric

This phase which is exhibited by materials composed of optically active molecules is essentially a nematic phase except that its structure has a screw axis superimposed normal to the director (Fig. 1.1b). The spiral structure imparts certain unique optical properties to the phase, like selective reflection of circularly polarized light, very high optical rotatory power, etc. Unlike the nematic, the cholesteric phase in certain compounds goes to the isotropic phase through another mesophase called the **Blue phase**. In recent years this mesophase has attracted the attention of both theoretical and experimentalists for some of its unique

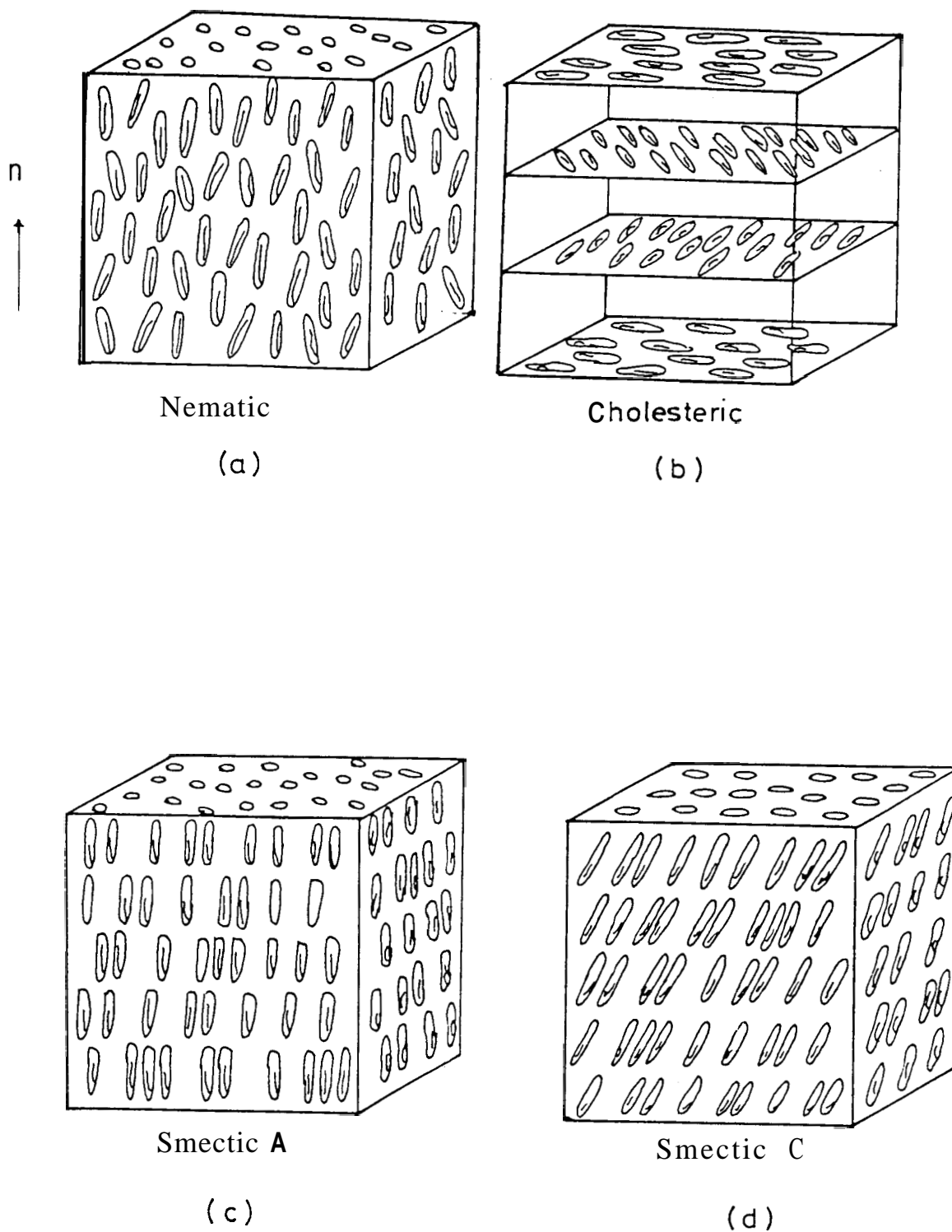


Figure 1.1

Schematic representation of the molecular arrangement in (a) nematic, (b) cholesteric, (c) smectic A and (d) smectic C phases. n denotes the director.

properties.

Smectic

It is characterised by a layered structure in addition to the orientational order of the nematic phase. Depending on the order within a layer and the inter-layer correlations, the smectics have been classified into several types. We shall mention here, in brief, the structure of two smectic phases, viz., smectic A and smectic C, as we will be mainly interested in these smectics in this thesis. (For a recent review on different types of smectic phases and their structural characteristics, see Ref. 4.)

In the smectic A phase the molecules are on the average upright with respect to the layer planes, the centres of the molecules within a layer being irregularly spaced in a liquid-like fashion (see Fig. 1.1c). The smectic A phase can therefore be looked upon as an orientationally ordered fluid with a one-dimensional mass density wave⁵⁻⁷ parallel to the director. The picture of the nematic or smectic A phase shown in Fig. 1.1a or 1.1c is in fact an idealized picture and a more realistic⁸ way of representing these phases is as shown in Fig. 1.2.

The smectic C phase can be regarded as a tilted form of smectic A. The molecules in each layer are tilted with respect to the layer normal (Fig. 1.1d).

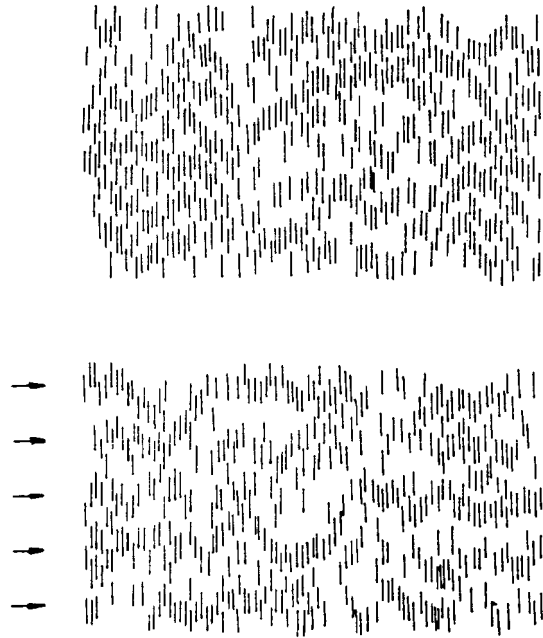


Figure 1.2

A realistic distribution of the molecules in the nematic (top) and the smectic A (bottom) phases. The arrows in the lower figure denote the crests of the density wave. (from Ref. 8).

Until recently it was believed that for thermotropic mesomorphism to occur, the molecules must be rod-like, but recently Chandrasekhar et al.⁹ have established for the first time that ordering of the symmetry axes of **disc-shaped** molecules can also give rise to stable mesophases. It is now known that these discotic or columnar mesophases exhibit a rich degree of polymorphism, comparable to that observed in rod-like systems. (For a recent review on liquid crystals of disc-like molecules, see Chandrasekhar.¹⁰) We shall not be referring to discotic phases any further in this thesis.

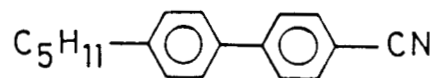
12 SEQUENCE OF TRANSITION

Some typical examples of mesogenic materials exhibiting one or more types of mesophases are listed in Table 1.1 along with the chemical formulae and the phase transitions exhibited by them.

If the transition to the liquid crystal phase occurs both on heating the solid phase and on cooling from a more disordered phase, then such a transition is referred to as enantiotropic. However, in several cases a liquid crystal phase is a metastable phase, i.e., the solid phase on heating directly transforms to the isotropic phase, but on cooling, the isotropic phase goes through a liquid crystal phase before becoming a solid. In such cases the transition is referred to as monotropic.

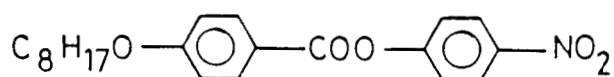
TABLE 1.1

- 1 4'-n-pentyl-4-cyanobiphenyl (5CB)



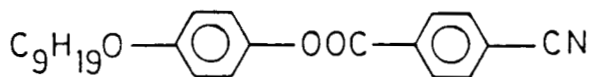
Solid $\xrightarrow{22^\circ\text{C}}$ Nematic $\xrightarrow{35^\circ\text{C}}$ Isotropic

- 2 4-nitrophenyl-4'-n-octyloxybenzoate (NPOOB)



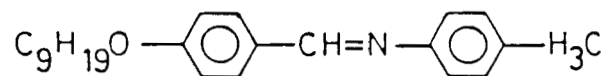
Solid $\xrightarrow{49.8^\circ\text{C}}$ Smectic A $\xrightarrow{61.2^\circ\text{C}}$ Nematic $\xrightarrow{67.5^\circ\text{C}}$ Isotropic

- 3 4-n-nonyloxyphenyl-4'-cyanobenzoate (90 PCB)



Solid $\xrightarrow{67^\circ\text{C}}$ Smectic A $\xrightarrow{95^\circ\text{C}}$ Isotropic
 $\downarrow 55.9^\circ\text{C}$
 Smectic C

- 4 N-(4-n-nonyloxybenzylidene)-4'-n-methylamine



Solid $\xrightarrow{72^\circ\text{C}}$ Smectic A $\xrightarrow{73^\circ\text{C}}$ Nematic $\xrightarrow{77.5^\circ\text{C}}$ Isotropic
 $\downarrow 64^\circ\text{C}$
 Smectic B

Since the discovery of liquid crystalline behaviour it is well known that the general sequence of phase transitions that are observed in a typical mesogen on cooling from the isotropic phase is :

Isotropic — Nematic — Smectic — Crystal .

Cladis¹¹ observed an interesting departure from this sequence. She discovered that in a binary liquid crystal system the nematic-smectic A transition becomes multivalued, i.e., a nematic phase appears at a temperature higher as well as lower than the temperature range of existence of the smectic A phase. The lower temperature nematic phase has been designated as **reentrant nematic** phase (**RN**) in analogy with the similar reentrant behaviour observed in condensed matter physics.^{12,13} This discovery has led to a variety of theoretical as well as experimental studies to understand the nature of the reentrant nematic phase. A feature which was common to most of the reentrant mesogenic compounds was that the constituent molecules possessed strongly polar cyano (CN) or nitro (NO₂) end group. Exceptions¹⁴ to this have been observed recently, but such instances are very few.

Another new and totally unexpected discovery was made in 1979 when studies conducted by the Bordeaux group¹⁵ led to the first observation of a transition between two polymorphic forms of the smectic A phase. This observation in a temperature-concentra-

tion diagram was established by Xray experiments.^{16a} So far four types of smectic A phases, namely, monolayer smectic A (A_1), bilayer smectic A (A_2), partially bilayer smectic A (A_d), and incommensurate smectic A (A_{iC}) are known to be exhibited either by a single component system or by binary systems of polar liquid crystals. Two other types of A phases, viz., antiphase (\tilde{A}) and crenelated phase (A_{cre}) are also known. However these are known to be biaxial^{16b} and hence cannot be classified as an A phase in the sense defined earlier.

1.3 EXPERIMENTAL SET UP

The results described in this thesis have been obtained using different experimental techniques, viz., miscibility methods, Xray diffraction and high pressure.

Miscibility

For obtaining high resolution temperature-concentration phase diagrams the major problem that was encountered was the availability of materials in relatively small quantities (~ 300 mg) from which a large number of mixtures (about 25-30 concentrations) had to be made with a reproducible accuracy of $\pm 0.01\%$ in concentration in order to carry out a complete mapping of the high resolution phase boundary. This was achieved by evolving a technique of careful weighing and sample preparation. The details of this procedure are explained

in Chapter III. Using this method high resolution temperature-concentration diagrams of systems exhibiting multicritical points have been obtained. The same technique has also been used to obtain T-X diagrams involving reentrant nematic systems which are discussed in Chapter V and phase diagrams involving A_d and A_1 phases which are discussed in Chapter VI.

Xray diffraction set up

Two types of Xray diffraction set ups have been used. All high resolution studies were conducted using a computer controlled Guinier Xray diffractometer. Employing a bent quartz monochromator in Johansson focussing geometry K_{α_1} and K_{α_2} lines were separated and only K_{α_1} was used for the experiment. The data acquisition as well as analysis was fully computerised. The temperature constancy during any data collection was ± 10 mK. The accuracy in the determination of wavevector corresponding to the Xray diffraction peak was $\pm 2 \times 10^{-4} \text{ \AA}^{-1}$. This set up has been used to study the smectic A_d -smectic A_2 transition. These studies have led to the first observation of the A_d - A_2 critical point discussed in Chapter IV.

For low resolution experiments, and in particular when a complete picture in reciprocal space was necessary to identify a phase, photographic technique was used. In particular, this set up has been useful in identifying the \tilde{A} and \tilde{C} phases whose Xray pictures consist of spots (corresponding to the transverse modulation within the layer)

which lie out of the Z-axis. It may be mentioned that all the scanning conducted using the computer controlled Xray diffractometer mentioned earlier was along the Z-direction, i.e., the equatorial direction.

High pressure set up

The high pressure studies were conducted using an optical high pressure cell. The phase transitions were detected by optical transmission technique. Using this set up the transition temperature at any pressure could be determined to a high degree of accuracy. The P-T diagrams of reentrant nematic systems described in Chapter V and the pressure behaviour of N-I transitions of cyclohexane materials discussed in Chapter VII were studied using this high pressure cell.

All the above experimental set-up are described in detail in Chapter II.

1.4 UNIVERSALITY OF REENTRANT NEMATIC-SMECTIC C-SMECTIC A AND NEMATIC-SMECTIC A-SMECTIC C MULTICRITICAL POINTS

The nematic-smectic A-smectic C multicritical point (or NAC point for short) has been of considerable current interest. It was first theoretically predicted^{17,18} and later found experimentally¹⁹ in the temperature-concentration (T-X) plane of a binary liquid crystal system. The experimental observation of the NAC point was followed by high resolution Xray,^{20,21} calorimetric^{22,23} and light scattering²⁴

experiments which initiated explicit comparisons with theoretical predictions. Brisbin et al.²⁵ obtained high resolution T-X diagrams of binary systems exhibiting the NAC point. On the basis of these diagrams they showed that the topology of the temperature-concentration diagrams in the vicinity of the NAC point is universal. Recently the NAC point in a single component liquid crystal system was obtained by Shashidhar et al.²⁶ in a P-T plane. Using expressions similar to those used by Brisbin et al. it was shown that the exponents derived from the P-T data for a single component system agreed exactly with those obtained from the T-X data of four binary systems. Thus it was established that the NAC **point exhibits universal behaviour**. A noteworthy feature of this result was that the scaling axes were found to be same as experimental axes (P, T in the case of Shashidhar et al.²⁶ and X,T in the case of Brisbin et al.²⁵) rather than linear combination of these.

Earlier, Shashidhar et al.^{27,28} in their efforts to look for an NAC point in a single component system observed another kind of multicritical point, namely, reentrant nematic-smectic C-smectic A point (or RN-C-A point). The striking features of the P-T diagram exhibiting the RN-C-A point were :-

- 1 The sequence of phase transitions on cooling were different from that of NAC case, the lowest temperature phase in the RN-C-A case was the reentrant nematic phase while in the

case of the NAC point the nematic phase was the highest temperature phase.

- 2 The singularities of the phase boundaries of the type seen near the NAC point were conspicuously absent near the RN-C-A point. The latter result was surprising. The symmetries of the different phases which exhibit the RN-C-A and NAC points being the same, it is expected²⁹ that both of them should belong to the same universality class and therefore should exhibit the same unusual features with regard to the topology of the phase boundaries. To resolve this problem, high resolution experiments have been undertaken to map accurately T-X diagrams near the RN-C-A point. These studies have shown that by bringing the temperature at which the RN-C-A point occurs closer to N-I transition in the T-X plane, the critical region could be enhanced so much so, the singularities of the phase boundaries in the vicinity of the RN-C-A point become more conspicuous. Detailed analysis of the boundaries yield exponents which are, within statistical uncertainties, exactly same as the exponents evaluated for NAC point in T-X as well as P-T planes. It is therefore established that the RN-C-A and NAC multicritical points exhibit the same universal behavior. These results are discussed in Chapter III.

1.5. SMECTIC A_d - SMECTIC A_2 - CRITICAL POINT

As mentioned earlier, materials with a strongly polar cyano (CN) or nitro (NO_2) end group exhibit smectic A polymorphism. The different forms of smectic A known so far are A_1 , A_2 , A_d and A_{ic} phases. Most of the above mentioned smectic polymorphisms have been successfully explained in terms of phenomenological model introduced by Prost^{30,31,32} and later developed by Prost and Barois.³³ The nature of the A_d phase and its relation to A_2 phase was addressed to theoretically by Barois et al.³⁴ They used the phenomenological model in the framework of mean-field theory to study phase diagrams exhibited by different systems. One of the important predictions of the theoretical phase diagrams is the existence of a gas-liquid type of critical point, namely, the A_d - A_2 critical point. It has been argued that since A_d and A_2 phases have the same macroscopic symmetry there cannot be a second order phase transition between them. The theory predicts that under certain conditions, the first order A_d - A_2 boundary should terminate at a critical point similar to the gas-liquid critical point. Although there have been some attempts³⁵⁻³⁷ to locate such a critical point, they were unsuccessful. Results of our high resolution Xray diffraction experiments which have led to the first observation of the A_d - A_2 critical point are described in Chapter IV.

1.6 COUPLING BETWEEN NEMATIC AND SMECTIC ORDERING IN REENTRANT NEMATIC SYSTEMS

The reentrant nematic phase, as mentioned already, was discovered by Cladis. Though initially observed in binary mixtures at atmospheric pressure or in single component systems at elevated pressures,^{38,39} later it was shown that a reentrant phase indeed exists at atmospheric pressure^{40,41} in single component systems. This has led to a variety of experiments, in particular a large number of phase diagrams of reentrant nematogens (in the P-T as well as T-X planes) have been obtained. As observed even in the earlier experiments⁴² the P-T diagrams of reentrant nematogenic systems showed some interesting features: (1) The nematic-smectic A boundary is elliptic or parabolic in shape, (2) There is a maximum pressure (P_m) up to which only the smectic A phase exists, and (3) P_m is uniquely related to range of the nematic phase at atmospheric pressure.

Another important feature which appears to emerge from the careful study of the P-T diagrams of reentrant nematic systems reported by Kalkura et al.⁴² was that the major axis of the elliptically shaped A-N phase boundary appeared to have the same tilt as the linear N-I boundary. This point was however not investigated quantitatively. In order to ascertain if this is the case, experiments have been undertaken to map out accurately both T-X and P-T diagrams of a number of single component as well as binary systems exhibiting

reentrant behaviour. The results of these studies which are presented in Chapter V show dramatically that the coupling between nematic and smectic ordering manifests in the phase diagrams exhibited by the reentrant nematic systems.

17 PHASE DIAGRAMS INVOLVING A_d AND A_1 PHASES

The experimental studies discussed in Chapter IV show that the first order A_d - A_2 transition can terminate at a critical point which is probably of gas-liquid kind. It has also been shown by Ratna et al.⁴³ that under certain other circumstances an incommensurate smectic A phase (A_{IC}) can intervene between A_d and A_2 phases. The situation concerning A_d - A_1 transition has also attracted considerable theoretical and experimental interest. Recently Prost and Toner⁴⁴ have used a dislocation loop theory to predict some novel features concerning the terminus of the A_d - A_1 boundary. Only some of the phase diagrams predicted by theory have been observed experimentally so far. The theory of Prost and Toner predicts in the mean-field limit an A_d - A_1 critical point which in principle should be similar to A_d - A_2 critical point discussed earlier. However, the theory also predicts that in the presence of fluctuations A_d - A_1 first order boundary can terminate in a nematic island. They also predict that this nematic island should always be separated from another nematic (**main domain** nematic). So far, A_d - A_1 critical point has not been observed experimentally. However an island of cholesteric or nematic

existing at the terminus of A_d-A_I boundary has been observed.^{45,46} Although no detailed study of phase diagrams involving such an island has been carried out, Chapter VI describes the phase diagrams obtained by studying binary and ternary systems involving A_d-A_I phases. The topological features of some of these systems are strikingly similar to some of the phase diagrams predicted theoretically by Prost and Toner.

1.8 PRESSURE STUDIES ON THE NEMATIC-ISOTROPIC TRANSITION IN CYANO CYCLOHEXYL CYCLOHEXANE MATERIALS

An important consequence of the part played by the end chains of a molecule in the stability of the mesophases exhibited by thermotropic liquid crystals is the occurrence of the alternations in N-I transitions⁴⁷ and a number of other properties such as order parameter,^{48,49} entropy of transitions,⁵⁰ excess specific heat,⁵⁰ splay elastic constant,⁵¹ dT/dP (rate of variation of temperature of N-I transition with pressure), etc. as the homologous series is ascended (i.e., increasing the number of carbon atoms in the end chain). This behaviour referred to as the odd-even effect,' which arises due to enhancement or decrease in the molecular anisotropy and molecular order accompanying increasing n , is found to be exhibited by thermotropic liquid crystals of low^{52,53} as well as large molecular mass.⁵⁴ In Chapter VII we describe the pressure studies on N-I transitions of four successive members of alicyclic cyclohexyl cyclohexane ($n=2$

to 5) homologous series (CCH_n).^{55,56} It may be noted that these cyclohexane materials possess negative diamagnetic anisotropy and exhibit unusual phase behaviour in that they show increased smectic stability for the shortest tail member whereas the nematic stability is greater for the members n=7 onwards. These pressure studies clearly show the odd-even alternation of $(dT/dP)_{N-I}$ consistent with a similar behaviour observed earlier for several liquid crystal systems of low molecular mass as well as main-chain polyesters.

The results discussed in this thesis have been published (or submitted for publication) in the following papers :

- 1 Universality of the reentrant nematic-smectic C-smectic A and nematic-smectic A-smectic C multicritical points. (in collaboration with R.Shashidhar and B.R.Ratna) - Phys. Rev. A, Rapid Commn., 34, 2561 (1986)
- 2 Smectic A_d-smectic A₂ critical point. (in collaboration with R. Shashidhar, B.R.Ratna, S.Krishna Prasad and G. Heppke) - Phys. Rev. Lett., 59, 1209 (1987)
- 3 Coupling between nematic and smectic ordering in reentrant nematic systems. (in collaboration with R. Shashidhar and B.R. Ratna) - Mol. Cryst. Liq. Cryst., 133, 19 (1986)
- 4 No reentrant nematic below smectic A₁. (in collaboration

with R.Shashidhar and P.E.Cladis) - Mol. Cryst. Liq. Cryst. Lett., 1, 177 (1985).

- 5 Phase diagrams involving A_d and A_1 phases. (in collaboration with R. Shashidhar, B.R.Ratna, Ch. Bahr and G. Heppke) (to be submitted)
- 6 Pressure studies on the N-I transitions in cyclohexanes. (in collaboration with R. Shashidhar) (to be submitted).
- 7 A nematic, smectic A_d and smectic A_2 critical end point in a binary system. (in collaboration with R. Shashidhar and B.R. Ratna) (to be submitted)

REFERENCES

- 1 For detailed account of structure and physical properties see, S.Chandrasekhar, Liquid Crystals (Cambridge University Press, 1977); P.G.de Gennes, The Physics of Liquid Crystals (Clarendon Press, Oxford, 1974)
- 2 G. Friedel, Ann. Physique, 18, 273 (1922)
- 3 L.J.Yu and A. Saupe, Phys. Rev. Lett., **45**, 1000 (1980)
- 4 G.W.Gray and J.W.Goodby, Smectic Liquid Crystals - Textures and Structures (Leonard Hill, USA/Canada, Heyden & Son, 1984)
- 5 K.K.Kobayashi, Phys. Lett., **31A**, 125 (1970)
- 6 W.L.McMillan, Phys. Rev., **A4**, 1238 (1971)
- 7 P.G.de Gennes, Solid State Commun., 10, 753 (1972)
- 8 R.Schaetzing and J.D.Litster, Advances in Liquid Crystals, Vol. 4, Ed. G.H.Brown (Academic Press, 1979), p. 147.
- 9 S.Chandrasekhar, B.K.Sadashiva and K.A.Suresh, Pramana, **9**, 471 (1977)
- 10 S.Chandrasekhar, Advances in Liquid Crystals, Vol. 5, Ed. G.H. Brown (Academic Press, 1982), p. 47
- 11 P.E.Cladis, Phys. Rev. Lett., 35, 48 (1975)
- 12 A.C.Anderson, W.Rease and J.C.Wheatley, Phys. Rev., 130, 1644 (1963)

- 13 G. Riblet and K.Winzar, Solid State Commun., 9, 1663 (1971)
- 14 G. Pelzl, S. Diele, I.Latif, W. Weissflog and D. Demus, Cryst. Res. Technol., 17, K78 (1982); S. Diele, G. Pelzl, I.Latif and D. Demus, Mol. Cryst. Liq. Cryst., 92, 27 (1983)
- 15 G.Sigaud, F. Hardouin, M.F.Achard and H. Gasparoux, J. de Phys., 40, C3-356 (1979)
- 16 a F.Hardouin, A.M.Levelut, J.J.Benattar and G.Sigaud, Solid State Commun., 33, 337 (1980)
b J. Prost, Advances in Physics, 33, 1 (1984)
- 17 J. H. Chen and T.C.Lubensky, Phys. Rev., **A14**, 1202 (1976)
- 18 K.C.Chu and W.L.McMillan, Phys. Rev., A15, 1181 (1977)
- 19 D.Johnson, D.Allender, R. De Hoff, C.Maze, E. Oppenheim and R.Reynolds, Phys. Rev., **B16**, 470 (1977)
- 20 C.R.Safinya, R.J.Birgeneau, J.D.Litster and M.E.Neubert, Phys. Rev. Lett., 47, 668 (1981)
- 21 C.R.Safinya, L.J.Martinez-Miranda, M. Kaplan, J.D.Litster and R.J.Birgeneau, Phys. Rev. Lett., 50, 56 (1983)
- 22 R. De Hoff, R. Biggers, D.Brisbin, R. Mahmood, C.Gooden and D.L.Johnson, Phys. Rev. Lett., 47, 664 (1981)
- 23 R. De Hoff, R. Biggers, D. Brisbin and D.L.Johnson, Phys. Rev., A25, 472 (1982)
- 24 S.Witanachi, J. Huang & J.T.Ho, Phys. Rev., A28, 434 (1983).

- 25 D.Brisbin, D.L.Johnson, H.Fellner and M.E.Neubert, Phys. Rev. Lett., 50, 178 (1983)
- 26 R.Shashidhar, B.R.Ratna and S.Krishna Prasad, Phys. Rev. Lett., 53, 2141 (1984)
- 27 R.Shashidhar, A.N.Kalkura and S.Chandrasekhar, Mol. Cryst. Liq. Cryst. Lett., 82, 311 (1982)
- 28 R.Shashidhar, S.Chandrasekhar and S.Krishna Prasad, Mol. Cryst. Liq. Cryst., 103, 137 (1983)
- 29 L.P.Kadanoff, in Critical Phenomena, Enrico Fermi Course LI, Ed. M.S.Green (Academic, New York, 1971), p. 100.
- 30 J. Prost, J. de Phys., 40, 581 (1979)
- 31 J. Prost, in "Liquid Crystals of One- and Two-Dimensional Order", Ed. W. Helfrich and G. Heppke (Springer-Verlag, Berlin, 1980), p. 125.
- 32 J. Prost, in "Symmetries and Broken Symmetries in Condensed Matter Physics", Ed. N. Boccara (IDSET, Paris, 1981), p. 159
- 33 J. Prost and P. Barois, J. Chirn. Phys., 80, 65 (1983)
- 34 P. Barois, J. Prost and T.C.Lubensky, J. de Phys., 46, 391 (1985)
- 35 F. Hardouin, M.F.Achard, C. Destrade and Nguyen Huu Tinh, J. de Phys., 45, 765 (1984)
- 36 F.Hardouin, M.F.Achard, Nguyen Huu Tinh and G.Sigaud, J. de Phys. Lett., **46**, 123 (1985)

- 37 S.Krishna Prasad, R.Shashidhar, B.R.Ratna, B.K.Sadashiva, G.Heppke and S.Pfeiffer, *Liquid Crystals*, 2, 111 (1987)
- 38 P.E.Cladis, R.K.Bogardus and W.B.Daniels and G.N.Taylor, *Phys. Rev. Lett.*, **39**, 720 (1977)
- 39 P.E.Cladis, R.K.Bogardus and D.Aadsen, *Phys. Rev.*, **A18**, 2292 (1978)
- 40 N.V.Madhusudana, B.K.Sadashiva and K.P.L.Moodithaya, *Curr. Sci.*, 48, 613 (1979)
- 41 F.Hardouin, G.Sigaud, M.F.Achard and H.Gasparoux, *Phys. Lett.*, **71A**, 347 (1979)
- 42 A.N.Kalkura, R.Shashidhar and M.Subramanya Raj Urs, *J. de Phys.*, 44, 51 (1983); A.N.Kalkura, *High Pressure Optical Studies of Liquid Crystals*, Ph.D. Thesis, University of Mysore, 1982
- 43 B.R.Ratna, R.Shashidhar and V.N.Raja, *Phys. Rev. Lett.*, 55, 1476 (1985)
- 44 J. Prost and J.Toner, *Phys. Rev. A* (in press).
- 45 P.E.Cladis and H. Brand, *Phys. Rev. Lett.*, 52, 2261 (1984).
- 46 F.Hardouin, M.F.Achard, Nguyen Huu Tinh and G. Sigaud, *Mol. Cryst. Liq. Cryst. Lett.*, 3, 7 (1986)
- 47 C.Weygand and R.Gabler, *Z. Phys. Chem.*, **48B**, 148 (1941); See also G.W.Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic, 1962)

- 48 H.Lippmann and K.H.Weber, Ann. Physik,**20**, 265 (1957)
- 49 A. Pines, D.J.Ruben and S.Allison, Phys. Rev.Lett., 33, 1002 (1974)
- 50 H.Arnold, Z. Phys. Chem. (Leipzig), 226, 146 (1964)
- 51 H.Gruler, Z.Naturforsch., **28a**, 474 (1973)
- 52 V.M.Feyz and E.Kuss, Ber.Bunsenges, Phys. Chem., 78, 834 (1974)
- 53 R.Shashidhar and G.Venkatesh, J. de Phys., 40, C3-396 (1979)
- 54 V.N.Raja, R.Shashidhar, S.Chandrasekhar, A.Blumstein, R.B.Blumstein and S.Kumar, Presented at the International Conference on Liquid Crystal Polymers, Bordeaux, July 1987 - Mol. Cryst. Liq. Cryst. (in press)
- 55 R.Eidenschink, D. Erdmann, J. Krause and L. Pohl, Angew.Chem., **89**, 103 (1977)
- 56 R.Eidenschink, D.Erdmann, J.Krause and L. Pohl, Angew. Chem. **90**, 133 (1978).