HIGH PRESSURE STUDIES OF LIQUID CRYSTALS

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BY

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CONTENTS

CHAPTER – 1

INTRODUCTION

Liquid Crystals are intermediate states of matter which possess long range ordering of the molecules (resulting in properties like optical, electric and magnetic anisotropy which are usually characteristic of solids) and also have the ability to flow and to form drops (as in the case of liquids). Liquid crystalline phases or mesophases may be produced in two different ways. Those formed by a change of temperature of the compound are called thermotropic liquid crystals while those formed by the effect of solvents are called lyotropic liquid crystals. We shall confine our attention here to the former type of mesomorphism only.

Thermotropic mesomorphism was first noticed by Reinitzer (1) at the end of the last century and since then several thousands of organic compounds have been found to exhibit this property. (2) A distinctive feature common to all these compounds is the geometrical anisotropy of the molecule. Till recently it was believed that only elongated (or rod like) molecules show thermotropic mesophases, but in 1977 Chandrashekhar et al (3) showed that pure compounds consisting of relatively simple disc like or plate like molecules also show mesophases.

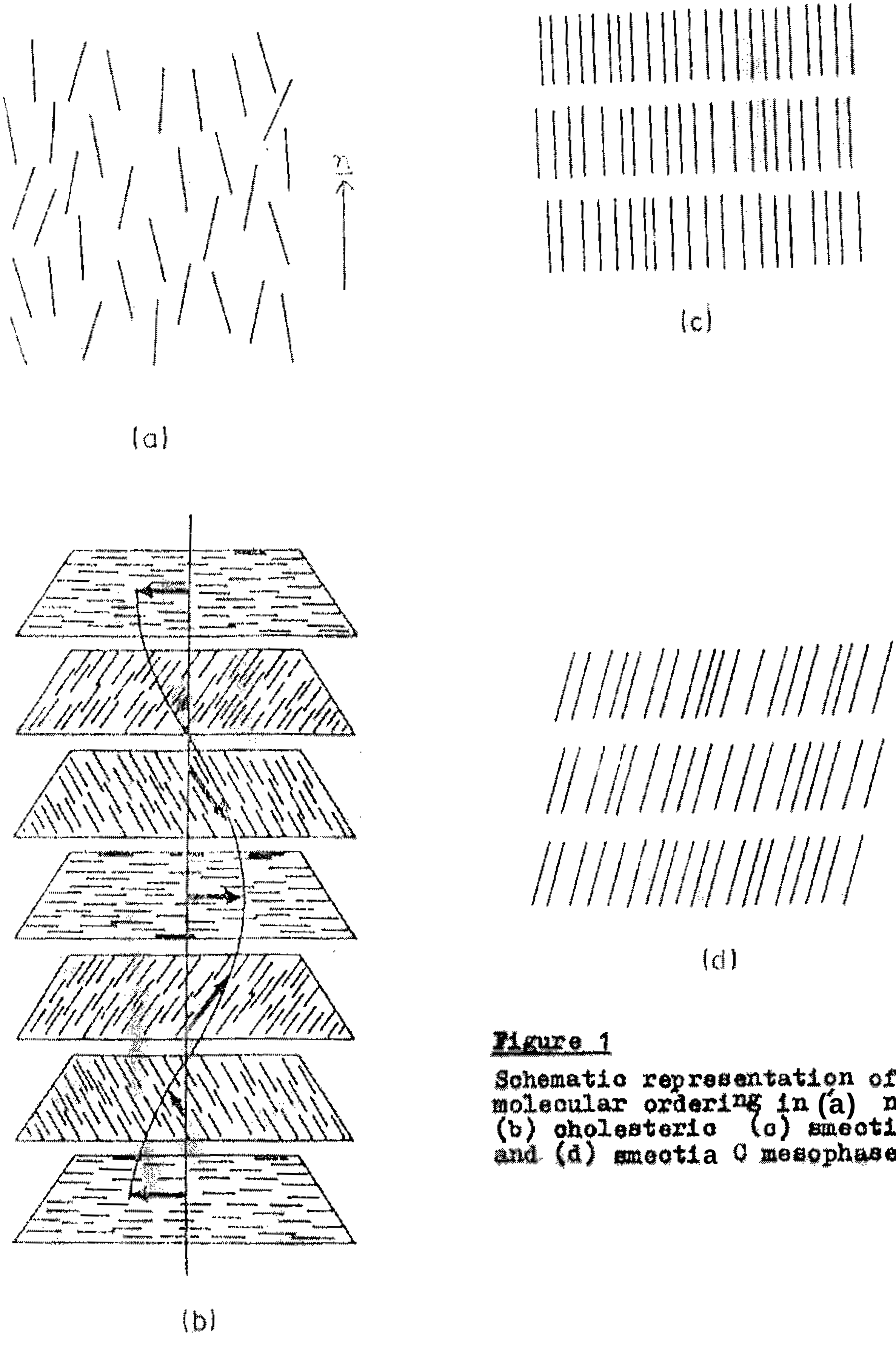

Figure 1

Schematic representation of molecular ordering in (a) nematic (b) cholesteric (c) smectic A and (d) smectic C mesophases.

Based on the molecular arrangements, thermotropic liquid crystals of rod like molecules are classified into three types, (4) nematics, cholesterics and smectics.

Nematics have a molecular arrangement as shown in fig 1(a). Here the molecules have a long range orientational order without any translational or positional ordering. On an average, the molecular axes tend to orient along a common axis called the director usually represented by n.

Cholesterics are also considered to be of the nematic type except that the director in this case twists about an axis perpendicular to it, resulting in a helical structure as shown in fig 1(b).

Smectics have stratified structures, the molecules being arranged in well defined parallel layers. They are classified into several types, smectic A, smectic B, smectic C, etc., depending on the molecular arrangement in each layer. For example, in Smectic A the molecules are normal to the layers, the molecular centres being irregularly spaced with each layer as in fig 1(c). Smectic B is similar to Smectic A but there is hexagonal close packed ordering of the molecules in each layer. Smectic C is a tilted form of smectic A as shown in fig 1(d). Several other smectic modifications,(5) are known, but their structures are not unambiguously determined. Attempts are being made to classify these higher order smectics on the basis of X-ray and neutron diffraction data.

The molecular arrangement in the recently discovered disc like mesogens is given in fig 2. The molecules in this case are stacked one above the other to form vertical columns, hence these mesophases are often called columnar phases.

The present thesis is concerned with an experimental study of the behaviour of thermotropic liquid crystals under high pressure.

The first high pressure studies on the mesophase transitions were carried out as early as 1899 by Hulett, (6) just a decade after the discovery of liquid crystals. He studied three compounds para azoxyanisole (PAA), para azoxyphenetole (PAP) and cholesteryl benzoate each up to about 300 bars by optical transmission technique. His phase diagram for PAA – reproduced in fig – 3 – is in excellent agreement even with the most recent determinations. Following Hulett, there were only two more pressure studies in the next forty years one by Puschin and Grebenschtschikow (7) in 1926 and the

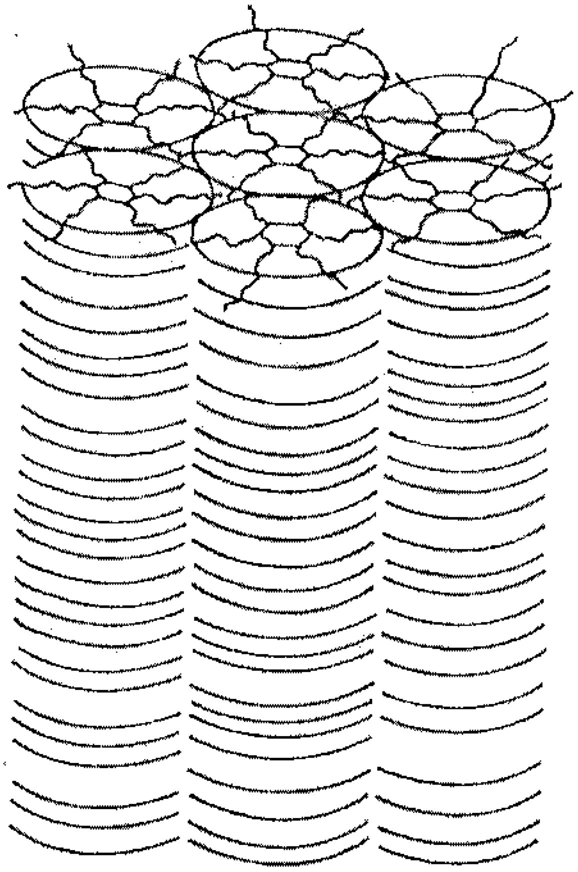

Figure 2: Schematic representation of the structure of the mesophase in disc like mesogens.

other by Robberecht (8) in 1938. But since 1970, there has been a considerable growth of activity in this field wherein a number of interesting and new phenomena like pressure induced mesomorphism (9), suppression of mesophases (10), change in the character of a transition from a first order to second order, (10-11) (tricritical behaviour).

Or from monotropic to enantiotropic (12), etc., which are of fundamental physical importance involving significant structural and thermodynamic implications, have been discovered. The various techniques used and the important results have been reviewed in a recent article on 'High pressure studies of liquid crystals' by Chandrashekhar and Shashidhar (13). However, much remains to be explored – for example, systematic investigations of the behaviour of the successive members of a homologous series of compounds are still rather scanty. The present work was undertaken with a view to investigating some of these problems.

The study of liquid crystals under pressure presents problems that are not normally encountered in the study of solid state. For example the sample is in the fluid state and needs a container which does not react with it and at the same time transmits pressure, the sample must be isolated from the pressure transmitting medium to prevent its contamination, the liquid crystalline transitions involve very low heats of transition and therefore somewhat difficult to detect, and confirmation of the new pressure induced phases requiring an optical observation. Bearing in mind all these aspects we have designed and fabricated a 200 ton hydraulic press incorporating a piston cylinder device suitable for the study of liquid crystals under pressure. In chapter II, we describe the details of the design, construction, working and calibration of the press. This high pressure assembly offers facilities to conduct a variety of experiments and has the following salient features –

i) Generation of pressures up to 20 kilobars over an area of 1".

ii) Use of an end load pressure to keep the pressure plate always under compression to prevent its bursting during the experiment.

iii) Use of a cooling assembly to keep the pressure plate always at room temperature while the sample cell assembly is heated to higher temperatures.

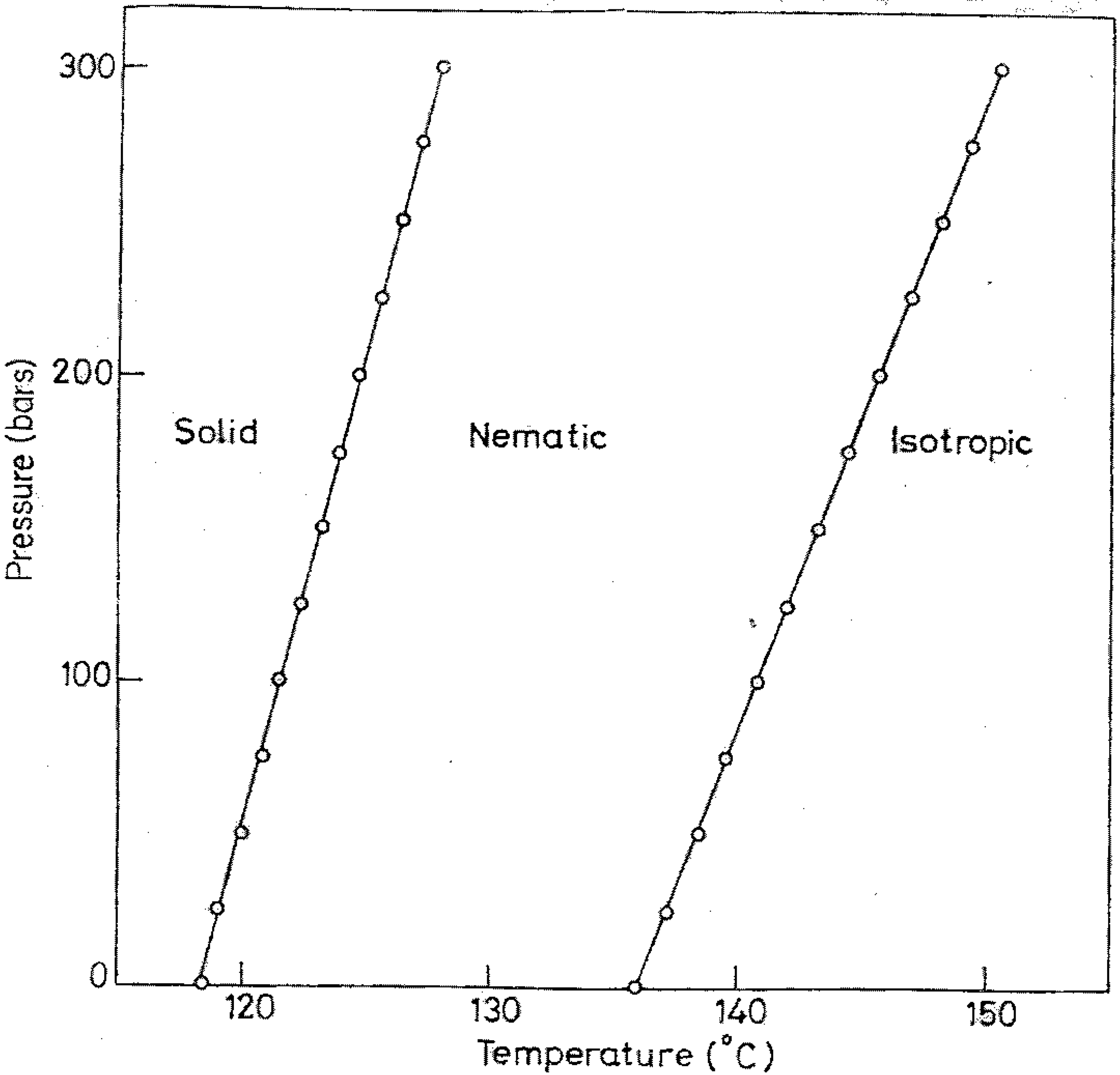

Figure 3

Phase diagram of PAA (after Hulett(6)).

iv) Fine controlling of pressures using relief valves even under static conditions.

v) Facilities to carry out experiments by Differential Thermal Analysis (DTA) technique.

vi) Facilities to carry out optical and volumetric studies.

The linearity of the pressure measurements was checked by determining the resistance variation of a manganin gauge with pressure using a Wayne Kerr bridge (model B642). The true pressures on the sample were determined by obtaining the phase diagram of freshly distilled CCl_4 and using it as a secondary standard. The accuracy of the absolute pressure measurements is reckoned to be of the order of ±2% over the entire range of our study.

Differential Thermal Analysis is a sensitive probe to detect the liquid crystalline transitions under pressure. The first accurate DTA experiments 'were those of Chandrashekhar et al (9) who observed for the first time the phenomenon of pressure induced mesomorphism using a new type of coaxial DTA cell designed by Reshamwala and Shashidhar (14). Subsequently they also confirmed a tricritical point in a smectic A – cholesteric transition. More recently other types of DTA cells have been designed by Klement and Cohen (15) who have studied PAA up to 2 kbar, and by Spratte and Schneider (16) who have obtained the phase diagrams of a number of compounds including PAA and PAP. Almost all the data presented in this thesis [except for those on the smectic C – smectic A (C-A) transition in chapter V] were obtained with a coaxial DTA cell essentially similar to that designed by Reshamwala and Shashidhar (14), but with appropriate modifications in dimensions to suit the 200 ton hydraulic press used in the experiments. In the second part of chapter II, we present the details of the design, working and calibration of this new coaxial DTA cell. The important features of this cell are:

i) Use of a Teflon sample cell which does not react with the sample,

ii) Isolation of the sample from the pressure transmitting medium by the Teflon cell and at the same time transmitting pressure to it,

iii) Use of talc as the pressure transmitting medium which is known to be hydrostatic up to about 90%,

iv) Immersion of the thermocouple junction well inside the sample facilitating the detection of even weak first order transitions,

v) Reproduction of transition temperatures to accuracy of ±1.5°C.

Using this new high pressure set up and the DTA cell, we have carried out systematic investigations of the Behaviour of liquid crystals under pressure.

In Chapter III, we present studies on the first six members of the 4, 4'–di-n-alkoxyazoxybenzene series. Para Asoxyanisole (PAA) and its higher homologues of this series are perhaps the most widely studied of all the liquid crystalline materials. A variety of techniques like calorimetry (17), dielectric studies (18), magnetic susceptibility (19), etc., have been employed to investigate the successive homologues of this series. A number of physical properties like order parameter'(20-21) the transition entropy (17), the nematic-isotropic transition (22), the excess specific heat, (17) show' a pronounced alternation as the homologous series is ascended, i.e., as the number of carbon atoms in the alkoxy end chain is increased. This is referred to as 'odd even effect'. But there are no systematic pressure studied on these compounds. The results of our investigation show that the dT/dP for the nematic-isotropic transition also alternates. In addition, we have observed in the case of the fifth homologue, a new pressure induced phase and suppression of an already existing phase and in the case of the sixth homologue a change of the character of transition from monotropic to enantiotropic.

In chapter IV, we describe the results of four compounds, the fifth to the eighth members of the series 4'-n-alkyl-4-cyanobiphenyls (nCB), as a function of pressure. These compounds are technologically very important because of their uses in electro-optical display devices. On account of this they have been studied very thoroughly. Birefringence (23), dielectric constants (24) and X-ray (25,26) studies have been reported on the successive members of this series. From the pressure studies we have observed again the alternation of the dT/dP for the nematic-isotropic transition whereas the dT/dP for the solid-nematic (or smectic) transition is roughly the same for all of them. Further the smectic A-nematic transition in the case of the eighth member, viz., 4'n-octyl-4-cyanobiphenyl (8CB) exhibits tricritical behaviour.

In chapter V, we discuss the results of the pressure studies on three smectogenic compounds. The majority of high pressure experiments on liquid crystals are devoted to the study of nematics, but with the recent discovery of the 're-entrant phenomenon', there have been studies on compounds exhibiting smectic A phases. Cladis et al (27-28) observed for the first time that 4'-n'octyloxy-4-cyanobiphenyl (8 OCB) exhibits in the pressure range of 1.6 to 1.8 kbars, the following sequence of transitions on cooling,

Isotropic → nematic → smectic A → nematic → solid

The lower temperature nematic is called the 're-entrant nematic' in analogy with similar phenomena observed in superconductors and He^3. The phase diagram of 8 OCB – typical of all compounds exhibiting re-entrant phenomenon – is given in fig 4. Recently the re-entrant phenomenon has been observed in pure compounds even at atmospheric pressures independently by Madhusudana et al (29) and by Hardouin' et al (30). The characteristic feature of all compounds exhibiting the re-entrance is that they are composed of molecules with the strongly polar $C \equiv N$ end group. The polarity of the molecules results in an antiparallel near neighbour correlation which in turn gives rise to a bilayer arrangement. Pressure studies were undertaken on another strongly polar compound, viz., 4-nitrophenyl-4'-n-octylooxybenzoate (NPOOB) to see whether it exhibits re-entrance. However, in the pressure range of our study there is no indication of any such behaviour. But this compound exhibits a pressure induced mesophase beyond a pressure of 2.3 kbar.

Chaper V also includes the results on to other compounds, viz., di-ethyl-p-azoxybenzoate (EPAB) and trans-1, 40cyclohexane-di-n-octyloxybenzoate (TCOB).TCOB exhibits

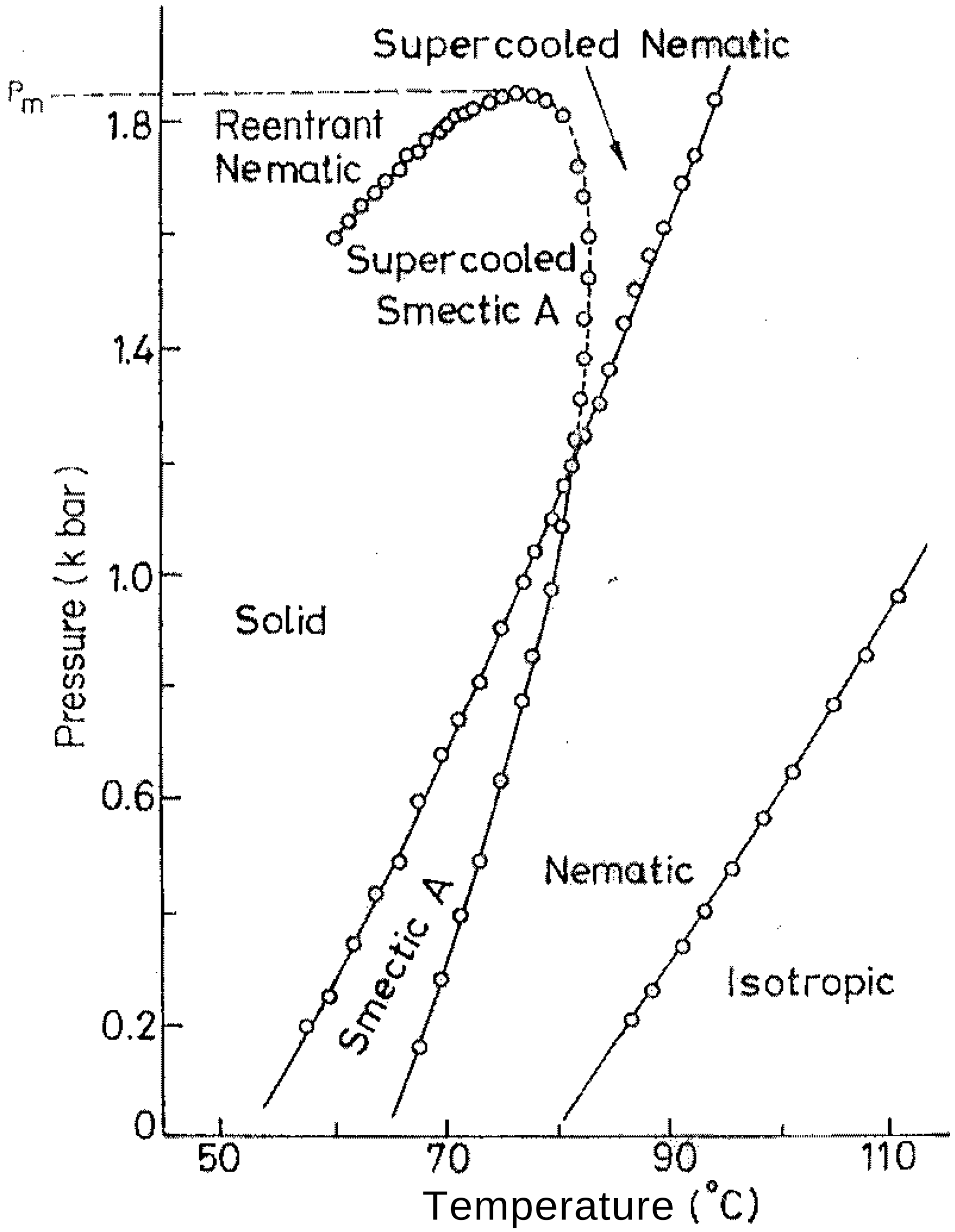

Figure 4: Phase diagram of 8 OCB (after Cladis et al[27])

two solid, two smectic B, smectic C and smectic A phases. All the transitions except the C-A transition were studied by the DTA technique. However, DTA fails to detect the continuous transitions, like the C-A transition, which involve no latent heat. We have obtained the phase diagram for this transition using a diamond anvil cell (31) and the optical transmission technique. The sample was sandwiched between two diamond anvils in an aluminum gasket and the pressure was transmitted to it through the anvils by a spring loaded lever arm assembly with graduated screw head. The pressures were measured by an indirect method. First an 'in situ' optical determination of the transition temperature of the sample in the cell was made and knowing the accurate P-T diagram of the sample the pressure was directly read out. At any fixed pressure the temperature was varied slowly and the intensity of the laser beam transmitted by the sample was monitored by a photocell. At the transition there was an abrupt change in intensity. This way the pressure and temperatures were measured to an accuracy of i15 bars and ±0.2°C respectively.

The pressure studies show that in TCOB, the smectic C phase gets bounded beyond a pressure of about 1.5 kbar. Also the range of the smectic B and smectic A phases in TCOB and that of the smectic A phase in EPAB increase with increase in pressure.

In chapter VI we present the first high pressure studies on the recently discovered disc-like mesogens. Four compounds belonging to benzene-hexa-n-alkanoate series the sixth to the ninth – have been investigated as a function of pressure. The results show that these compounds also exhibit phenomena similar to those observed in rod like systems – for example, pressure induced mesomorphism, suppression of the mesophases, change in the character of the transition from monotropic to enantiotropic, etc. the sixth homologue which is non-mesomorphic at atmospheric pressure exhibits a pressure induced phase while the seventh and eighth members lose their mesomorphism at higher pressures. The ninth member presents a very interesting phase diagram wherein the monotropic mesophase first becomes enantiotropic with the application of very small pressures and then with further increase of pressure the mesomorphism disappears.

We have already pointed out that though the DTA technique is useful in detecting weak first order transitions, it is not suitable for studying second order (continuous) transition of C-A type. In such cases it is more convenient to employ the optical transmission technique which has been used successfully by a number of investigators recently. For example, Keyes et al (11) used it to observe, for the first time, a tricritical point in a smectic A – cholesteric transition. More recently Cladis et al (27) employing the same type of optical cell studied the interesting phenomenon of re-entrant behaviour. As mentioned earlier, we used a diamond anvil cell and optical transmission technique to detect and track the continuous C-A transition in TCOB as a function of pressure. However, this cell has a drawback in that it does not give the pressure acting on the sample directly. Hence we have designed a new optical cell assembly which could be incorporated in the piston cylinder device of the 200 ton hydraulic press.

In chapter VII, we describe the details of the design, working and calibration of the new optical cell. Briefly the cell assembly consists of a Teflon body with sapphire windows. The sample is sandwiched between two sapphire rods in an aluminum gasket. The phase transitions are detected by monitoring the intensity of the light transmitted by the sample. Besides, this cell can be used to study various other properties like the variation of the birefringence and hence the order parameter, light scattering, variation of the pitch of a cholesteric as functions of pressure. The cell also facilities the microscopic observation of a thin layer of the liquid crystal sample under pressure so that the pressure induced phases can be identified from the optical textures exhibited by them. Experiments are in progress in this direction with the new optical cell.

Some of the results discussed in this thesis have been published in the following papers:

1. High pressure studies on 4 –n-alkyl-4-cyanobiphenyls,(in collaboration with R. Shashidhar). Presented at the Seventh International Liquid Crystals Conference, Bordeaux, France, 1978. J. de Physique, 40, C3-396 (1979)
2. Disc like mesogens (in collaboration with S. Chandrasekhar, B.K. Sadashiva, K.A.Suresh, N.V.Madhusudana, S.Kumar and R.Shashidhar). Presented at the

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4. High pressure studies on some smectic liquid crystals (in collaboration with R.Shashidhar and A.N.Kalkura). Presented at the Eighth International Liquid Crystals Conference, Kyoto, Japan (1980)
5. On the fabrication of a 200 ton hydraulic press (in collaboration with R.Shashidhar and R.V.Ramani) (to be submitted to High Temperatures – High Pressures)

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