

Preface

Liquid crystals are intermediate states between crystals and isotropic liquids and thus have intermediate physical properties between them; i.e., the fluidity of liquids and the anisotropy of crystals. Between 1850 and 1888, researchers in different fields of science found that several materials behaved strangely at temperatures near their melting points. It was observed that the optical properties of these materials changed discontinuously with increasing temperatures. W. Heintz, in 1850, reported that stearin melted from a solid to a cloudy liquid at 52°C, changed at 58°C to an opaque and at 62.5°C to a clear liquid. Some biologists observed anisotropic optical behaviour (a property of crystalline phase) in "liquid" biomaterials. An important invention of the time was microscope fitted with hot stage, by Otto Lehmann, a German physicist and an expert in crystal optics.

In 1888, an Austrian botanist named **Friedrich Reinitzer**, working in the Institute of Plant Physiology at the University of Prague and interested in the biological function of cholesterol in plants, was looking at the melting behaviour of an organic substance related to cholesterol. (The chemical structure of cholesterol was still unknown. Today we know that the observed substance was cholesteryl benzoate). He observed, as W. Heintz did with stearin 38 years, before that the substance melted to a cloudy liquid at 145.5°C and became a clear liquid at 178.5°C. Discussion with Lehmann and others led to the identification of a new phase of matter called the *liquid crystal phase*. But this new phase of matter was challenged by many important scientists like Walter Nernst and Gustav Tamman. They argued that the phenomena could be due to the formation of emulsion of two distinct phases or compounds. Later Emil Bose and Max Born independently suggested a theoretical description of liquid crystals as molecules with permanent electric dipoles.

From 1945 to 1958 there was a *pause* in the exploration in the liquid crystal world. In 1958 Glenn Brown, an American chemist, published an article in *Chemical Reviews* on the liquid crystal phase causing a resurgence in liquid crystal research.

Thermotropic liquid crystals are formed by rod-like molecules (calamitic liquid crystals) or disc-shaped molecules (discotic liquid crystals). Calamitic mesogens, in addition, form lamellar (smectic) phases while discotic mesogens form columnar phases. These basic molecular structures can be modified in different ways giving rise to new structural features of the mesophases (i.e., polycatenar liquid crystals, sanidic liquid crystals). Liquid crystal molecules normally rotate freely along this symmetry axis, unless there is no symmetry requirement. From this viewpoint, molecules with shapes deviating from a rod, such as board or bent shape, have been thought of as bad molecules for forming liquid crystals. If such molecules freely rotate about their long molecular axes, the excluded volume becomes large and violates the liquid crystallinity. For these reasons, only a very few bent-core molecules have been synthesized before the discovery of their polar switching. It should be noted, however, that Vorländer, who is a pioneer in the field of liquid crystal synthesis, synthesized several bent-core liquid crystals and reported their mesogenic properties in 1929, mentioning that the thermal stability of the mesophase is low compared with that of the straight-core analogues. After a long time, Matsunaga and coworkers revived the synthesis of bent-core mesogens in 1991. One of the molecules, 1,3-phenylene bis[4-(4- n-octyloxyphenyliminomethyl) benzoate], opened a new era of liquid crystal science, although they did not realize the physical importance of this molecule before the discovery of polar switching in this molecule.

Takezoe's enlightening lecture at the 6th International liquid crystal conference in 1996 at Kent, Ohio in U.S., has sown the seeds for new area of research of banana liquid crystals. He reported ferroelectric properties of a new type of liquid crystalline phase, in which chirality is manifested by achiral bent-shaped mesogens. Because of the sterically induced packing of the bent molecules new smectic modifications can occur which have no counterpart in the field of calamitic liquid crystals. On the other hand, structural features of the new mesophases can lead to unusual physical properties. As a consequence of the special molecular packing of bent molecules, smectic layers with C_{2v} , C_2 , and possibly also C_{1h} or C_1 symmetry could occur giving rise to ferro-, ferri- or antiferroelectric properties. The ferro- or antiferroelectric switching and the second harmonic generation (SHG) activity of some phases offer, in principle,

interesting possibilities for a practical application. As shown in the literature the polar order of bent molecules in smectic layers can induce a chirality of the smectic layers although the individual molecules are achiral. This type of chirality can lead to the formation of helical superstructures.

The recent literature in the field of liquid crystals shows that “banana-shaped” mesogenic materials represent a bewitching and stimulating field of research that is interesting both academically and in terms of applications. Numerous topics are open to investigation in this area because of the rich phenomenology and new possibilities that these materials offer.

In spite of being very new arena of about 10 years, the field of banana-shaped liquid crystals has been an active and fruitful research area for both academic and applied interests within Materials Science. Today, “banana-shaped” liquid crystals occupy one of the most exciting areas of research in both mesogenic materials and supramolecular chemistry. More than 500 papers have been published within 10 years, including review articles. A review of literature in the last few years quickly envisages that of all the molecular based materials synthesized thus far, the vast majority contains Schiff base linkage and usually V-shaped or bent shaped molecules possessing C_{2v} symmetry. Most of the above discussion is compiled in **chapter 1**.

A net spontaneous polarization and hence ferroelectricity (or antiferroelectricity) have become the resultant material properties in molecules with a bent angle of about $\sim 120^\circ$. The molecules with a bent angle of about $\sim 120^\circ$ can be realized in molecules derived from resorcinol or 1,3-disubstituted phenyl derivatives and are actually abbreviated as banana or bent shaped liquid crystals. Similarly the molecules derived from 1,2-disubstituted phenyl ring are abbreviated as V-shaped liquid crystals. The liquid crystalline behaviour of these two classes of bent-core molecules, viz., **V-shaped**, and **Banana shaped** are different Hence the possible positions of linkages through covalent bonds for disubstitution in a benzene ring are 1,2; 1,3; and 1,4 with a promesogenic moiety which can give rise to bent or V-shaped molecule, banana or bow shaped

molecule and rod like molecule respectively and manifest molecular assemblies with short and long range orders to exhibit liquid crystal behaviour. In order to investigate the influence of bent angle of the molecule on banana liquid crystal behaviour, we focused our attention to synthesise series' of compounds with 1,3- as well as 1,2- disubstituted phenyl core at the centre . The central phenyl core was extended with rod like molecular moieties through imine linkage. The imine linkage, otherwise susceptible to decomposition due to moisture and ultraviolet light, was stabilized with the introduction of *o*-hydroxyl group. The influence of substituent on the central core was also attended. Compound with pyridinyl central core was also synthesised. All the general experimental methods are presented in **chapter 2**

The compounds synthesized were analyzed for chemical composition by spectroscopic methods and characterized for the liquid crystalline behaviour using differential scanning calorimetry and thermal microscopy. These results are presented and the findings are discussed in **chapter 3** under appropriate heads.

The work that is carried out during the last few years is presented in this small thesis. The compilation of the references used in each chapter has been presented at the end of the respective chapters themselves to aid quick search of the source. All the figures and tables are placed embedded in their respective discussions themselves (and also at the end of the theses), to facilitate smooth, quick and uninterrupted review.