INTRODUCTION

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Liquid crystals represent an intermediate state of matter which exhibits mechanical properties of liquid and optical properties of crystalline solid. In 1888, an Austrian botanist, Reinitzer (1) observed the first thermotropic 'liquid crystal' cholesteryl benzoate. However, Otto-Lehmann (2) was the first to make a systematic study of such substances and proposed the name 'liquid crystals' for such compounds. A more satisfactory nomenclature has been proposed by Friedel (3,4) who is of the opinion that the name 'liquid crystals' is not a good one as the substances are neither perfect crystals nor perfect liquids. He described this state as a 'mesomorphic state' (Greek- mesos- intermediate, morphe- form), meaning a state intermediate between the crystalline solid and the amorphous liquid state. From this are derived the terms 'mesomorphs', 'mesoforms' and 'mesophase'. However, the popular name liquid crystals still prevails.

1. CLASSIFICATION

Liquid crystals are conveniently divided into two chemically distinct types. Thermotropic liquid crystals are obtained by melting crystalline solids comprised of rod-shaped (calamitic) or disc-shaped (discotic) molecules. Depending on the orientational and positional organisation of the molecules, these states may be nematic, smectic or columnar.

Lyotropic liquid crystals are obtained by dissolution of amphiphilic molecules containing balanced hydrophobic and hydrophilic groups in a solvent, mainly water. The state of these materials is determined by their concentration, and the most familiar are those obtained on adding surfactants to water. The surfactant molecules undergo reversible self-assembly into larger aggregates, which in turn self-organise over a larger scale into liquid crystals.

Certain macromolecules of either synthetic or biological origin like DNA molecules also show mesophase. The mesophases that are seen in aqueous solutions of rod-shaped DNA molecules are almost identical in their structure and properties to those of calamitic liquid crystals. DuPont's ultra-high strength polyaromatic amide fibre Kevlar is spun from a lyotropic mesophase obtained in concentrated sulphuric acid.

The investigations carried out in this thesis deal with only thermotropic mesophases.

2. THERMOTROPIC MESOPHASES.

On the basis of the molecular arrangements Friedel (5) classified thermotropic liquid crystals into two broad classes, smectic and nematic. Often the cholesteric phase is described separately, but it is also known that this is a twisted nematic mesophase. To these two classes, was added a new class of discotic liquid crystals invented by Chandrasekhar et al (6) in 1977. Host of new discotic liquid crystals are added to this class, subsequently.

2.1 Smectic mesophases (S)

The term smectic originated from the Greek word "smectose" meaning soap like and was coined by Friedel (5) as smectic mesophase is viscous, turbid liquid with reminiscent properties of soaps.

Smectic liquid crystals have stratified structures and different kinds of molecular arrangements are possible within these layers. Depending on the molecular arrangement and the extent of interlayer correlation, smectics can be classified into different groups.

Smectic A : Smectic A phases have a layer structure. Inside the layers the molecules are parallel, on an average, one to each other with their long axes perpendicular to the layer plane (Fig. 1). They have the possibility for rotation around the long and short molecular axes, translational diffusion, and, within the layer, no long - range order with respect to the positions.

Smectic C : Smectic C phases are closely related to smectic A phases. The most important difference is the tilt of the molecular long axes with respect to the layer normal (Fig. 2). The mobility of the molecules is similar to that of the smectic A phases, however, the rotation around the long axis is slightly more hindered than in smectic A phases.

If the molecules are chiral then the Sc phase has a helical twist of the director. The tilt precesses around the layer normal. This phase is called chiral smectic C phase or smectic C* phase.

Sackmann and Demus (7) have classified smectic phases according to the textures observed in the mesophases. They identified seven smectic phases from S_A to S_G by miscibility studies. deVries and Fishel (8) have reported the eighth possible smectic phase SH.

Review on 'Phase Types, Structures and Chemistry of Liquid Crystals' by Demus (9) describes various smectic phases from S_A to S_M. The books "Smectic Liquid

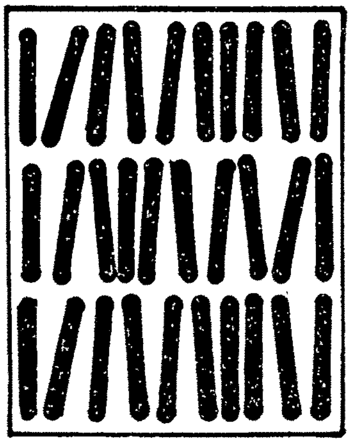


Fig.1 Structure of smectic A phases.

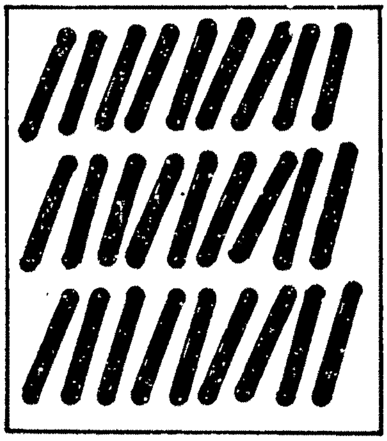


Fig.2 Structure of smectic C phases

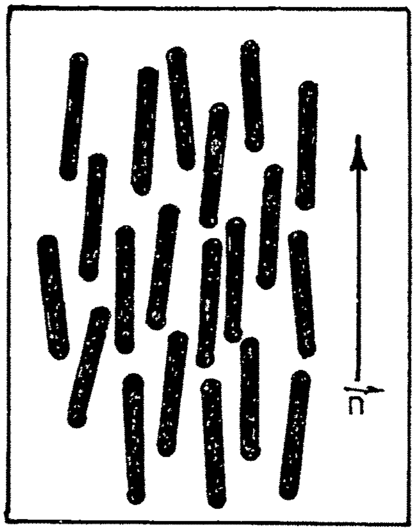


Fig.3 Structure of nematic phase

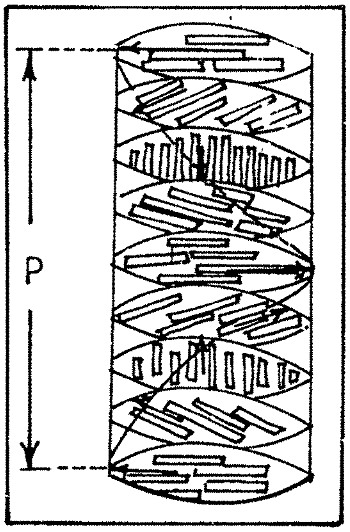


Fig.4. Structure of cholesteric phases(N*) : p = pitch of the helix

Crystals" (10) and "Texture of Liquid Crystals" (11) provide detailed accounts of all smectic phases.

Levelut et al. (12) have designated smectic O phase in 1-(methyl) heptyl terephthalidene bis aminocinnamate. Bennemann et.al (13) have reported some mesogenic chiral compounds, which show a smectic Q phase just below the clearing point. Recently, Bennemann, Heppke and Lotzsch (14) have carried out structural investigation of smectic Q phase.

2.2 Nematic Mesophase (N)

The word 'Nematic' is derived from a Greek word 'Nema' meaning thread The molecules in the nematic phase tend to be parallel to a common axis called the director and possess a long range orientational order (Fig. 3).

2.3 Cholesteric (Ch) or Chiral Nematic phase (N)*

The cholesteric phase was observed in cholesterol derivatives hence they derived this name cholesteric phase. It is twisted nematic phase as it possesses the sturcture of layered nematic liquid crystals twisted about an axis perpendicular to the molecular layers, which results in helical structure (Fig. 4)

Nematogens with chiral centre also exhibit cholesteric phase (15-17) hence, they are called 'Chiral Nematics'. Gray (17) has reported an optically active deuterated compound exhibiting cholesteric phase. The addition of optically active materials to nematic liquid crystals also gives cholesteric liquid crystals.

Cholesteric liquid crystals have helical structure hence they behave in an unique and in most striking way not observed in other types of liquid crystals i e reflection of iridescent colours. Certain cholesteric compounds can selectively scatter light into different colours. The colour of the reflected light can be determined by (a) pitch of helix (b) by temperature (c) the angle of the incident beam. Physical effects which wind or unwind the helix such as temperature, mechanical disturbance like pressure or shear and traces of organic vapours, result in various colour changes.

In contrast to smectic and nematic compounds cholesteric liquid crystals are optically negative. They generally have three types of textures.

(i) Focal Conic Texture :

When an isotropic liquid is cooled, the texture obtained is focal-conic. The term is derived from the conic sections that are usually observed in case of smectics The focal-conic texture nucleates in discrete points from where it grows in all the directions i.e radial growth until whole film is covered.

(ii) Plane Texture or Planar Texture :

In this texture, the sample is uniformly aligned with the twist axis perpendicular to the plane of the film. However, alignment discontinuities can show reflected colours For perpendicular incidence the wavelength of light at the centre of the reflection band is equal to the wavelength of the pitch multiplied by refractive index.

(iii) Blue Phases :

Blue phases appear in a narrow range of temperature (typically less than 0.5 ^{o}C) between the N* phase and the isotropic liquid phase, provided the pitch of the N* phase is relatively short (< 3000 A^{o}) .

In 1956, Gray (18) described phenomena of blue phase and in 1969 Saupe (19) confirmed the optical properties noted by others and proposed a cubic model for the blue phase.

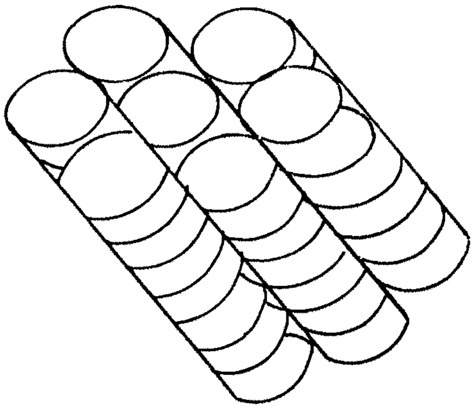
In spite of this work, the blue phase remained a relatively unknown phenomena upto 1978, but the situation changed drastically with the publications of a series of papers by Stegemeyer et al (20-22) during the period 1978-80. This work attracted number of scientists (23-27) working in the liquid crystal field.

2.4 Discotic Mesophases.

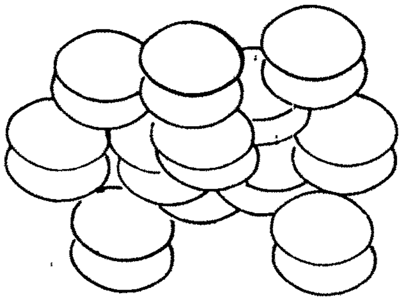
The first discotic liquid crystal was synthesized and identified in 1977 by Chandrasekhar et al (6). Discotic phases may be classified into two fundamental types : columnar and nematic (fig. 5). The thermodynamic, optical and X-ray studies (28) led to the conclusion that these compounds are entirely new type of liquid crystals. Usually, these phases are formed from molecules having more or less flat aromatic cores with normally six, but sometimes four lateral substituents, like alkoxy or ester (or more complex) group, with atleast five carbon atoms. However, Abied et al (29) and Vora et al ., (30) have reported disc like molecules with only three substituents.

Development of discotic liquid crystalline system is becoming an increasingly prominent feature of current liquid crystalline research. Certain forms of highly chiral pentyne compounds have been well documented and many of which are known to show discotic nematic phases. (31-35). Cook et al (36) have synthesized the first discotic liquid crystalline derivative of a ferrocene and tetrathiafulvalenyl- phthalocyanine.

Synthesis of discotic liquid crystals with unpaired spins (37) non-discoid metal complexes (38) and derivatives of pentaerythritol (39) have been reported recently.



SCHEMATIC REPRESENTATIONS OF THE
TILTED COLUMNAR STRUCTURE.



SCHEMATIC REPRESENTATIONS OF THE
NEMATIC PHASE OF DISC—LIKE MOLECULES

Fig.5

3. SEQUENCE RULE AND REENTRANT BEHAVIOUR

In the liquid crystalline state, Sackmann (40) derived the rule of the phase sequence by systematic observation of the sequences of different phases in polymorphic compounds. This rule in polymorphic compounds predicts a stepwise decrease of order with increasing temperature and the reverse with decreasing temperature. That means, according to this rule, the smectic phases generally are low-temperature phases with respect to the nematic phases. Within the smectic state with increasing temperature first the 'herring - bone' structures, then the layer structures with less pronounced positional order and at higher temperatures layer structures without positional order appear. Considering all structures known in calamitic substances, a hypothetical sequence can be derived :solid crystal -H-K-E-G-J-F-L-I-B_{hex} - M-C-A-N- isotropic. In compounds with association behaviour or compounds with several flexible chains (in general, compounds which cause effective " molecule polymorphism" in dependence of the temperature) certain phase sequences may be reversed, a situation called " reentrant " behaviour. There are compounds or mixture with the sequence N_{re}-S_A-N-Is (41, 46) or N-S_A-Is(47, 48), even with double reentrance N_{re}-S_{Are}-N_{re}-S_A-N-Is (49, 50).

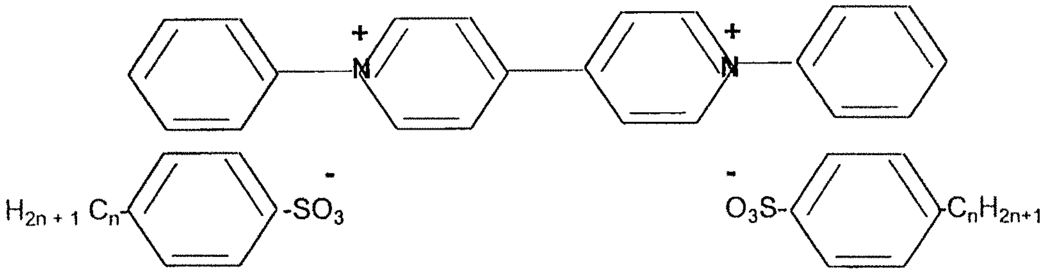
Destrade et al (51, 52) have reported reentrant cholesteric phases in polar mesogens Reentrant behaviour has also been observed in discotic materials (53) Subramaniam et al (54) have reported reentrant isotropic phases in polypeptide solution.

Recently, Weissflog et al . (55) have synthesized two new six-ring double-swallow tailed mesogens. One of them shows the very unusual phase sequence cryst-smectic C-cubic-isotropic-nematic-isotropic.

4. IONIC LIQUID CRYSTALS :

There are only a few reports concerning ionic thermotropic liquid crystals. Some liquid crystal polymers with the pyridinium side chain (56) and those with alkyl ammonium salt as principal chain have been reported (57).

Haramoto et al ; (58) have reported the new type of ionic liquid crystal materials shown below :



5. LIQUID CRYSTALLINE SUPRAMOLECULES.

Recently, much attention has been paid to the self assembly of complementary building blocks. The assembly of the components is effected and controlled by intermolecular forces such as hydrogen bonding, ionic and charge transfer interactions and metal complexation. Thermotropic liquid crystalline phases have been induced by hydrogen bonded molecules, possesing amphiphilic character. Mesophase generation in amphiphilic systems is ascribed to hydrogen bonding interaction between the polar head groups and to the spatial separation of polar and apolar groups. Supramolecular polymeric structures, based on non-covalent bonding of complementary components have been synthesized by various groups (59 - 63). The emergence of supramolecular chemistry i.e. chemistry beyond the molecule initiated by Lehn (64), addresses goals involving well defined macromolecules relevant to bio-chemistry.

Macrocyclic liquid crystals are adding a new dimension to this entire field which so far has been concerned with liquid, glassy and crystalline states. Liquid crystalline properties for molecular trees were first reported in 1988 by Friberg et al (65).

Recently, it has been demonstrated that low-molar-mass macrocyclics based on conformationally flexible rod-like mesogens exhibit a higher ability to generate liquid crystalline phase than do their low-molar-mass linear and both their linear and cyclic high molecular mass homologues (66).

Macrocyclics of a certain size are more rigid than are the corresponding linear homologues as well as both their high molecular mass and linear and cyclic compounds.

This novel class of liquid crystals opens numerous possibilities for the design of new macromolecular and supramolecular architectures based on liquid crystalline macrocyclic building blocks.

6. METALLOMESOGENS.

Metal containing liquid crystals are known as metallomesogens. The first thermotropic metal-containing liquid crystals were reported by Vorlander (67) in 1910. He found that the alkali-metal carboxylates, $R\text{-}(CH_2)_n\text{-}COONa$ forms classical lamellar phases on heating. Since then many new types of mesogenic metal complexes have been synthesized. Many examples of liquid crystalline metal complexes have been reported over the years and many of these are discussed in the review articles by Giroud-Godquin and Maitlis (68) and Espinet et al (69). Giroud and Muller - Westerhoff (70) were the first to use d-block elements to obtain metallomesogens. Varieties of monodentate ligands, such as cyanobiphenyls (71), nalkoxystilbazols (72), monostilbazols (73), distilbazols (74), 4-substituted pyridines (75), Ferrocenes (76) etc. have been used to obtain metal chelates.

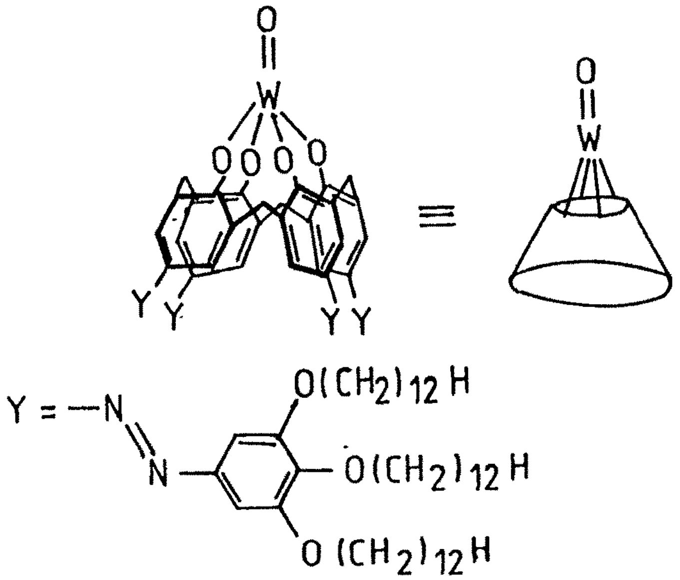
Bidentate ligands such as β-diketones and N-salicylideneamine derivatives exhibit calamitic or discotic mesophases depending upon the number and nature of the substituents. Polydentate ligands such as derivatives of phthalocyanines, porphyrins or annulenes predominantly exhibit discotic phases. However, not all the metal chelates show liquid crystalline behaviour. A majority of complexes with linear, square planar and square pyramidal geometries have so far been found to be mesogenic though a few metallomesogens with octahedral and tetrahedral geometries have also been reported in literature (77-81).

In addition to above, a large number of other metallomesogens are known. Sadashiva and co-workers (82,83) have also reported liquid crystalline behaviour in some homologous series of β-diketones and a few of their Cu(II) and Pd(II) complexes. Shimizu et al (84) have given the first example of a discotic metallomesogen having an Al nucleus. In 1996, Yada et al (85) have reported the synthesis and deorganization of an Aluminimum based dodecyl sulfate mesophase with a hexagonal structure.

Maldivi et al (86) have synthesized for the first time, metallomesogens giving an authentic columnar mesophase near room temperature in the pure state. This result is promising, because it shows that it is possible to lower transition temperatures of metallomesogens without disturbing their mesomorphic properties.

Recently, synthesis of novel liquid crystalline organometallic polymers have been reported by Bunz (87).

An extensive investigation has been conducted into the mesomorphic behaviour of calix[4]arene based bowlic liquid crystals. The calix[4]arene metallomesogens based on Tungsten$_{(VI)}$ oxocalix[4]arenes (88) display highly stable columnar liquid crystal phases. This was achieved by attaching alkyl chains to the lower rim of the calixarene and then capping the four hydroxyl groups on the upper rim with the tungsten-oxygen group. Because of their bowl-like shape, these calixarenes stack together a bit like paper cups, as shown below



to form columnar mesophases that are stable over a spectacular range of about 200 °C. Host-guest effects indicate head-to-tail order within column in which the tungsten-oxo groups protrude into the cavities of the neighbouring mesogens. Recently, Xu et al (89) have successfully developed new methodology to produce optically pure chiral bowlic liquid crystals. Reviews on 'Mesogenic Calixarene' by Malthete (90) 'Liquid Crystalline Calixarene' by Swager and Xu (91) and 'Bowlics' by Lam (92) have also appeared in literature.

7. MIXED MESOMORPHISM

Liquid crystals with low crystal-mesophase transition temperatures and with wide phase length have been primary goal of organic chemists in recent years. Since the occurance of single component, room temperature liquid crystal with wide mesophase range is rare, it is necessary to mix two or more low melting materials which may give room temperature mesomorphic mixture with wide mesophase range Number of workers have studied and reported the formation of mixed liquid crystals in the case where one or both the components are non-mesogenic (93-97). Dave and Vora (98) have reviewed the work of Dave et al (95,96) on mixed mesomorphism and have derived an order of end group efficiency in the nematic mesophase as under :

$-NO_2$ > -OEt > -OMe > n-PrO- > $-NMe_2$ > Me=C1 > F=Br > H

Many mixtures have been reported where a mesogen or other compounds were added to low melting mesogens, either to decrease the melting point, or to increase the mesophase range or to change the electric conductivity and dielectric- anisotropy (99-101)

Extensive studies have been carried out for mixed mesomorphism of smectic type Vora and Changawala (102) and Padmini et al; (103)reported binary systems consisting of a smectogen exhibiting polymorphism and non-mesogenic Schiff base, in which they observed that smectic phase changed to nematic phase even when the concentration of the non-mesogenic Schiff base was lower.

Arora et al, (104) and Neubert et al, (105) have reported creation of nematic phase in smectogen by the addition of the second component which is also mesogen. This work has vindicated the results of Vora et al, who reported such behaviour of the binary phase diagram for the first time.

Recently, number of research papers on the induction of the different type of mesophases (106-113) have also appeared in the literature.

8. AMPHOTROPIC OR AMPHITROPIC LIQUID CRYSTALS :

Currently, there is growing interest in compounds which have amphiphilic character and liquid crystallinity i.e compounds which contain the two types of ordering effect. Such compounds have been called amphotropic or amphitropic.

Many efforts have been made to produce amphotropic liquid crystals (114-118) In this context, tetraethoxycholesteryl semisuccinate has been reported (119), which combines the hydrophilic oligoethylene glycol group with the hydrophobic rigid cholesteryl moiety. However, several previous attempts were made to introduce rod-like molecular units into the hydrophobic part of oligoethylene glycol amphiphiles, and with one exception (120) all the compounds described previously exhibited only lyotropic properties after the addition of water (121-123). The amphotropic behaviour of simple alkane-1, 2-diols has recently been reported (124-126) Their combination with rigid cores gives rise to extended thermotropic and lyotropic mesomorphic ranges (127-130).

In order to clarify further the relation between molecular structure and amphotropic behaviour, Tschierske et al, (131) have recently reported new amphiphilic oligoethylene glycol derivatives incorporating different rigid cores and oligo-oxyethylene chain of different lengths. Borisch et al; (132) reported molecular design of amphitropic liquid crystalline carbohydrates-amphiphilic N-methyl-glucamides exhibiting lamellar, columnar or cubic mesophases.

9. LIQUID CRYSTALLINE TWINS :

Liquid crystalline twins are mesomorphic compounds which posses two rigid anisometric units linked with each other. The recent interest in twins and larger oligomesogens has been promoted by both their ability to act as model compounds for polymers and their quite different properties in comparison to conventional low molecular mass mesogens. A great majority of reported twins (133-141) and oligomesogens (142-144) consist of calamitic units which are connected via their terminal chain. Vora et al, (145) have reported dicholesteryl esters and carbamates with flexible spacers. Discotic (146,147) and macrocyclic derivatives (148,149) have also been described. Laterally fixed calamitic twins (150,151), trimesogens and tetramesogens (152,153) have only recently been reported. Griffin et al., have prepared methylene-bridged 'ligated twins' (154,155). Twins which are joined by thio, sulfinyl and sulfonyl bridges have been described by Dehne et al., (156). Weissflog et al., (157) and Tschierske and Andersch (151) also reported on laterally connected dimesogens with longer spacer units. However, the dimesogens synthesized by the different groups differ in their chemical structures, in the lengths of the connecting units and in their connecting topology. Therefore, a direct comparison of the mesomorphic properties of the various compounds is not possible.

10. FERROELECTRIC LIQUID CRYSTALS. (FLC)

The advent of a fast switching, bistable, electro-optic device configuration based on ferroelectric properties of liquid crystals has aroused interest in the synthesis of optically active smectic liquid crystals. The steric shape of a molecule and its dipolar character govern the formation of ferroelectric liquid crystals (FLC). Materials which possess following criteria exhibit ferroelectric properties (158-161).

(i) an alkyl-aryl-alkyl systems

(ii) strong terminal lateral dipoles

(iii) atleast two aromatic rings

(iv) a chiral centre which reduces the symmetry of the phase

Ferroelectricity is observed in materials which exhibit tilted smectic phases. The most important smectic phase type derived from chiral compounds is that with the designation C*. Because of the twisted structure the C* phases show strong optical activity and selective reflection of circularly polarised light.

Examination of the structures of materials which typically exhibit ferroelectric smectic phases shows that the optical center is normally at one end of the molecule This helps the centre to rotate freely, independently of the rest of the molecule which is also rotating.

Restricting this freedom of rotation of the chiral centre enables increasing of spontaneous polarisation.

Besides, the orientationally disordered crystal phases of optically active materials exhibit ferroelectric properties. This is attributed to the lowered symmertry of the structural environment of the phase. Two materials exhibiting the same phase but with the opposite helical twist senses can be blended together in proportions to produce a smectic liquid crystal phase (C*, J* or F*) which has infinite pitch length. The phase can still posses a spontaneous polarisation and be ferroelectric (162).

Ferroelectric metallomesogens are a new type of liquid crystals which have unique properties arising from the presense of metal atoms. In 1995, Espinet et al, (163) have reported metal containing ferroelectric liquid crystals.

Ferroelectric liquid crystalline phases have shown a potential as electrically active media in a variety of applications such as displays, light valves, spatial light modulators, optical processing and pyroelectric detectors.

10.1 Spontaneous Polarization

Overall net spontaneous polarization is strongly influenced by the strength of lateral dipole associated with the optically active centre (164-166). However, the effect of lateral dipoles other than those linked directly to the chiral centre on the magnitude of net polarization is not yet clear. The strength of spontaneous polarization can be increased considerably by restricting the freedom of rotation of the chiral centre in relation to the molecule as a whole. This can be achieved by moving the branch closer to the core thus creating a direct interaction between the two via dipolar coupling and restricted rotation. However, this can have detrimental effect on the stability of the ferroelectric phase and which may also be lost altogether in certain cases.

The dipolar nature of the chiral centre strongly influences the strength of spontaneous polarization, and therefore its position in relation to the tilt direction will also determine the direction of spontaneous polarisation. Thus, as the number of atoms in the spacer group is increased incrementally, not only will the helical twist sense alternate, but also the direction of spontaneous polarization will alternate back and forth .with respect to the tilt orientation for a given homologous series.

In applications it is usually necessary to produce eutectic mixtures which exhibit the required phase at room temperature. To obtain high spontaneous polarization, it is important to mix materials which have the same direction of the polarization, but not necessarily the same twist sense.

In the design of materials suitable for applications it is necessary to take a number of factors into account.

These include:

(i) the gross molecular shape.

(ii) the aliphatic to aromatic constituent ratio and their distribution.

(iii) the direction of the polarisability of the delocalized electrons.

(iv) the placement of the chiral center and its relation to helical twist sense.

(v) the relationship between the directions of the tilt and the spontaneous polarization.

11. ANTIFERROELECTRIC LIQUID CRYSTALS . (AFLC)

A new chiral smectic liquid crystal phase exhibiting an anticlinic ordering of the molecular orientation in successive layers has been discovered and designated as antiferroelectric mesophase.

Extensive studies have been carried out to clarify the origin of the antiferroelectric phase (167-169). It was reported that the antiferroelectric S_{CA}* phase is stabilized by a molecular pairing via a dipole-dipole interaction between two molecules (170). Recently, the importance of a dipole component parallel to the smectic layer was also pointed out (171). The helical pitch of AFLCs is fairly short compared with conventional FLC However, the chiral interaction is still so weak that the helicoidal pitch is very long as compared to the smectic layer spacing i.e. the molecular length.

With a view to the construction of new types of display devices (172,173) many AFLC compounds have been developed and the correlation between the molecular structure and the appearance of the antiferroelectric S_{CA}* phase has been investigated. As a consequence, some empirical rules for the design of AFLC compounds have been reported (174,175). According to these rules, a core structure composed of three phenyl rings more reliably induces the antiferroelectric phase than compounds with two phenyl rings. Most of the AFLC compounds have two ester groups, which align in the same direction and in the same sense. This structure effectively induces polarization and conjugation along the molecular long axis in antiferroelectric molecules (176). In practice, however, it is not yet clear how to design new FLC compounds which show the stable S_{CA}^* phase.

Recently, number of new materials exhibiting this phase have been synthesized (177-181)

12. THE EFFECT OF CHEMICAL CONSTITUTION AND MESOMORPHISM

Considerable interest has been shown from the very begining to find out the correlation between chemical constitution and mesomorphism. Gray (182,183) and Demus et al; (184-187) have given quite a detailed account of effect of chemical constitution on mesomorphism.

12.1 The Effect of Terminal Substituents On Mesomorphism.

Terminal groups present in the molecule have their own importance because of their polarity. It has been found that, terminally substituted compounds exhibit more stable mesophases compared to unsubstituted mesogenic compounds.

Any terminal group which increases the molecular polarisability without increasing the molecular breadth too much, increases the thermal stability of the resulting mesophase. The terminal group efficiency order which has been compiled (182) for smectic phase in rod-like aromatic system is :

-Ph > -Br > -Cl > -F > $-NMe_2$ > -Me > -H > $-NO_2$ > -OMe > -CN

and the nematic group efficiency order is :

-Ph>$-NHCOCH_3$ >-CN > - OCH_3 > $-NO_2$ > -Cl > -Br >$-N(CH_3)_2$ > $-CH_3$ > -F>-H

These orders give a broad idea about the probability of obtaining a particular type of mesophase.

Gray (183) and Dave and Vora (188) have studied the effect of substitution in cholesteryl benzoates, and obtained a group efficiency order for the different substituents in the cholesteryl systems.

Demus et al, (184) have synthesized terminally swallow tail type compounds and established that by selecting proper geometry of molecules, the liquid crystalline property can be maintained in such systems.

According to the systematic studies by Gray and Harrison (189) on alkyl 4-(p-substituted benzylideneamino) cinnamates, all the branched chain esters have lower liquid crystal stabilities than the unbranched chain esters. Matsunaga et al; (190,191) have carried out systematic studies on the effects of branching of the ester alkyl group on the mesomorphic properties.

Thirty-eight non substituted and laterally fluoro-substituted 4-Nitro,4-isothiocyanato-,4-fluoro-,4-trifluoromethyl-, and 4-trifluoromethoxyphenyl 4-(5-alkyl-1,3,2-dioxaborin- 2- yl) benzoates were synthesized and their phase transition temperatures and enthalpies of transition measured by Dabrowski et al., (192). The influence of both terminal and lateral substituents in both benzene rings (in the acidic and phenolic moieties) on the phase transition temperatures in general and on the stability of the smectic A phase in particular are compared by them.

Recently, Ogawa (193) has reported the effects of terminal mesogens on thermal properties of dimeric, trimeric, and tetrameric model compounds for main chain liquid crystalline polymers.

12.2 The Effect of Lateral Substituents on Mesomorphism

Lateral substituents may force apart the molecules and may thus reduce the intermolecular lateral cohesions but at the same time side substituents may increase the intermolecular attraction. Normally, the first effect predominates i.e. a lateral substituent decreases the mesophase thermal stabilities. However, if the substituents do not have fullest breadth increasing effect as in the case of the 5-substituted-6-n-alkoxy-2- napthoic acids (194) then the second effect predominates. i.e. the thermal stabilities of substituted mesogens increases.

The lateral group efficiency order which has been compiled (182) for smectic phase in rod-like aromatic system is :

$-I > -Me > -NO_2 = -Br > -Cl > -F > -H$

and the nematic group efficiency order is :

$-NO_2 = -I > -Br > -Me > -F > -H$

Mesomorphic properties of 2,6- ; 1,5- and 1,4- ; substituted naphthalene derivatives were studied by Gray and Jones (194) Wiengand (195) and Dave et al ; (196,197). These studies show that the order of mesophase thermal stabilities in naphthalene ring substitution is :

2,6- > 1,5- > 1,4-

Increase in the molecular breadth have three pronounced effects.

(i) Lowering of the temperature at which mesophase appears.

(ii) Decreasing the stabilities of the mesophase.

(iii) Destroying any smectogenic property regardless of alkoxy or alkyl group chain length.

Vora et al, (198,199) have studied number of homologous series with bulky methoxy group as a lateral substituent. They have found that contrary to common observations lateral methoxy group does not depress much crystal-mesomorphic transition temperatures, but the mesomorphic-isotropic transitions are drastically reduced.

Demus et al (185-187) have reported compounds with lateral long chain substituents and established new molecular concept for liquid crystals. They have found that the nematic state is mainly stabilized by steric repulsions and that the attractive forces play only a secondary role.

Gray et al, (200-202) have reported laterally chloro and fluoro substituted compounds. Chloro substituted compounds could be expected to be useful in two frequency switching devices, due to its greater polarity. Number of research papers (203-206) on the effects of lateral fluoro substituents on mesomorphic properties have also appeared in literature.

Bayle et al ; (207-209) have reported influence of a lateral aliphatic chain on the ordering in some nematic compounds, new laterally alkoxy branched metallomesogens with a large nematic range and change of the lateral chain conformation in the solid and nematic phase in laterally substituted nematogens.

Recently, Weissflog and Hohmuth (210) have reported the first two ring mesogens having a lateral aromatic branch and corresponding polysiloxanes.

13. APPLICATIONS

Liquid crystals are used in many fields particularly in the field of electro-optical applications (211). The technology using these materials became successful because of its passive nature which provided the combined characteristics of low power and viewability in bright light.

Liquid crystal displays (LCDs) have many advantages over other display types. They are flat and compact, possess extremely low power consumption (microwatts per square centimeter in the case of the twisted nematic effect), their color and contrast does not fade with an increase in the illumination intensity, they work both in transmissive and reflective modes in a wide operating temperature range and with a long life time. Besides that, LCDs are the most economically produced display systems. LCDs have a brilliant future in high definition TV Systems, personal computers, measuring devices etc. The most widely used electrooptic effects in display are the twist, super twist, and guest-host modes.

Among other applications they distinguish displays for measuring tools, office equipment, clocks, cameras, telephones and thermometers, car dashboards, games, consumer products, avionics, etc.

Their potential applications cover optical data processors, image amplifiers, incoherent to coherent images and wavelength converters, associative memories, spatial filtering, optical correlators, etc. Television image can be projected on to a large screen without loss of intensity using liquid crystal image converters . Such screens are necessary at traffic control points, flight control centers, etc.

A liquid crystal display device is made by sandwiching a liquid crystal mixed with some dopant between two glass plates coated with current conducting transparent material. such as tin oxide. Electric and magnetic fields are capable of inducing molecular re-orientation in liquid crystals. Which are reflected in variety of optical changes i.e. by applying electric current to the plates, the cell becomes opalescent and by switching it off, the cell becomes transparent in microseconds. The advantages of liquid crystal displays are low operating voltages, low power consumption, ability to withstand high levels of light and low cost. Disadvantages are difficulty in cell fabrication, life time and viewing angle considerations.

Ferroelectric liquid crystals have been widely explored for display applications due to its unique properties of bistability, threshold behaviour, high speed even at very low voltage, large electrooptical response, etc.

A review on the use of liquid crystals in laser optics (212,213) also appeared in the literature. Owsik et al., (214) have reported the use of chiral liquid crystals in laser engineering.,

Antiferroelectric liquid crystals are also gaining considerable attention because of their characteristic tristable switching (215) applicability for display devices (216-218).

Kiefer (219) has reviewed the physical properties, electro-optical effects, and applications of ferroelectric liquid crystal polymers. Full colour image has been demonstrated on a high frame rate, binary, ferroelectric liquid crystal display or spatial light modulator (SLM) by Rankyn et al. (220). Recently, Patel (221) has fully discussed ' Liquid Crystal Devices and Devices for Liquid Crystals.'

Cholesteric liquid crystals exhibit a colour-temperature response mechanism on the molecular scale. This effect has been made use of widely in thermography i.e. for mapping the surface temperature distribution in operation devices which reveals any hidden structural characteristics by location of heat or conduction paths. Cholesteric liquid crystals have also been used in aerodynamic testing, to detect short circuit, in disposable thermometers as temperature sensors to detect tumors, to detect solvent vapours such as benzene and chloroform in the ppm concentration, for colour changing clothes, etc.

In addition to these applications, liquid crystals have been used as stationary phase in gas-liquid chromatography, in spectroscopic studies, in cosmetic formulations, lubricants, adhesives and protective coatings on metals. They have also been used as solvents in many chemical reactions.