CHAPTER 1

INTRODUCTION

"Liquid crystals are beautiful and mysterious" : P.G.de GENNES

Though most of the solids melt to form isotropic liquids, there are certain organic chemicals which do not have a single transition from solid to liquid, but pass through a series of transitions involving new phases. The physical properties of these phases are intermediate between crystalline solid and isotropic liquid. The first such phase (the so-called cholesteric phase) was discovered over a hundred years ago by Reinitzer [1,2] and Lehmann [3-5]. Since these substances flow like ordinary liquids, but exhibit anisotropic properties like crystalline solids, Lehmann in 1890 gave the name "Liquid Crystals" to these compounds. Friedel [6,7] suggested the term "mesomorphic phase" or "mesophase" to the liquid crystalline state of matter. Thousands of organic chemicals are known to form mesophases [8,9]. According to Brown [10] about 5% of the known organic compounds have one or more liquid crystal phase. Few organo-metallic [10,11] and some inorganic chemicals [12] show liquid crystalline properties as well.

The molecules of the compounds showing mesophases are non-spherical (generally rod like or disc like) in shape and as such have at least one non-degenerate principal axis. In the crystalline state not only the centre of mass of the molecules form a three - dimensional lattice, but the principal axes of the molecules also tend to be parallel. These substances, when heated, lose part or whole of their 3-dimensional positional order and the orientational order of the axes at different temperatures, giving rise to various different forms of liquid crystalline phases. These changes of state are generally reversible with temperature, but in some cases mesophases are produced only on cooling (monotropic transition). There are many excellent books and review articles on liquid crystals which give details regarding molecular structure and physical properties of the compounds exhibiting mesophases, of which I have listed only a few [8,9,11,13-21]. A beautiful article on hundred years of thermotropic liquid crystals has been compiled by Demus [22]. Recent developments in the field of liquid crystal research and application are also available [23,24].

1. Classification of Liquid Crystals:

Broadly speaking there are two types of liquid crystalline mesophases, viz, Lyotropic and Thermotropic.

1.1a Lyotropic:

Liquid crystalline phase can exist intermediate between solid state and an isotropic solution. The amount of solvent is then the most important variable. The mesophases thus formed are called lyotropic liquid crystals [25-29]. Solutions of soap and water are prototypical examples of lyotropics and their mesomorphic phases appear as a function of either concentration or temperature. Lyotropic liquid crystals play an important role in living systems [30]. However, no technical applications of lyotropic system for display devices are known as yet [31]. Since this dissertation is only concerned with thermotropic liquid crystals, I shall not discuss this type of mesophases further.

1.1b Thermotropic mesophase:

Thermotropic liquid crystals are those where transitions in different mesophases occur due to the change of temperature. Friedel [32] from his detailed optical and x-ray studies classified the thermotropic liquid crystals into three types: nematic, cholesteric and smectic.

1.2 Nematic mesophase:

The nematic mesophase is a fluid where the molecules have long range orientational order. The word nematic has come from the Greek word νη̄μα which means thread. When a thin layer of nematic sample is observed between crossed polarizers under microscope, a characteristic pattern known as texture, which is usually thread like is seen. The nematic liquid crystals do not possess long range translational order, thus showing fluid character of nematic phase, but they have long range orientational order of the long axis of the molecules. Although the centre of mass of the molecules are distributed at random as an ordinary liquid, the molecules still have a tendency to align themselves in a preferred direction, known as the "director" denoted by $\overset{\leftrightarrow}{n}$. Thus this phase is uniaxial with respect to all physical properties. The axis of uniaxial symmetry has no polarity i.e. $\overset{\leftrightarrow}{n}$ and $-\overset{\leftrightarrow}{n}$ are equivalent. According to Maier-Saupe theory [33] the anisotropy of the molecular polarizability is responsible for the occurence of the liquid crystalline phase. Recent x-ray studies [34,35] indicate that in certain nematic liquid crystals a large number of molecules are arranged in groups [36]; in each group molecules are parallel to each other, and the centre of molecules are lying in a well defined plane. These so-called cybotactic groups may be thought of as smectic fluctuation in the nematic phase.

1.2a Cholesteric or chiral nematic phase:

Cholesteric liquid crystals are formed by optically active molecules. Many cholesterol esters form these type of liquid crystals. Actually cholesteric mesophase is nothing but a nematic type liquid crystal except that it is composed of optically active molecules. In addition to the long range structure there exists a spatial variation of the director leading to the helical structure [37]. The helical structure can be described by an variable intrinsic director,

$$n_x = \cos(q_o z + c)$$

$$n_y = \sin(q_o z + c)$$

$$n_z = 0$$

c being a constant.

The sign of q_o distinguishes between left- handed (leavo type) and right-handed (dextro type) chiral nematics. The longitudinal distance in which a full rotation of director is completed is known as pitch L of the helix, normally defined as

$$L = 2\pi/|q_0|$$

However, since $\overset{\leftrightarrow}{n}$ and $-\overset{\leftrightarrow}{n}$ are equivalent,

$$L = \pi/|q_0|$$

when $q_0 = 0$ i.e. L is infinite leads to the nematic phase.

No liquid crystal sample has been found so far which posseses both nematic and cholesteric mesophases. Also, application of external magnetic or electric field may change a cholesteric phase to nematic one. On the other hand adding a small amount of cholesteric compound to a nematic substance causes it to exhibit cholesteric phase. Hence, cholesteric phase is a variation of nematic phase and may be called chiral nematic phase [38-40].

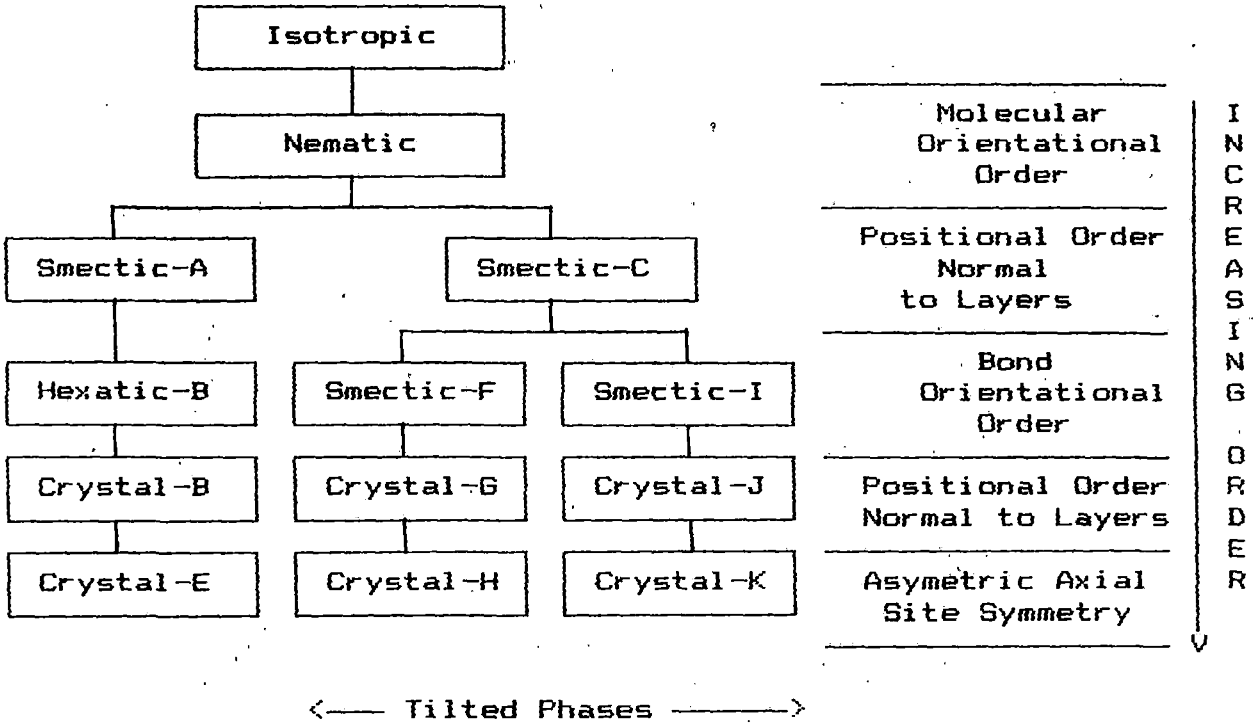
1.3 Smectic mesophase:

The smectic mesophases are generally more viscous than nematic. In addition to the long range orientational order the molecules are arranged in equidistant planes. The long axis of the molecules are parallel to the preferred direction $\overset{\leftrightarrow}{n}$ which may be normal to the planes or tilted by a certain angle. In some smectic phases, the molecules are mobile in two directions (in the layer plane) and can rotate about its long axis. The interlayer attractions are weaker than the lateral forces between the molecules and hence the layers can slide over one another thus showing fluid behaviour. At least eight thermotropic smectic phases have been identified [41-50]. The smectic phases have been designated as follows [51].

$$S_A, S_B, S_C, S_D, S_E, S_F, S_G, S_H, ...$$

Since, in the present work I am concerned with nematic and smectic A phases only, I will not go into details of other smectic phases. However, I am giving classification of smectics according to Pershan [19] in figure 1.1.

Figure 1.1 Classification of smectics according to Pershan [19].



1.3a Smectic A phase:

In smectic A phase the long axis of the molecules lie almost parallel to one another within the smectic layers and the director is normal to the layer plane. The layers can slide over one another. The molecules are generally free to rotate about their long axis and the distribution of the molecular centres in the layer plane is random [44,52,53]. Due to the infinite fold rotational symmetry about an axis parallel to the direction normal to the layer, smectic A phase at thermal equlibrium are uniaxial [54]. Recent works [55-61] have revealed that smectic A phase can be subdivided into several distinct phases such as monolayer Smectic A_1, bilayer Smectic A_2, partially bilayer Smectic A_d, and smectic antiphase Smectic $\tilde{A}$. To have more information regarding this polymorphism in smectic A some recent publication may be consulted [62-70].

1.4 New liquid crystalline phases.

1.4a Discotic phases:

In addition to the liquid crystalline phases discussed, recently disc-shaped molecules have been synthesized that exhibit a new class of columnar liquid crystalline phases [71] in which the molecules are stacked in parallel columns, these columns forming a two dimensional array. Previously, very similar disc-like mesogens had been identified in petrolium and coal tar [72,73]. In recent years significant amount of research have been performed with disc like molecules [74-78].

1.4b Re-entrant phase:

One of the most interesting phenomena exhibited by liquid crystals is the formation of "re-entrant phase", analogous to similar phases observed in superconductors and ^{3}He. In 1975 the re-entrant phase sequence in liquid crystals was discovered by Cladis et al [79]. In certain terminal polar compounds such as octyloxy cyano biphenyl (8OCB) this behavior is readily induced either by the application of elevated pressure or by making appropriate binary mixtures with second materials such as hexyloxy cyano biphenyl (6OCB). Since its discovery, the re-entrant nematic phase has been studied extensively. This phase has been observed in mixtures [79-80] as well as in single compounds at high pressure [81-82] or at atmospheric pressure [83]. The re-entrance of liquid crystalline phases is not restricted to the binary systems of terminal polar compounds only but has been observed for terminal non polar compounds as well [84-87]. Re-entrant smectic phases have also been reported in terminal polar compounds [88]. In binary mixtures of terminal non polar compounds the phase sequence S_A- S_C- S_A has been detected [89-90]. The re-entrant nematic phase has been observed in some pure compounds at atmospheric pressure [83,91-97]. A multiple re-entrant polymorphism have also been found in a pure substance [98].

The mechanism of the formation of the nematic phase at lower temperature has been explained by Cladis [99-101]. A more complete theoretical discussion by taking attractive forces and hard core repulsions by Longa and de Jeu [102], showed that there can exist a lower temperature nematic phase. Based on the molecular point of view, S. Chandrasekhar [103] has discussed qualitatively the re-entrantrant phenomenon. Luckhurst and Timmi [104] have developed a molecular theory for re-entrant nematic and smectic A mesophases by extending McMillan's treatment of the smectic A phase [105].

1.4c The injected (or induced) smectic phase:

One of the fascinating features of binary liquid crystal mixtures is the formation of so-called injected (or induced) smectic phases from components which show only nematic phases in their pure states [106,107]. The formation of injected smectic phase is accompanied by a marked deviation of the nematic-isotropic transition temperature from a linear dependence on composition. Induced smectic phases are often formed in binary mixtures of one compound having a strong terminal polar group and another compound having non polar terminal group. [108-123]. Evidently, dipole - induced dipole interactions play a major part in this phase stabilization. There is some evidence of charge transfer complex being formed with polar molecules acting as acceptors [108,118,124]. Recently, however, injected smectic phase has been observed in mixtures of other type of molecules [125-127]. Mixtures of two cyano compounds have been found to induce smectic C phase [125,126]. A quantitative theory of injected smectic phase is difficult since it would require the inclusion of position dependent attractive and repulsive interactions for both the components. Wagner [128] has tried with limited success to explain the phase diagram of mixtures showing injected smectic phase using McMillan's [105] theory for smectics. He however could not reproduce the nematic-isotropic phase boundary. A molecular model of the induced smectic phase has also been discussed by de Jeu et al [129].

1.5 Objective and scope of this work:

Cyano compounds and their mixtures are widely used in commercial devices. The cyano biphenyls are quite stable, easily available and have rather large birefringence and other anisotropic properties, and hence are ideal components for electro-optical display devices. To have a liquid crystal at room temperature with desired properties for a display device, often two or more pure compounds are mixed. The physical properties of such mixtures can not be interpolated from the properties of the pure components, notable examples being formation of injected (or induced) smectic phase in a mixture of pure nematogens, and exhibition of re-entrant nematic phase in a mixture of liquid crystal chemicals which do not show such phase in their pure form. The presence of induced smectic phase in the operational temperature range of the display device must be avoided. However, its presence at a lower temperature is advantageous since it decreases the bend to splay elastic constant ratio thus increasing the sharpness of the electroptical display device. Hence, measurement of physical properties of cyano compounds and their mixtures is very important from the view point of selection of proper liquid crystal materials for display devices.

I, therefore, undertook to study a few pure cyano biphenyls and several mixtures containing cyano biphenyl by small angle x-ray diffraction technique, for determining the order parameters and layer thickness or apparent molecular length in their respective mesophases. I also determined the refractive indices and density of most of these mixtures for which no such data was available before. I have extensively studied two mixtures, showing injected smectic phase, over their entire composition range. I have also fitted the experimental order parameter values in the smectic phase with those calculated from McMillan's theory by varying α and δ parameters in the potential. I have been able to successfully explain the variation of the layer thickness with composition for these mixtures. No x-ray diffraction studies on aligned samples of these mixtures showing either re-entrant nematic phase or injected smectic phase is available in the literature. Such study is essential for the determination of orientational order parameters. Previously reported but unexplained anomalous entropy change in one of the mixtures has been explained successfully. I have also studied mixtures (6OCB/8OCB) showing re entrant nematic phase and have shown that even in the mixture of 6OCB/8OCB which has no smectic phase, x-ray diffraction photographs indicate strongly the presence of smectic fluctuations.

X-ray diffraction data from monodomain samples of alkoxy cyanobiphenyl (n = 9,10,11,12) in mesophase have been analysed to determine the order parameters and layer thickness. Powder photographs from nOCB (n = 9,10,11,12) have been analysed to estimate the unit cell parameters of these crystals assuming these to be monoclinic.

Finally, an experimental set up for the determination of bend and splay elastic constants has been successfully designed and constructed by me. This was used to determine the bend to splay ratios of five nematogens. Priest's spherocylindrical model has been successfully tested using our x-ray data for length, width and order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ for these compounds.

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