

Chapter II

Review of Literature

Survey about bent shaped liquid crystals in quest for chirality in achiral molecules followed by proposed plan of research work.

2. Banana shaped Liquid crystals: till date from the beginning

With the synthesis of bent shaped molecules of Schiff base derivatives of resorcinol, by Matsunaga *et al.* [1] the common convention of rod like molecules exhibiting liquid crystalline behaviour has been modified where they have reported only conventional liquid crystalline phases in these bent shaped molecules. However in 1996 the discovery of ferroelectric characteristics in achiral bent shaped molecules presented in **Figure 2.1**, possessing C_{2v} symmetry, which not only exhibit liquid crystalline polymorphism but also distinct switching characteristics, has motivated many of the liquid crystalline scientists to design and synthesize new materials for possible potential applications in emerging opto-electronic technologies. Hence the uncommon distinct molecular structure, the unconventional mesomorphic properties, the occurrence of a spontaneous symmetry breaking in some cases, the biaxial smectic phases and the special switching behaviour of some of their mesophases immediately attracted great interest. Hence, such materials are of great importance because of their possible application in switchable nonlinear optical devices. Bent or banana or V-shaped molecules as shown in **Figure 2.1** exhibiting banana mesomorphism has attracted much attention in the last decade because of its distinct properties [2-10]. For macroscopic polarization in smectic layers, the bent shape of the molecules can preferably be packed in a distinct direction viz., the bent direction to manifest the long range correlation of the lateral dipole moments.

2.1. Chirality in Achiral Molecules: ferroelectricity and antiferroelectricity:

Is molecular chirality essential for a liquid crystal to exhibit (anti) ferro electric property?

One of the most exciting of the new FLC research areas was reported by Takezoe at the 6th International Liquid Crystal Conference 1996 in Kent, Ohio that burst into prominence, a new type of mesophase called banana liquid crystal phase i.e., achiral banana (or bow or bent) shaped molecules (figure 2.1) exhibiting liquid crystalline behaviour (anisotropic fluid) as well as ferroelectricity (or antiferroelectricity) in liquid crystalline phase with large spontaneous polarization. In 1996 Takezoe, Watanabe and coworkers [2-7] in Japan carried out

detailed experimental studies in bent shaped molecules (figure 2.1) to discover that the molecular chirality is not a necessary condition for the existence of ferro or antiferroelectricity in liquid crystalline smectic phases. They discovered that bent or banana shaped molecules exhibit banana liquid crystalline phases and possess ferroelectric order. Moreover this banana shaped achiral molecules [8-10, 12-15] assembling in tilted smectic layers, which manifest the polar order parallel to layers, exhibit distinct ferroelectric properties in the high temperature liquid crystalline phase. This breaking discovery was the beginning of a lot of activity to investigate the structure and properties of these new mesophases, which are not comparable with smectic phases formed by calamitic mesogens. The term ‘‘banana-shaped mesogens’’ is used as a synonym for this new field of liquid crystals; and hence this field has attracted much attention in recent years because of academic importance and commercial applications.

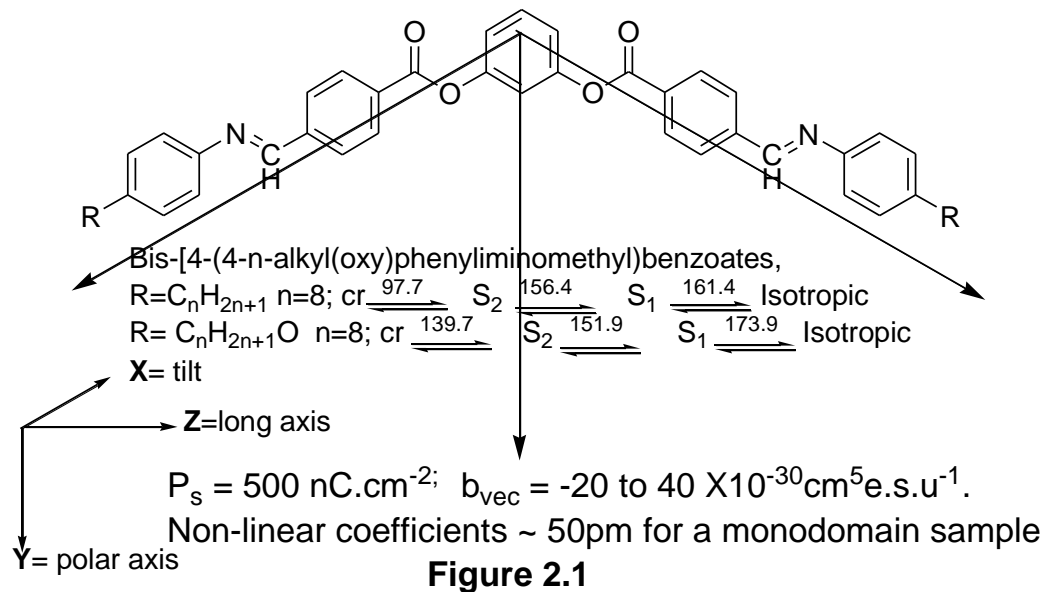


Figure 2.1: Molecule in which Takezoe et al found ferroelectricity.

So far eight banana phases, B1 to B8, have been identified and in two of these phases, B_2 (S_1 of **Figure 2.1**) and B_5 , the polarization direction is inverted in alternating layers, and hence both the phases are antiferroelectric in the absence of applied electric field. Of those eight banana phases, B_2 phase is the most common and widely studied phase in bent core liquid crystals. Four different supramolecular packing arrangements are found to exist with two of them can form chiral conglomerates (SmC_{AP} , SmC_{SP}), while the other two appear as

racemates (SmC_sP_A , SmC_AP_F) [16, 17]. Ferroelectric switching is also observed in these phases, with a field-induced transition from antiferroelectric to ferroelectric. The observed saturation values for the spontaneous polarization are high ($P_s = 350 \text{ nC/cm}^2$) (and in some compounds as large as 1000 nC/cm^2). In addition, the nonlinear second-order susceptibility for second harmonic generation (SHG) is very large ($d_{11} = 10 \text{ pm/V}$) and the SHG properties are comparable to inorganic materials. Moreover these materials exhibit liquid crystalline behaviour.

2.2. Materials suitable for ferroelectricity:

Introduction of polar symmetry [11] in a system is the necessary requirement for the formation of ferroelectric liquid crystal which can be obtained by the introduction of the essential requirements viz., chirality of the molecules and their tilted association in smectic layers, leading to reduced symmetry, to form conventional ferroelectric liquid crystals in 1976. However in 1996, the necessary requirements has been replaced by the shape factor, i.e., banana shaped achiral molecules, to induce polar C_{2v} symmetry which has been implicated by the efficient, tilted packing of the banana shaped molecules into a smectic layer, with the direction of spontaneous polarization parallel to two-fold symmetry axis. Hence the tilt of the molecules on the one hand and the polar order of the bent molecules on the other hand are two independent symmetry breaking factors, which cause a chirality of the smectic layers, where the handedness depends on the tilt direction of the molecules. These materials have become potentially promising candidates for basic as well as application oriented research in this decade and shall continue to do so in future as evidenced by the stream of reports appearing in literature currently.

2.3. Design of the molecules:

The possibility of designing and using achiral bent shaped liquid crystalline molecular materials suitable for technical applications in future depends on the understanding of structure–property relationships. Even though a good number of new achiral liquid crystalline molecules are synthesized, few of them have been

examined for their electro-optic and NLO characteristics [4-10] a large pool of substances is a very important condition for extensive physical measurements. Few of the important challenges are chemical stability to atmospheric conditions, position of substituents which can affect leading to loss of banana liquid crystalline behaviour, influence of substituents to enhance NLO characteristics etc. The bent shape of these molecules results from a central 1,3-phenylene (or modifying the ring C by 2,7-naphthalene [4] unit) and compounds with five, six or seven aromatic (or heterocyclic) rings have been synthesized [12, 13]. Nonetheless, most banana-shaped liquid crystals reported up to now correspond to five-ring mesogens with a 1,3-phenylene central unit as shown in **Figure 2.2**.

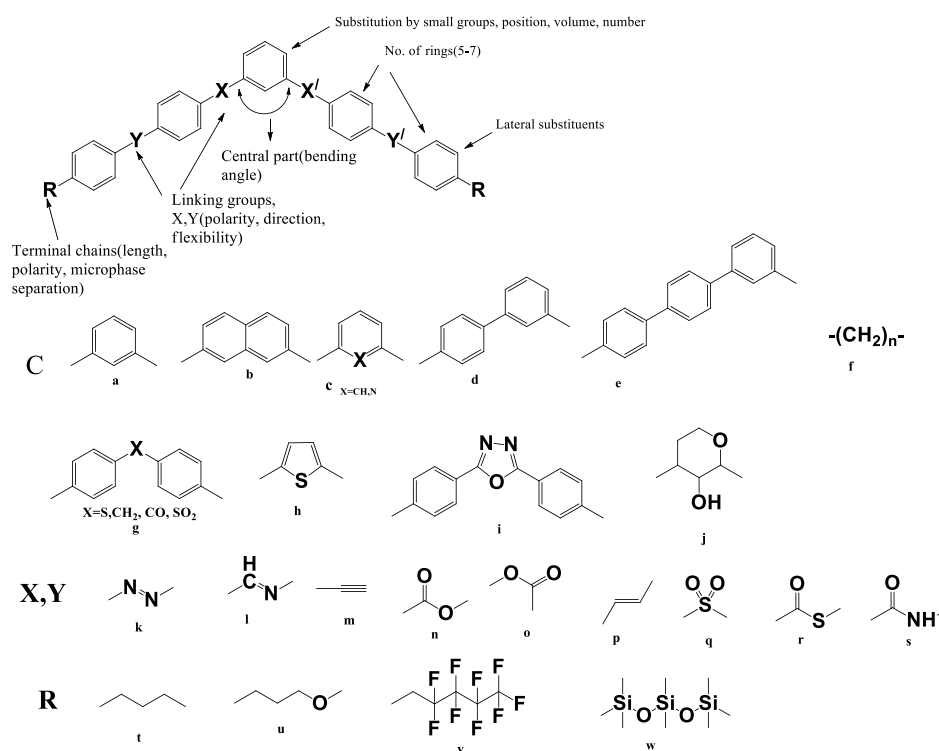
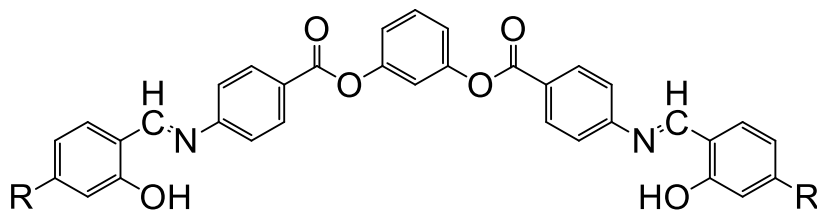


Figure 2.2: Skeleton of a banana shaped liquid crystal (top). Central bent core C (a-j), linking groups X,Y (k-s) and end chain R (t-w) (bottom) used so far in designing banana shaped liquid crystal.

On the basis of this general formula, different chemical modifications can be considered and according to the available data [12, 13] each alteration can lead to a change in or even to the loss of the liquid crystalline properties. The reasons for this are still not clear. The influence of the nature, position and direction of the linking groups X, Y, X' and Y' appears very strong. In fact the compounds with

azomethine and carboxylic linkages ($Y = -N=CH-$, $X = -COO-$, $X' = -OOC-$, $Y' = -CH=N$) exhibit banana liquid crystalline phases, while the simple inversion of the sense of linking groups, $X (-CH=N-)$ and $X' (-N=CH-)$, leads to the disappearance of these mesophases. It appears that connecting groups correspond to an alternating distribution of the electronic density throughout the molecules which favour the liquid crystalline properties.

The nature and position of the lateral substituents have strong influence on the liquid crystalline properties of the banana-shaped compounds. However the major drawback in all these compounds exhibiting banana phases is their limited hydrolytic, thermal, and photochemical stability due to the presence of the $CH=N$ group which can be overcome either by replacing the imine linkage by ester linkage ($Y=COO$) or by the introduction of O-hydroxy group with imine linkage promoting to form intermolecular H-bonding to yield a stable molecule. The physical studies reported in SmC^* materials, are being complicated by the hydrolytic instability of the molecules. As pointed out earlier the resorcyldiene aniline core actually seems superior to the benzylidene aniline core with respect to exhibiting tilted phases, mesogenicity, and is more stable towards hydrolysis. Recently new achiral electro-optically active bow-phase materials [14, 15] (figure 2.3) are reported, exhibiting potentially useful high strength analog electro-optics in standard LC cells (V-shaped switching). If the linkages ' Y ' = *resorcyldiene* and ' X ' = $-COO-$ between the phenyl rings of figure 2.2 respectively are swapped, the molecule in figure 2.3 becomes a molecule shown in figure 2.4. The O-hydroxyl groups in the ring of figure 2.4 not only promotes H-bonding and thereby stabilizing the compound but can also promote metal complexation to replace the non-liquid crystalline inorganic materials.



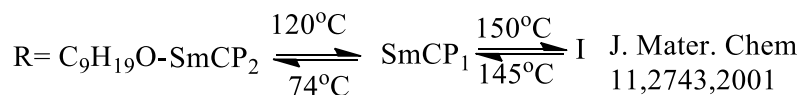
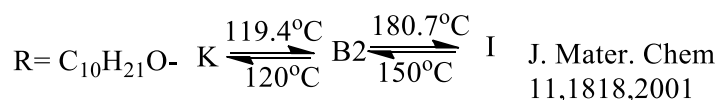


Figure 2.3: Reported molecule containing ester and imine as linking group.

Modification of the initial structure with an O-hydroxyl group, attached at position 2 of the phenyl ring B (**Figure 2.4a**) yielded banana liquid crystalline phases. Further by introducing lateral substituents in the central ring 'C' like nitro group with its large dipole moment and pronounced electron-attracting ability offers a path to drastically change the electron distribution in the aromatic core. This has been used to enhance NLO-effects such as second harmonic generation (SHG) in liquid crystals and in liquid crystalline polymers. Further, the introduction of a nitro group on position 4 of the central ring (figure 2.4b) induces new mesophases. We synthesized few homologues in our laboratory the preliminary studies [18] of which are encouraging. Hence systematic studies are to be performed in a particular homologous series to arrive at the importance of the lateral substituents attached to the central ring. Rao *et al.* have also reported the effect of fluoro substituent on 4-position of the central diamine core.

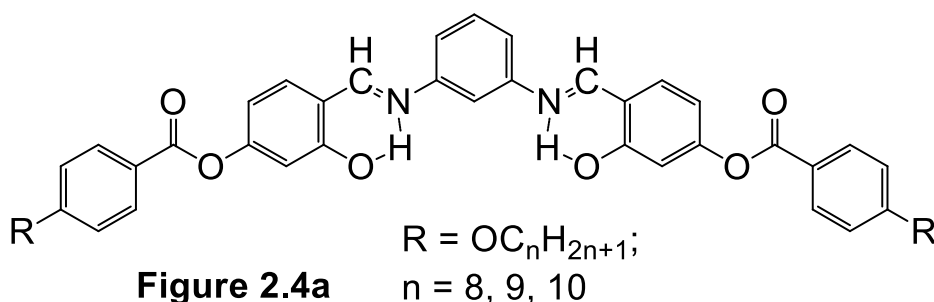


Figure 2.4a: Modification of molecule in fig.2 with an O-hydroxyl group.

The studies on the influence of substituents on the intermediate or outer rings are very few and meagre [19]. The influence of chain length played an important role in the nature of banana phases exhibited by bent shaped compounds.

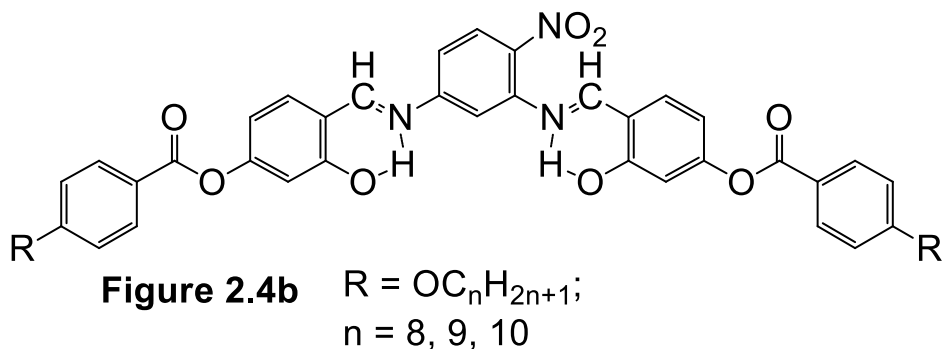


Figure 2.4b: Five ring compound containing nitro group as substituent.

Influence of chain length on fluoro substituted banana shaped liquid crystals was reported by Rao et.al [18b].

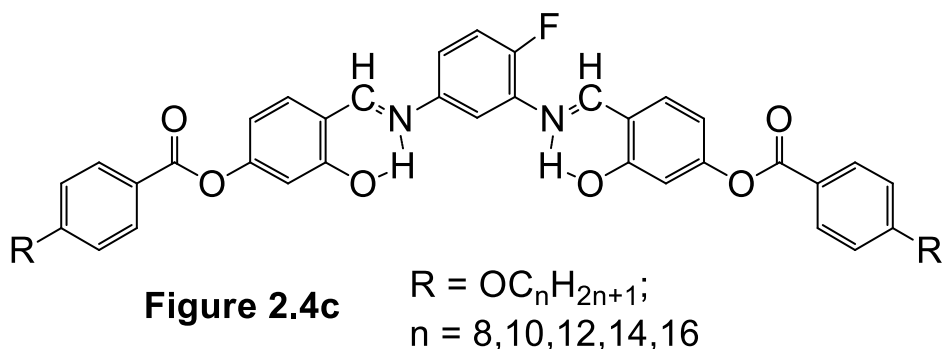


Figure 2.4c: Five ring compound reported by Rao et al containing fluoro group as substituent.

Banana-shaped compounds depending on the length of the alkyl or alkyloxy or alkylthio terminal chains, show two or three different mesophases which is rather subtle and complex unlike that in calamitic mesogens. Nevertheless, in a homologous series, the short homologues produces an intercalated banana “B6” and/or a two dimensional “B1 phase” while the long chain derivatives show a switchable lamellar “B2 phase”. Depending on the length or on the nature of the terminal chains, other systems present [20, 21] a more complex evolution of the polymorphism.

The influence of a lateral fluorine or chlorine or methyl substituents in the terminal or outer phenyl ring gave evidence of the subtle relationship between the chemical structure and mesomorphic properties of banana compounds. Further, lateral substituents can cause steric effects and thereby the Van der Waals volume of the substituents is usually more important with respect to phase behaviour than

dipolar interactions. The more detailed influences of lateral substituents depend on the structure of the rigid core and the position of the substituents. Further lateral substitution in calamitic or conventional liquid crystals enhances the molecular width and leads to a larger interpenetration of the terminal chains and decrease in molecular layer spacing and sometimes the nature of phase also changes. Generalizations are difficult; since the effects differ between polar and non-polar mesogens. Moreover the molecular organization of bent-shaped compounds is a result of a complex and subtle balance between the electrostatic interactions and the Van der Waals interactions developed by the aliphatic chains. Thus the distribution of the electrostatic potential maximum (extrema) along the molecule will strongly influence the molecular arrangement and the nature of the mesophases. Hence sufficient data is necessary to arrive at generalized conclusions between structure-property relationship and their suitability in practical applications.

Weissflog *et al* [13] from Germany, reported antiferroelectric current response while Heppke *et al* [20] observed ferroelectric current dynamics in several other homologues. The discovery of the spontaneous formation of macroscopic chiral domains in smectic phases in achiral bow-shaped molecules by Clark, Walba and co-workers [14, 16, 17] in USA has dramatically enlarged the scope of the research on chiral/polar smectics. These materials exhibit several completely new phases of matter, (based on recent history) and are quite likely to have more surprises in store. Using detailed electro-optic investigations they gave evidence [14, 16, 17] that polar packed molecules are tilted with respect to layer normal. Most of the materials, which have been reported to exhibit banana liquid crystalline phases invariably, possess Schiff's base imine linkage and a major drawback of these compounds is their limited thermal, hydrolytic and photochemical stability. Hence all the physical studies can be complicated by the hydrolytic instability of the molecules. Even though Tschierske *et al* reported banana liquid crystalline mesogens, exhibiting ferroelectric and antiferroelectric properties, without Schiff's base units [23-25], variations in the substituents on the bis-Schiff's base bent-core system have proven remarkably useful for providing interesting polar smectics. The resorcyldiene aniline core, present in

calamitic ferroelectric liquid crystals, actually seems superior to the benzylidene aniline core with respect to mesogenicity, and is more stable towards hydrolysis. This core also played a key role in the first discovery of antiferroelectric phase from achiral molecules, being the core present in the pioneering Soto-Bustamante-Blinov anticlinic bilayer antiferroelectric phase (SmAP_A) [11]. Hence introduction of *o*-hydroxyl group to Schiff's base imine linkage not only stabilizes the material to hydrolysis but also enhances the tilted phases due to transverse dipole moment.

2.4. Influence of terminal chain lengths:

The investigation of the relationship between the molecular structure and mesomorphic properties is very important and essential to liquid crystal chemistry. Hence designing a bent shaped molecule with systematic structural variation and synthesis of such designed compounds has to be carried out for systematic investigations in a large number of compounds of different homologous series exhibiting liquid crystalline behaviour to examine the relationship between the chemical structures and their physical properties, particularly the polar orders in the bent-core mesogens. For that purpose, new synthetic methods have to be developed; a large number of compounds are required for any generalizations to be arrived. Excellent reviews [26, 27] appeared recently describing the chiral and polar properties of the compounds, ferroelectric and/or antiferroelectric properties, chirality and optical properties, molecular structure in different phases, origin of chirality, influence of substituents, nature of central core, number of phenyl rings, influence of nature and position of substituent in central core as well as outer rings in the wings of bent molecule.

Since the discovery of polar switching in a bent-core liquid crystal [1] extensive research activity has led to a new era of liquid crystal science particularly in view of polarity and chirality [26, 27]. Lee *et al.* reported [28-32] the emergence of ferroelectricity and antiferroelectricity which is dependent on the number of carbons and position of the chiral carbon along the terminal chains in banana shaped molecules of two homologous series of chiral bent core mesogens viz., 1,3-phenylene bis[4-(4-alkoxyphenyliminomethyl)]benzoates **Figure 2.5a** and their oxygen analogues possessing ω -(S)-amyloxy terminal groups, **Figure 2.5b**.

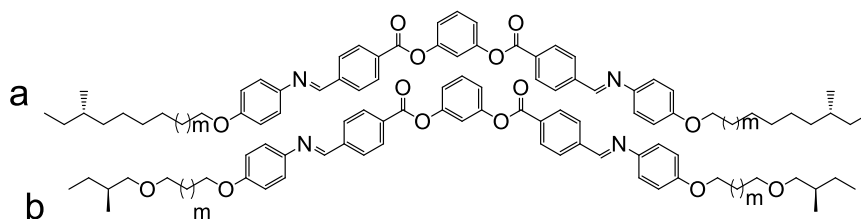


Figure 2.5: 1,3-phenylene bis[4-(4-8-alkoxyphenyliminomethyl)- benzoates]

Figure 2.5: Lee et al reported five ring compound containing chiral carbon in the terminal chains.

These achiral molecules spontaneously resolve into chiral domains and exhibit ferroelectric and antiferroelectric phases depending on odd and even of the end chain length in two homologous series (eight compounds) of bent-core liquid crystals. They further demonstrated that the interlayer steric interaction is very important for the selection of polar orders. Since many bent-core mesogens exhibit the antiferroelectric phase, such studies are expected to provide guidelines for the molecular designs to realize the ferroelectric phase.

Several bent core compounds **Figure 2.6**, without imine linkage was reported by Tschierske *et al.* [33-36] in recent years. They also reported several polyphilic molecules composed of a bent aromatic core, oligo (siloxane) units, and alkyl segments were synthesized, and the self-organization of these molecules was investigated. Most materials organize into polar smectic liquid crystalline phases. With increasing segregation of the silylated segments, the switching process of these mesophases changes from antiferroelectric for the nonsilylated compounds via super paraelectric to surface-stabilized ferroelectric.

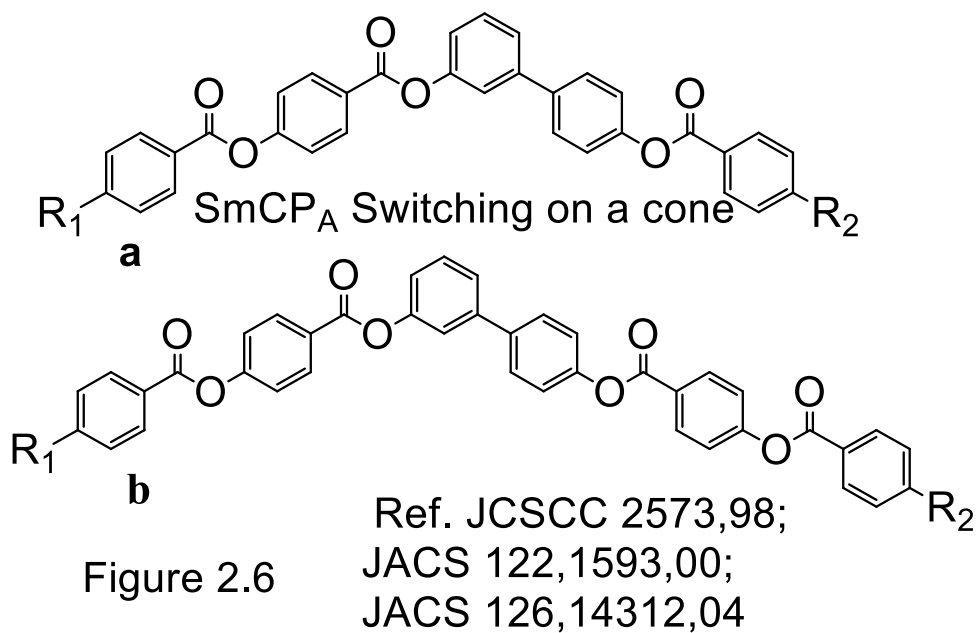


Figure 2.6

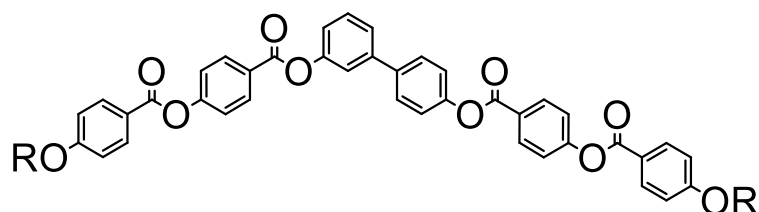
Figure 2.6: Tschierske et al reported several bent core compound without imine linkage.

They had proposed that the siloxane sublayers stabilize a polar synclinal ferroelectric (SmC_sP_F) structure, based on the response to electric field and the escape from a macroscopic polar order as well as steric effects leads to a deformation of the layers with formation of disordered micro-domains, giving rise to optical isotropy. The spontaneous formation of chiral domains with opposite handedness is another striking feature. For two compounds, a temperature-dependent inversion of the optical rotation of these domains was found, which is associated with an increase of the tilt angle of the molecules from $<45^\circ$ to $>50^\circ$. This observation confirms that it is a new source of optical activity in supramolecular systems. With the increasing alkyl chain length the phase segregation is lost and a transition from smectic to a columnar phase. In the columnar phase, the switching process is antiferroelectric and takes place by rotation of the molecules around the long axes, which reverses the layer chirality; that is, upon application of an electric field, the racemic ground-state structure is switched into a homogeneous chiral structure.

The presence of cis double bonds (**Table 2.1**) which increase the flexibility of the chains, does not decrease the clearing temperatures significantly, but drastically reduces the melting points, leading to bent-core mesogens with glassy polar

smectic phases [36]. Also branching of the chains is of great importance and can give rise to low melting points and glassy materials [36b]. Even more importantly, branching can lead to a transition from AF to FE smectic phases [4b] as well as to B7 subtypes due to changes at the interlayer interfaces.

Table 2.1: Comparison of the mesophases shown by compounds containing different types of terminal chains



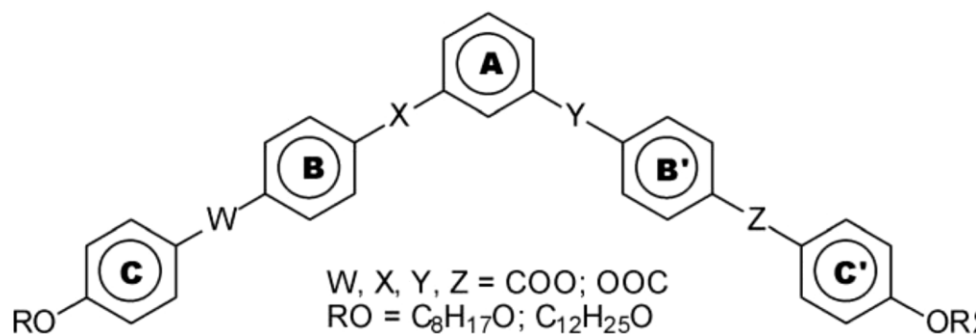
The Terminal Chain (R)	Phase transitions(°C)	References
C ₁₀ H ₂₁	Cr 119 Col _r 166 I	23
C ₁₂ H ₂₅	Cr 106 SmCP _A 159 I	36d
(CH ₂) ₉ CH=CH ₂	Cr 99 Col _r 146 I	36e
(CH ₂) ₁₀ CH=CHCH ₃ (cis)	Cr 28 SmCP _A 125 I	36a
(CH ₂) ₅ -CH=CHC ₅ H ₁₇ (cis)	Cr 28 SmCP _A 122 I	36a
(CH ₂) ₁₁ OOCCH=CH ₂	Cr 50 SmCP _A 102 I	36a
(CH ₂) ₁₁ OOC(CH ₃)=CH ₂	Cr 50 SmCP _A 107 I	36a
(CH ₂ CH ₂ O) ₄ CH ₃	Cr 22 SmCP _A 62 I	36a
(CH ₂) ₁₁ SiMe ₂ OSiMe ₂ OSiMe ₃	Cr 87 USmCP _A 142 Col _{ob} PA155I	36c
(CH ₂) ₆ C ₄ F ₉	Cr 127 SmCP _A 213 I	23

2.5. Effect of linking groups in bent core molecules:

The role of direction of the linkage groups on banana shaped liquid crystals has been reported by Weissflog *et al.* [37] as detailed in **Table 2.2**. For this reason they have synthesized two series of isomeric five-ring bent core mesogens with equal length of the terminal chains (octyloxy and dodecyloxy), which contain only carboxyl linkage groups. All possible 10 isomers are presented which are different from each other by the direction of at least one linkage group. The

mesophase behaviour and the physical properties vary significantly and the influence of direction of the carboxyl linkage groups in both series of isomeric compounds is demonstrated. The direction of connecting groups between aromatic rings in calamitic liquid crystals can also influence the mesophase behaviour, but not as prominent as in these compounds.

Table 2.2: Influence of direction of ester linkage on mesophase behaviour.



W	X	Y	Z	Cr		SmCP		Col		I
COO	COO	OOC	OOC	•	109	•	119	-		•
COO	OOC	COO	OOC	•	157	-		-		•
OOC	COO	OOC	COO	•	152	-		•	162	•
OOC	OOC	COO	COO	•	191	-		•	189	•
COO	COO	COO	COO	•	105	-		•	140	•
COO	COO	COO	OOC	•	120	•	112	-		•
COO	COO	OOC	COO	•	110	•	133	-	168	•
COO	OOC	COO	COO	•	142	•	158	•	144	•
COO	OOC	OOC	COO	•	146	-		•	168	•
OOC	COO	COO	COO	•	138	-		•		•

Novel five ring bent core systems possessing only ester as connecting groups between the aromatic phenyl rings was reported by Weissflog *et al.* [37] and different lateral substituents at the central phenyl ring viz., 1,3-phenylene bis[4'-(4''-alkoxyphenoxy)carbonyl]benzoates **Figure 2.7a** and isomeric 1,3-phenylene bis-[4'-(4''-dodecyloxybenzoyloxy)benzoates **Figure 2.7b** with alkyl chain length of octyloxy or larger are presented. They demonstrated that the influence of

lateral substituents on the banana mesomorphism is much more pronounced than in the calamitic compounds.

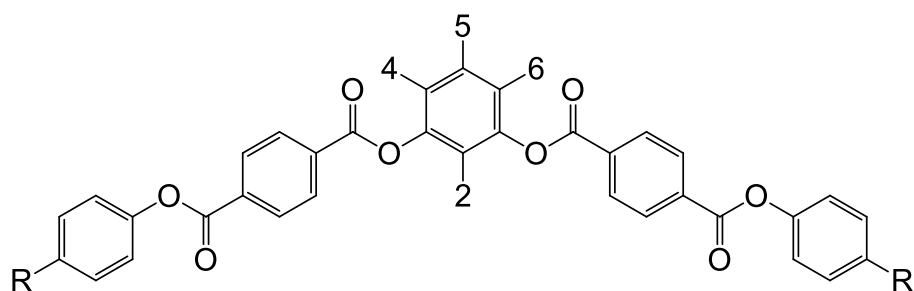


Figure 2.7a $R=OC_nH_{2n+1}$ $n= 8,12,14,16$

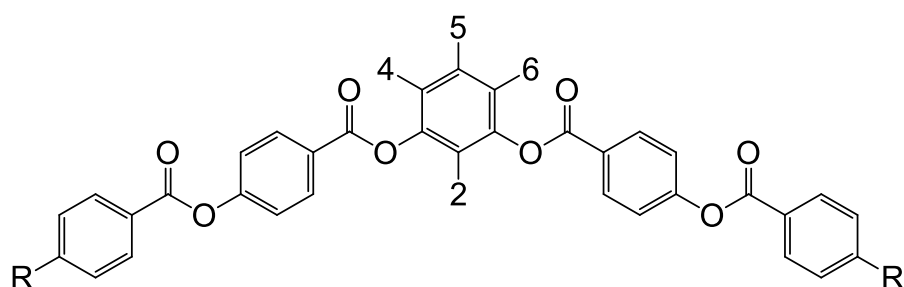


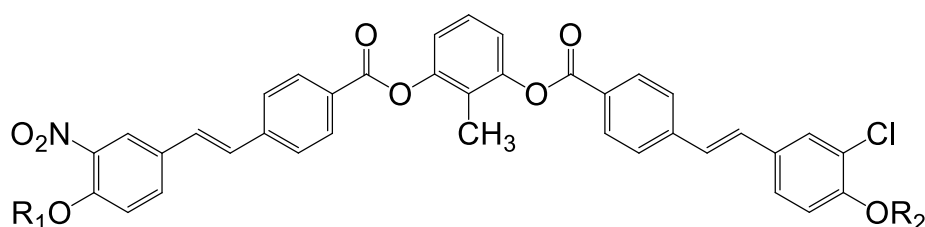
Figure 2.7b $R=OC_nH_{2n+1}$ $n= 12$

Figure 2.7: Five rings bent core system reported by Weissflog et al.

They also found that mesomorphism strongly depends on the position of the lateral substituents. Compounds, derived from 4-cyano-, 4-chloro- and 4,6-dichloro-resorcinol, show polymorphism variants where polar phases (SmAP, SmCP) occur together with nematic and conventional smectic phases, e.g. SmA–SmAP, SmA–SmC_SP_A–Col_{ob}–SmC_SP_A, N–SmA–SmCP_A, SmA–SmC–SmCP_A and SmC–SmCP_A. On the basis of the behaviour of two series of materials, the occurrence of different polar-switching mechanisms had been demonstrated. Apart from the usual mechanism by director rotation around the tilt cone, the polar switching can also take place through collective rotation of the molecules around their long axes in SmCP_A, and SmCP_F phases, which corresponds to a field-induced switching of the layer chirality viz., coupling of reversal of layer chirality with field reversal. A remarkable finding is the polar switching in the crystalline modification of long-chain, bent-core compounds with a methyl group in 2-position, which is accompanied by a clear change of the optical texture and by a relatively high switching polarization (approx. 600 nC/cm²). It was found for selected laterally substituted bent-core compounds that, above the transition

temperature of a polar to a non-polar phase, the non-polar phase can be transformed to the polar phase by application of an electric field, which was proved for the transitions isotropic–SmCP_F, SmA–SmCP_F and isotropic–CrII polar phase.

Recently, two different types of homologous series of compounds **Figure 2.8 and 2.9**, exhibiting orthogonal polar smectic A phases were reported by Gomola *et al.* [38, 39]. Three series of asymmetric bent-core compounds were synthesized and their mesomorphic properties were studied. All the compounds in these series possess 2-methylresorcinol as a central unit, nitro and/or chloro substituents in the outermost rings with a stilbene moiety as linking group between two outer phenyl rings as a main element in the structure. Molecules of series 1 and series 2 possess only saturated terminal chains while those of series 3 have one or both unsaturated chain(s). All the compounds exhibit the isotropic to uniaxial orthogonal phase with ferroelectric properties SmAP_R phase transition and the B1_{RevTilted} phase at lower temperatures. For compounds with one olefinic terminal chain, the temperature range of the SmAP_R phase was found to be narrower in comparison to compounds with both saturated terminal chains. Dielectric investigation inferred that both the SmAP_R and B1_{RevTilted} phases and two different types of dynamical behaviour were observed.



Series 1: R₁ = C₁₂H₂₅; R₂ = C_nH_{2n+1}, n = 5,7,8,10-16,18

Series 2: R₁ = C₁₂H₂₅; R₂ = C_nH_{2n+1}, n = 13-16

Series 3: R₁ = C₁₁H₂₃; R₂ = C_nH_{2n+1}, n = 11,12,14,16,18

Figure 2.8

Figure 2.8: Homologous series of five ring compound reported by Gomola *et al.* The symmetric compounds with 2-acetyl groups exhibited polarization randomised non-tilted smectic A (SmAP_R) and room temperature non-tilted smectic (SmAP_A) phases, which is the first example of polar biaxial Smectic A to polar uniaxial smectic A phase.

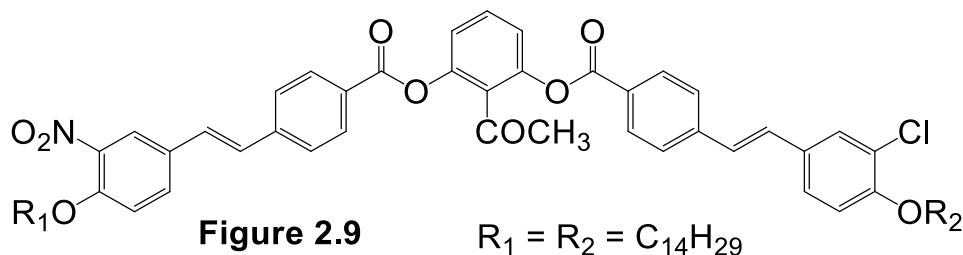


Figure 2.9: Five ring bent molecule with ethylene linkage reported by Gomola et al.

Nguyen *et al.* [40], Weissflog *et al.* [41] reported the five ring banana shaped molecules derived from isophthalic acids, as shown in **Figure 2.10b** and **2.10c**, apart from different substituted compounds (**Figure 2.10a**). Several mesophases with switching properties are detected by a combination of several linking groups and different selected substituents either on the outer ring or on the central ring. Their studies revealed new structural modifications and also the importance of alkyl chain length on banana polymorphism. They demonstrated the importance of the nature of lateral substituent and its position on the central ring in influencing the liquid crystalline properties. Further they also reported the importance of the nature and the sense of the linking groups and also the sense of bridging group of the central linking group in deciding the rigidity of the molecule and conformational freedom in exhibiting switchable banana phases. They reported B1, and B6 phases in lower homologues and B2 phase in higher homologues in bent shaped molecules possessing a thio ester linkage. They also reported ferroelectric switching behaviour for a B7 phase in fluoro substituted bent-core molecules in peripheral positions on the aromatic core, ortho to each of the two terminal alkoxy chains. This special substitution pattern seems to be a quite useful structural unit for the formation of ferroelectric switchable banana phases, which was evidenced in fluoro substituted compounds [42, 43]. Nguyen *et al.* reported [40g] derivatives of esters of isophthalic acids (**Figure 2.10b**), which exhibited conventional SmC and nematic phase, while the compounds substituted with a fluorine atom ($X = F$) exhibited switchable phases. The fluorine derivatives exhibited four smectic phases without in-plane order but the structure of the mesophase are not yet known. The derivatives of isophthalic acid esters with five-ring banana-shaped mesogens [41a] (**Figure 2.10c**), which are

distinguished by the linkage between the aromatic rings and the bromine substitution in the 4-position, decreases the melting and clearing temperatures as compared to those of the analogous unsubstituted compounds which exhibited B2 phase. The synthesis of new bent-core derivatives (**Figure 2.10d**) with ethylene linkage in banana branches instead of an imine or ester linkage and incorporating lateral substituents like fluorine or iodine atoms were reported by Mieczkowski *et al.*[44] which exhibited B7 and B2 phases with anticlinic ($\text{SmC}_{\text{A}}\text{P}_{\text{A}}$) or synclinic ($\text{SmC}_{\text{S}}\text{P}_{\text{A}}$) interlayer structures, depending on the central ligand and lateral substituent and also found lower transition temperatures than the unsubstituted analogues. The $\text{SmC}_{\text{A}}\text{P}_{\text{A}}$ phase exhibited strong optical activity and chiral domain segregation could be induced by applying a weak electric field in these compounds. The homologous series of $\text{N,N}'$ -bis[4-(4-*n*-alkoxybenzoyloxy)benzylidene] phenylene 1,3-diamines, shown in **Figure 2.10e**, exhibited interesting mesomorphism [41b]. The lower homologues ($n = 1-6$) form a intercalated B6 phases, the middle homologues ($n = 5-10$) form the two dimensional B1 phases, whereas the long chain members shows the switchable B2 phase. Therefore, systematic studies of homologues series are necessary for the clear understanding of the phase behaviour. Pelzl *et al.* reported [41c] a novel chiral banana shaped mesogens, derived from 4-chloro resorcinol (**Figure 2.10f**), exhibiting nematic phase with unusual optical and electro-optical properties. Kovalenko *et al.* [40] reported first examples of achiral banana shaped compound (**Figure 2.10g**) possessing perfluoroalkyl chain in the terminal position and lateral substituent at the top (or 5-position) of the central benzene ring exhibited B2 and SmA phases, characteristics for a bent and rod shaped molecules with reduced clearing and melting temperatures. Pelzl *et al.* reported [41d] the first banana phase, B6, found in Vorlander's achiral banana shaped compounds synthesized during 1900-29, which is shown in **Figure 2.10h**.

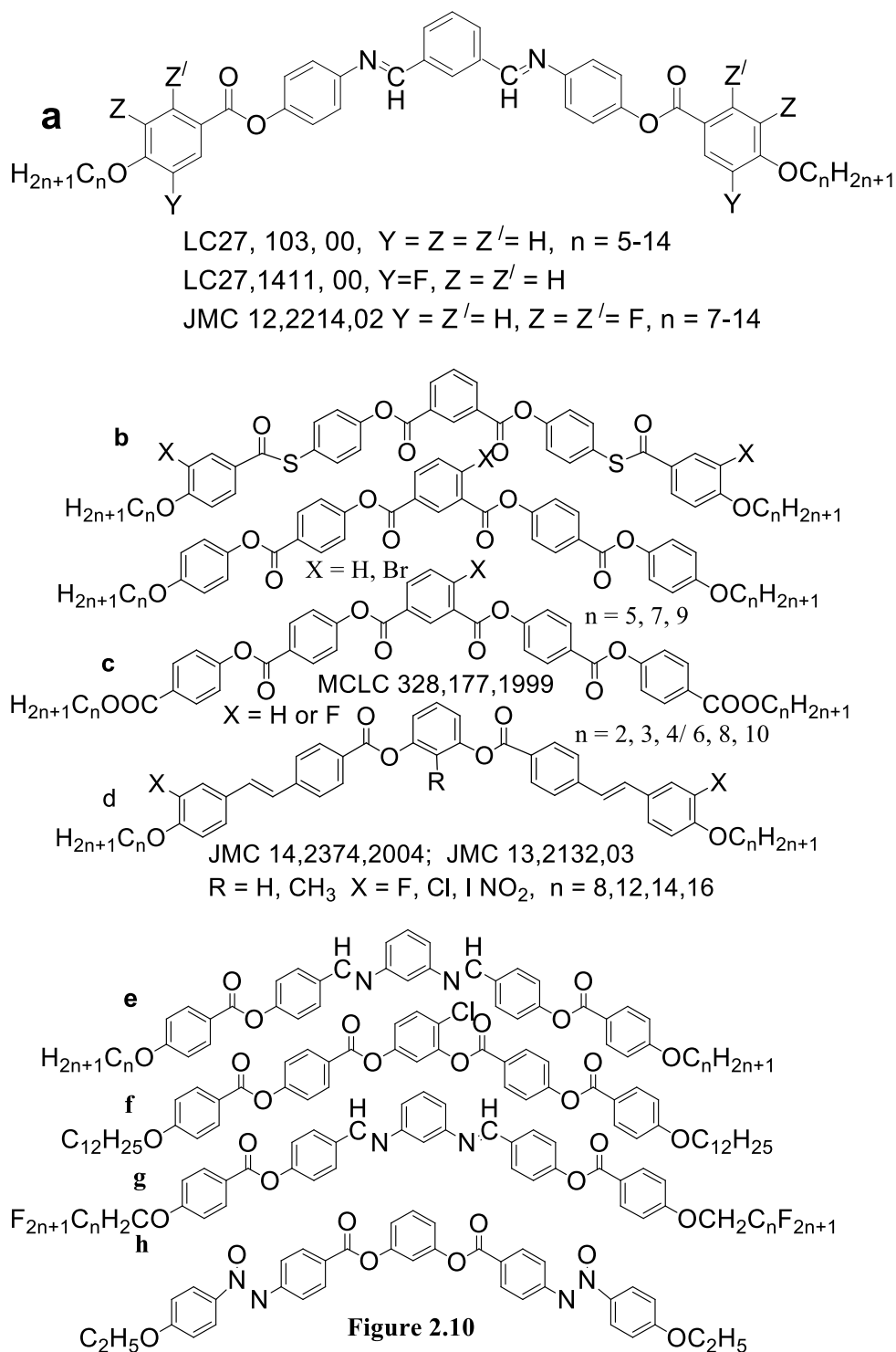


Figure 2.10a-e: Nguyen et al, Weissflog et al reported various five ring compounds; **f:** Pelzl *et al.* reported a novel chiral banana shaped mesogens, derived from 4-chloro resorcinol; **g:** Kovalenko *et al.* reported first examples of achiral banana shaped compound possessing perfluoroalkyl chain in the terminal position; **h:** Vorlander's compound in which B6 phase was reported by Pelzl et al.

Prasad *et al.* reported [45] first examples of achiral bent-core molecules (**Figure 2.11**) of five aromatic rings, linked through an azo linkage and with an imine and/or ester linkage, exhibiting B1 and B2 banana mesophases relatively at low transition temperatures and with wide temperature ranges. The B2 phase of these materials is identified to be the anticlinic–antiferroelectric, Sm_CAP_A phase. The observation of bent-core phases in azo compounds assumes significance from a new dimension, namely photochromism, with the introduction of the –N=N– linkage, to this field.

Figure 2.11

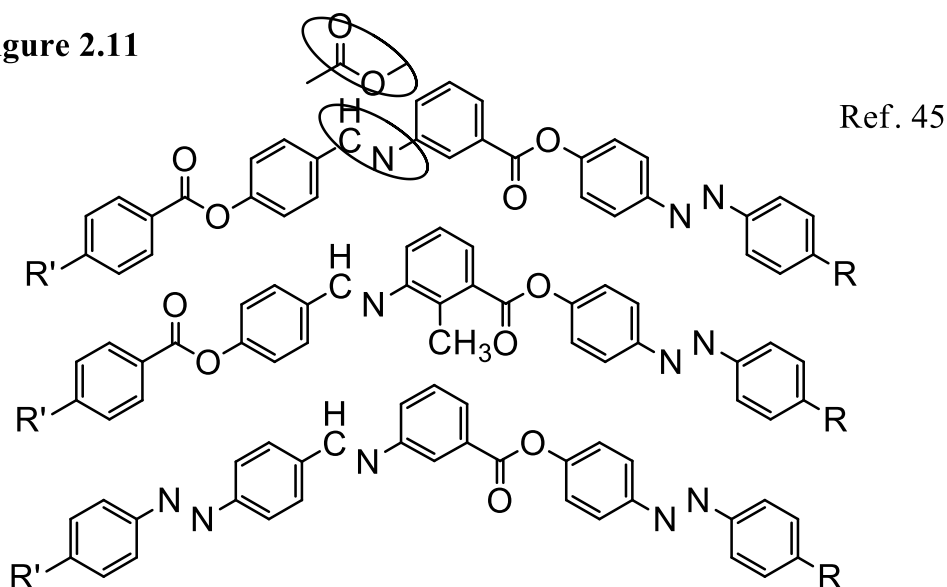


Figure 2.11: Prasad et al reported first examples of five ring bent core molecules linked by an azo linkage.

2.6. W-shaped compounds:

A new corner developed in banana liquid crystal when a W-shaped molecule PBPBTB exhibiting a sequence of different ferroelectric and antiferroelectric mesophases with anticlinical coupled double banana shape was reported by Kumar *et al.*[46a]. Molecules with analogous shaped dimer also exhibit a switching between ferroelectricity and antiferroelectricity [46b].

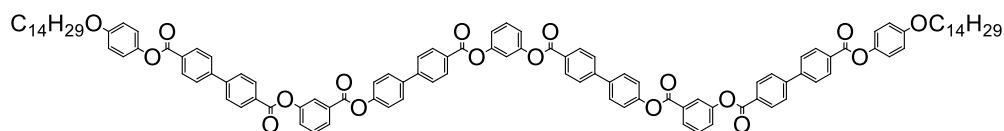


Figure 2.12a

Figure 2.12a: Kumar et al reported W-shaped molecule.

Rao *et al.* has reported W-shaped molecule (figure 2.12b) possessing a nitro group and two OH groups ortho to imine linkage to promote intramolecular hydrogen bonding, which deviates significantly from the typical V-shape of other bent core molecules. The compound exhibits chiral filament like domains [47] and also chiral domains of opposite handedness which can be seen in the birefringent phase by slightly decrossing the polarizers. This compound exhibits an unusual smectic mesophase with additional in plane order (Sm X2).

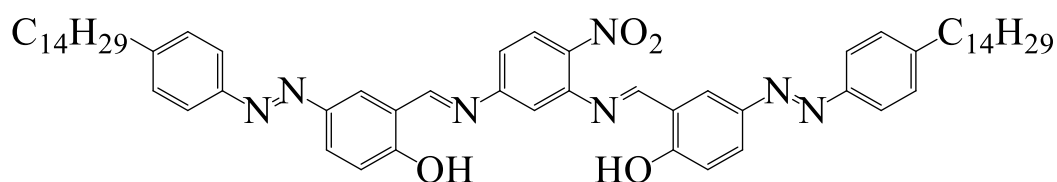


Figure 2.12b: Rao et al reported W-shaped molecule with an azo linkage.

2.7. Effect of substituents on banana shaped mesogens:

Sadashiva and coworkers reported several compounds exhibiting banana liquid crystalline behaviour during the last few years. The effect of a number of lateral substituent on the mesophase formed by compounds composed of achiral banana-shaped molecules viz., derivatives of resorcinol possessing seven aryl rings with ester linkages was first reported by Sadashiva *et al.* [52-58]. The synthesized compounds and the reported phases are shown in **Table 2.3**.

Table 2.3					

Chain length (n)	X	Y	Z	Phase sequence	Ref.
	H	H	H	B2, B1, B6	53
	F	H	H	B2, B1, B6	
5-12,	CH ₃	H	H	B2, B1, B6	

14,16,18					
	C ₂ H ₅	H	H	B2, B1, B6	
	H	F	H	B2, B1, B6	
7-12	H	H	H	B1 or B2	56
	H	F	H	B1	
10,11,12	H	Cl	H	B1	
	H	CH ₃	H	B1 or B2	
	H	OCH ₃	H	B1 or B2 monotropic	
5-12, 14,16,18	H	F	CN	B1 or B7	55
5,8-12, 14,16,18	F	H	CN	B1 or B7	55
8-12, 14,16,18	F	H	CH ₃	B1 B2	57
4-12	H	CH ₃	H	B2, B1, B6	58

Sadashiva *et al.* [59] also reported the synthesis and characterization of several compounds composed of highly polar unsymmetrically substituted esters of five ring bent core molecules, having the general molecular structure (**Figure 2.14**), exhibiting partial bilayer biaxial smectic A -uniaxial smectic A transition. The unsymmetrical molecule contains an n-alkoxy chain in one of the wings of the bent-core, while the other arm is terminally substituted with a highly polar cyano group. The partial bilayer biaxial smectic A (SmA_{db}) phase in which the bent cores of two neighbouring molecules overlap in an antiparallel orientation as in the case of highly polar lath-like molecules.

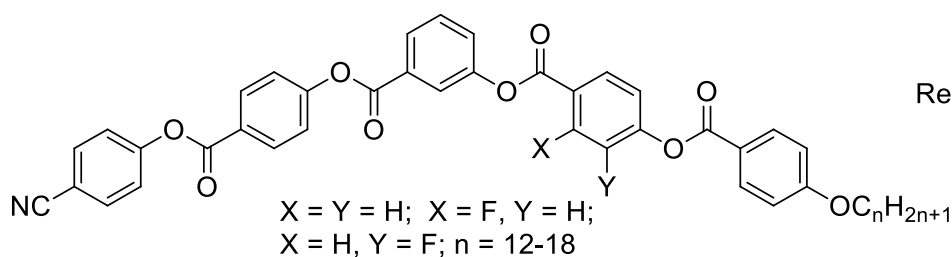
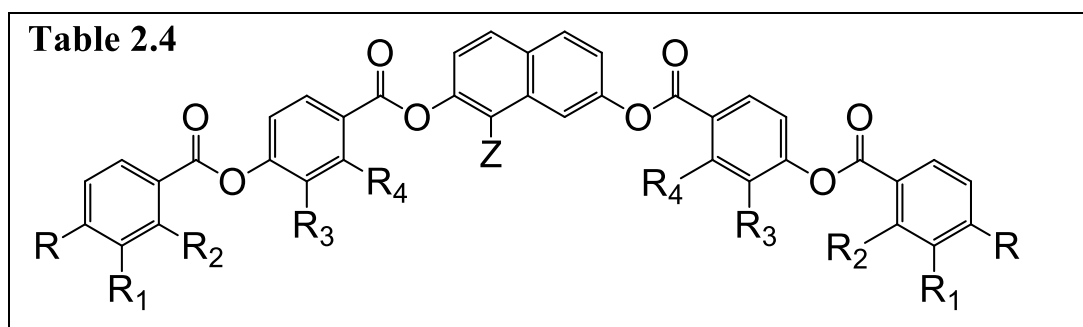


Figure 2.14

Figure 2.14: Sadashiva et al reported five ring system containing polar group in the terminal chain.

Reddy *et al.*, Thisayukata *et al.* reported the homologous series of bent shaped compounds containing 2,7-dihydroxynaphthalene [5,53,60] and 1,3-dihydroxybenzene (resorcinol) [60] as a central bridging unit with lateral fluoro substituent(s) on the inner or outer phenyl rings. Some of the homologous compounds exhibit switchable B2 phase. The lower homologous compound display only nematic phase and B1 phase where as higher homologous compound exhibits B2 and monotropic B3 phases or columnar phases depending upon the number and position of fluoro substituents. The lateral fluoro-substituents not only lower the clearing transition temperature of the parent compound but also in lower homologous series displays monotropic nematic phase. The compounds with lateral fluoro substituent meta to ester linkage of the end phenyl ring exhibit B3 phase. The work can be summarized as follows. They have synthesized derivatives of resorcinol and 2,7-naphthol with either two or three rings in the wings of the molecule and studied structure-mesomorphism relationship with different substituents either on the central core ring or in the rings of the wing as shown in **Table 2.4**. The salient features are that some of these compounds are to exhibit ferroelectric properties, chiral behavior, biaxial phases, columnar phases and, calamitic phases depending on the position and nature of substituent. All the compounds are esters and are thermally stable. Several novel columnar (switchable and non switchable), ferroelectric and anti ferroelectric phases have been reported in the banana shaped mesogens derived from symmetric 2,7-dihydroxynaphthalene and 1,3-dihydroxyderivatives (**Table 2.4**) [53, 60].



Chain length(R)	R1	R2	R3	R4	Z	Phase variants	Ref
n = 5-12, 14,16, 18	H	H	H	H	H	B1 or B2	60
n =1-12, 14,16, 18	H	H	H	F	H	B1,N or B2	
n=4-12, 14,16, 18	H	H	F	H	H	B1,N or B3, B2	60
n = 7-9	H	H	H	H	H	B1	61

Chain length(R)	R1	R2	R3	R4	Z	Phase variants	Ref
n = 5-12,14,16,18,6-Me-8*	H	H	H	H	H	Sm3,Sm2, Sm1	3, 5
n = 6, 8, 10,12	H	H	H	H	H	BX,	62 62 62 62
n = 6, 8, 10,12	H	H	H	H	CH ₃	B2,	
n = 6, 8, 10,12	H	H	H	H	CN	B2'-B2''-N	
n = 6, 8, 10,12	H	H	H	H	Cl	B2	

2.8 Calamitic compounds with a spacer in the central unit:

Watanabe *et al.* reported [48, 49] interesting mesophases (banana leaf like textures in $(C_2H_2)_5$ spacer), exhibited by the dimeric systems (**Figure 2.13a**) depending upon the number of carbon atoms (parity) in the spacer joining the two aromatic fragments with alkyl or alkoxy end chains. Further such achiral systems exhibit antiferroelectric or nonferroelectric switching behaviour under the influence of triangular wave electric field provided the odd alkylene spacer (which genuinely promotes bent shape) and tail parts of the dimer segregate to form smectic layers. Moreover second harmonic generation studies [48] confirmed the growth of macroscopic polar order under the influence of electric field in dimeric molecules. The homologous series of symmetric dimeric liquid crystals, where two-ring or three-ring mesogenic units are connected by a bis (carbonyloxy) propylene spacer (**Figure 2.13b, c**), exhibited conventional calamitic smectic phases [50]. The most interesting result is the inverse phase sequence SmA to SmC has been observed with increasing temperature in compounds of three ring mesogenic units. Ferroelectric switching behaviour is also reported [51] in bent shaped mesogens (**Figure 2.13d**) possessing non-mesogenic units linked by alkylene spacer by interchanging the ester linkage with imine linkage unit in the non mesogenic unit.

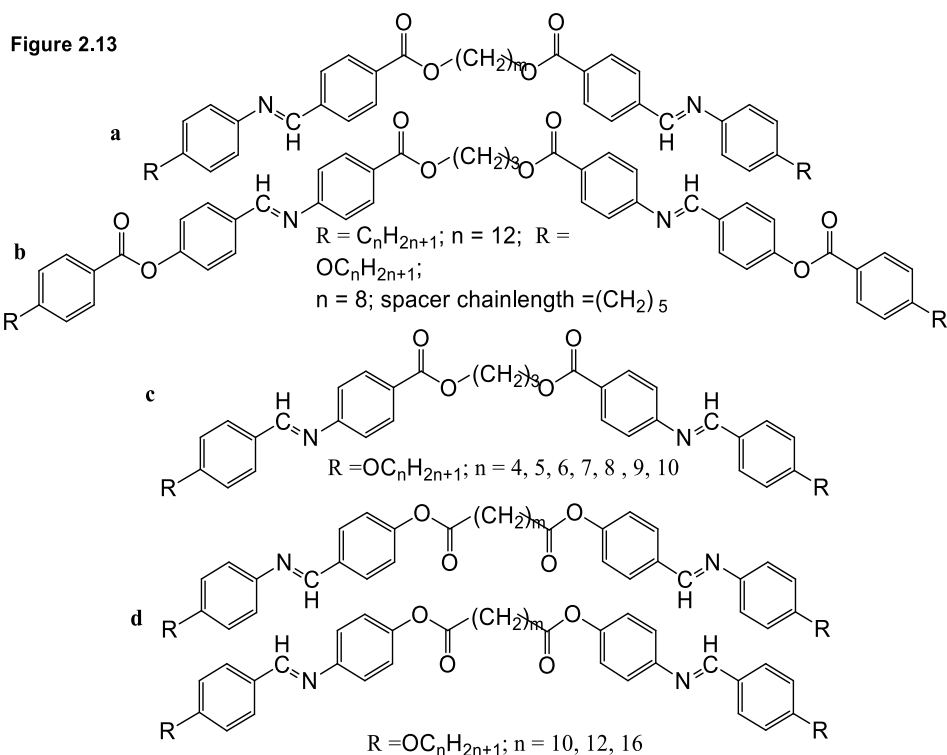


Figure 2.13a-d: Watanabe et al reported banana leaf like textures in dimeric systems.

2.9. Four-ring bent shaped liquid crystals:

The reported results on four-ring bent-core compounds till date are meagre and there were no sufficient and specific report in literature to understand or speculate their mesophase behaviour. The reported results pointed towards the classical phases exhibited by calamitic compounds and hence the speculation suggested that they may not be able to form typical banana-phases (SmAP, SmCP) spontaneously because the required shape/steric as well as core-core interactions between bent molecules are too small and are not sufficient enough to induce banana mesomorphism. Hence the four-ring bent-core molecules has been classified as intermediate between the banana-shaped (five or six or seven ring systems) and hockey stick (i.e., calamitic mesogens with an alkyl end chain in the meta position of a calamitic molecule) shaped compounds. The design and synthesis of four-ring architectures exhibiting mesomorphism and further investigations on these compounds are at the boundary between calamitic and banana-shaped liquid crystals to make them a new field of liquid crystal research opening many new questions. Hence it is a significant challenge to design and

tune the four-ring bent-core molecules to obtain banana LC phases at the primary level and then to generate nematic phases at a distinct level.

Bent core mesogen derived from oxadiazole (**Figure 2.15**) as central core with a bent angle of $\sim 134^\circ$ which is larger than the common bent angle of 120° found in 1,3-substituted phenyl or 2,7-substituted naphthalene derivatives exhibiting LC polymorphism have been reported by Kang *et al.* [63]. This compound exhibits nematic, SmC and an optically isotropic uniaxial Bx phase with randomly distributed domains of opposite handedness. The Bx phase under the influence of electric field transformed into a birefringent phase with homochiral SmC_{APF} structure.

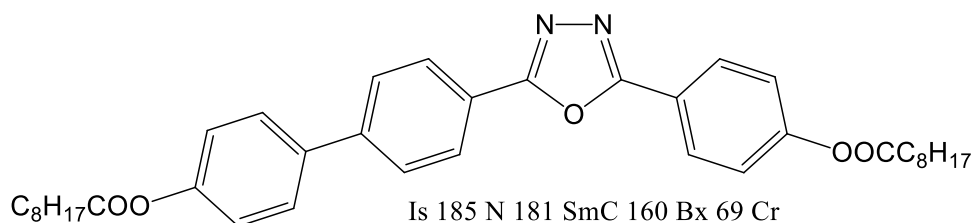
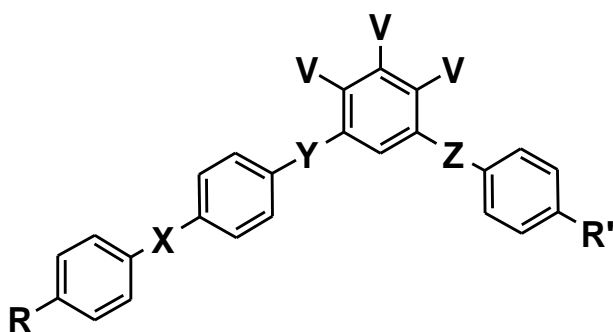


Figure 2.15

Figure 2.15: Kang et al four ring molecule containing oxadiazole moiety.

The four-ring compounds that had been reported in literature consisting of four aromatic phenyl rings in a bent core are compiled in **Table 2.5**. Majority of these four-ring compounds are unable to exhibit liquid crystalline behaviour, while very few of them are mesogens.

Table 2.5: Chemical structure and mesophase behaviour of bent core four ring mesogens reported in the literature



R	X	Y	Z	V	R'	Mesophase behaviour	Ref
							.

C ₁₂ H ₂₅ -	COO	CH=CH	OOC	H	-OC ₁₂ H ₂₅	Cr 108 Is	64
NC-	--	OOC	OOC	H	-OC ₁₀ H ₂₁	Cr 141 Is	65
C ₇ H ₁₅ O-	COO	COO	COO	H	-OC ₈ H ₁₇	Cr 130 Is	66
C ₁₀ H ₂₁ O	CH=CHC	CH=N	OOC	H	-OC ₈ H ₁₇	Cr 96 Is	
-	OO						
H	-N=N-	N=N	OOC	H	-OC ₁₂ H ₂₅	Cr 107 Is	67
C ₁₀ H ₂₁ O	--	OOC	OOC	F	-OC ₁₂ H ₂₅	Cr 88 Is	68
-							
C ₁₂ H ₂₅ O	COO	COO	OOC	F	-OC ₁₂ H ₂₅	Cr 70(N41)	69
-							
C ₁₂ H ₂₅ O	---	COO	COO	F	COOC ₈ *	Liq.Cryst. ^a	68
-				H ₁₇			
^a Cr 99 SmC _a * 137 SmC* _{ferri} 141 SmC* _{ferro} 166 SmA* 213.5							

Weissflog *et al.* reported novel asymmetric four-ring bent-core compounds derived from N-benzoylpiperazine (**Figure 2.16**) exhibiting SmA, SmC and SmI phases. In compounds exhibiting SmA and SmC phases polar structures can be induced under the influence of external electric field. Some compounds exhibit SmI phases, which are found to be polar ferroelectric phases and are switchable under the influence of electric field. This is the first example of non-chiral ferroelectric SmI phase (**Figure 2.16**).

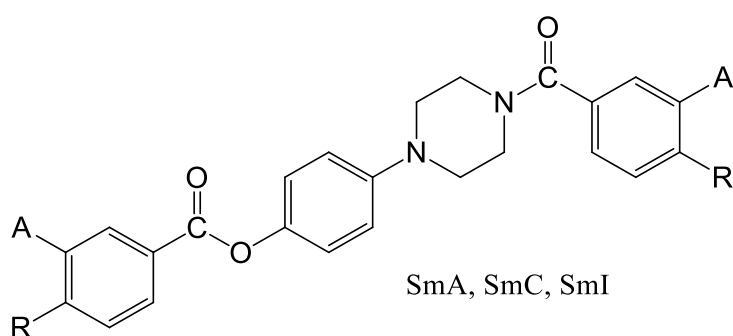


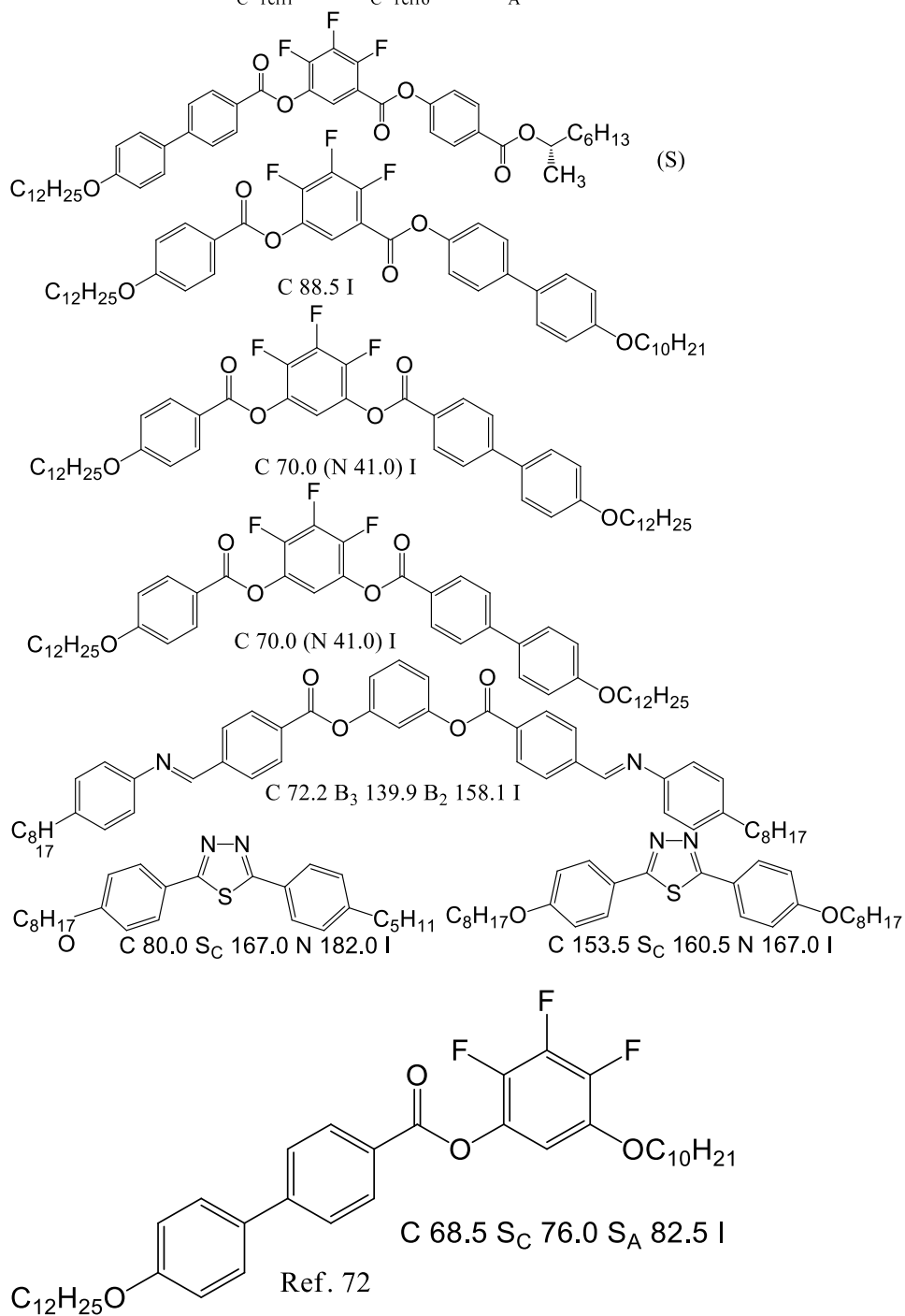
Figure 2.16: Weissflog et al reported asymmetric four ring compound derived from N-benzoylpiperazine.

2.10. Nematic phases in bent core mesogens:

Hird *et al.* [70] reported chiral SmC and nematic phases. Hird *et al.* reported [71] fluoro substituted four-ring bent-core material i.e. molecules with only four rings

in the core with a biphenyl moiety, exhibiting mesomorphism at high temperatures. The compound exhibited conventional SmA, ferro-, ferri-, and antiferroelectric SmC phases resulting from the molecular chirality and not due to the bent shape. The compound with conventional directions of ester groups based on banana-shape of parent compound is non-mesogenic, with a rather high melting point which may be masking liquid crystal phases and further the bend position is in not the right place for conventional mesomorphism. Increase in chain length and modification in the direction of linking ester moiety revealed the monotropic nematic phase at a lower temperature. The nematic phase exhibited very unusual optical textures and when viewed between crossed polarizers exhibited domains of opposite handedness present in equal proportions. The electro-optic switching of the nematic phase induces a fan-like texture that shows an unusual switching behaviour. Further no homeotropic texture could be observed in the nematic phase. Structures of the banana shaped liquid crystals reported which shows nematic phases are presented below (figure 2.17).

C 99.5 S_C*_{ferri} 137.5 S_C*_{ferro} 166.0 S_A* 213.5 I



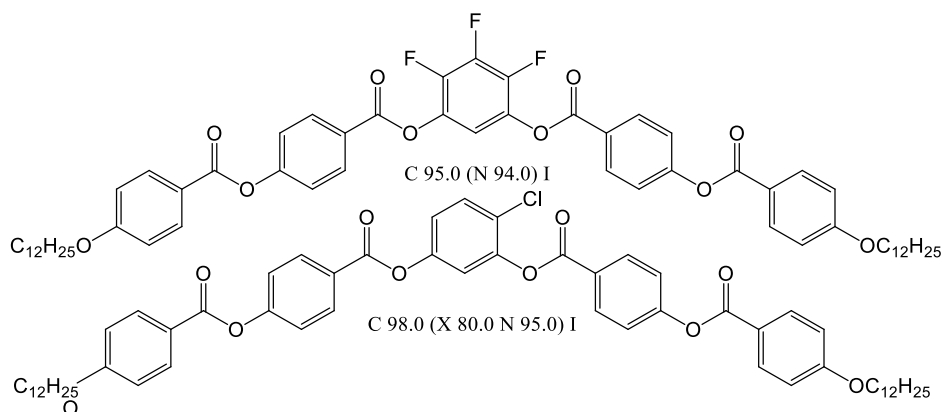


Figure 2.17: Some banana shaped liquid crystals exhibiting nematic phase.

2.11. Cybotactic clusters in the nematic phases:

C. Tschierske et al. [73] reported cybotactic clusters in the nematic phases of five ring bent core compounds. nematic phases are similar to ordinary nematic phases with only nearest neighbour correlation (N) whereas long chain compounds form SmC-type cybotactic clusters and these cybotactic nematic phases (N_{cyb}C) can be regarded as strongly fragmented SmC phases. The following are the series of compounds:

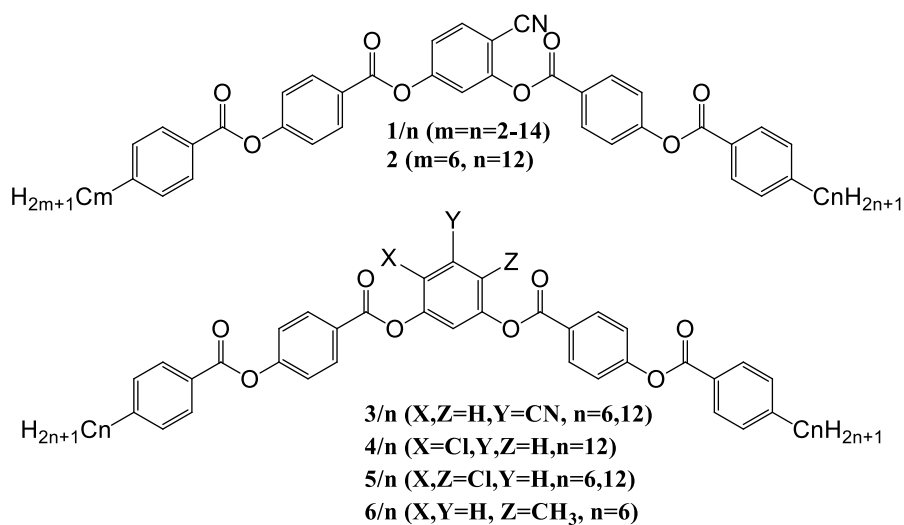


Figure.2.18: Tschierske et al reported compounds with cybotactic clusters in nematic phase.

O. Francescangeli et al. reported cybotactic cluster in nematic phase in a bent shaped molecule containing oxadiazole moiety in the central unit as shown in **Figure.2.19** [74]. Further the discovery of fluid cybotactic nematic phases (formed by Sm-C like clusters viz., N_{cyb}C phase) with ferroelectric response and field induced biaxiality in the nematic phase of bent-core mesogens derived from

symmetrical 3,5-diphenyl-1,2,4-oxadiazole unit is reported [73-78]. The transition from normal to skewed cybotactic nematic phase exhibited by some bent-core nematic mesogens as evidenced by small angle X-ray studies [76] is correlated to N_U-N_B phase transition by optical textures [79]. However only recently asymmetric achiral four-ring bent-core compounds of N-benzoylpiperazine derivatives [80], low melting unsymmetrical four-ring bent-core 1,3-disubstituted phenylene derivatives [81], 4'-amino phenyl-3-aminobenzoate derivatives exhibiting smectic phases have been reported [82,83].

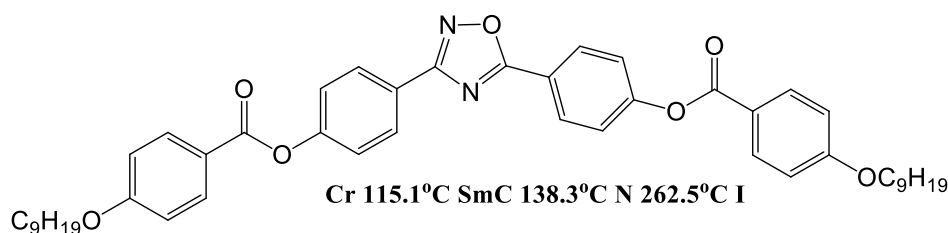


Figure.2.19: Tschierske et al reported cybotactic clusters in nematic phase in compounds with oxadiazole moiety.

2.12 Stripe patterns and elastic constants in the nematic phases:

Nematic phases composed of a mixture of rod-like and bent-core compounds are also interesting as they often exhibit unusual physical properties [84-88]. For example, there are some reports on the unusual elastic properties in the mixture of rod and bent-core liquid crystals. In particular, Dodge et al. showed that addition of a small concentration of bent-core liquid crystals in a calamitic compound can reduce K_{33} by a factor of two or more [84,85]. Kundu et al. reported anomalous trends in the temperature dependence of splay (K_{11}) and bend (K_{33}) elastic constants in the nematic phase of mixtures of 4-n-octyloxy 4-cyanobiphenyl (8OCB) and a bent-core compound and explained the results on the basis of their mutual orientation [86] in the presence of short-range smectic fluctuations. Recently Dozov theoretically showed that a spontaneous symmetry breaking phase transition inside the N phase is possible because of mutual tendency of banana-shaped molecules to induce a local bend director with a negative bend elastic constant [89]. Dhara et al. [90] measured the splay (K_{11}) and bend (K_{33}) elastic constants in the nematic phase of a bent-core liquid crystal as shown in **Figure.2.20**. They have observed that in the vicinity of the nematic-isotropic transition temperature K_{33} is proportional to the square of the order parameter. In

the nematic range K_{11} increases monotonically with decreasing temperature, whereas K_{33} is practically independent of temperature and is smaller than K_{11} . K_{33} exhibits a pretransitional slow divergence toward the transition temperature to the smectic phase and becomes slightly larger than K_{11} . The small K_{33} is explained on the basis of strong coupling of the bent shape of the molecules with the bend distortion.

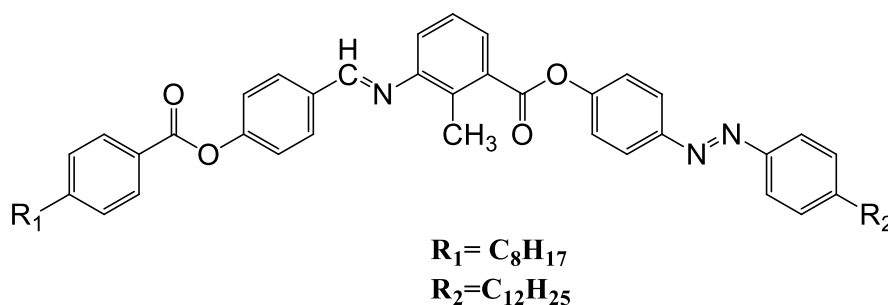


Figure: 2.20: Dhara et al reported K_{11} and K_{33} in nematic phase of a bent core liquid crystal.

Dhara et al. [91] again reported temperature-dependent measurements of splay (K_{11}) and bend (K_{33}) constants of mixtures of rod-like and bent core molecules. K_{11} remain almost constant for all the mixtures whereas K_{33} is always lower than K_{11} and further decreases with increasing concentration of bent-core molecules in the mixtures.

2.13 Density Functional Theory study:

As suitable X-ray quality crystal could not be grown, quantum chemical calculation based on density functional theory (DFT) has been performed to investigate the electronic structure of the 2F-14 (figure 1). Full geometry optimization has been carried out without imposing any constrain with the Gaussian 09 program package [92]. Spin-restricted DFT calculation has been carried out in the framework of the generalized gradient approximation (GGA) using Becke3-Lee-Yang-Parr exchange-correlation functional i.e. B3LYP [93, 94] hybrid functional and 6-31G (d, p) basis set.

Motivation of this work:

The discovery of the concept of spontaneous polarity and chirality of bent-core liquid crystals has stimulated new research corner in the area of liquid crystals because of its great potential in applications owing to their polar packing which in turn account for their polar switching. There are many reports on new bent-core compounds of five and six rings exhibiting polar smectic and nematic phases in literature. The challenge of finding novel mesophases, explanations for the novel optical textures observed and the description of new phenomena in these materials have attracted the interest of researchers throughout the world. The structure property relationship for the four-ring banana shaped liquid crystals has not yet been understood, although numerous number of bent-core materials were synthesized and extensively studied. Most of the reports on banana shaped liquid crystals are molecules with five or more rings. The four-ring bent-core compounds exhibiting banana mesomorphism is till eluding and remained unexplored. Further the manifestation of nematic phase in these bent core compounds is negated by the core-core interactions, incompatibility of the aromatic and aliphatic moieties and prevention of the flip-flop rotation by the shape factor of the molecules. Hence in this thesis, novel unsymmetrical four ring bent-core compounds shall be designed which will be followed by their synthesis and further investigations shall be carried out to understand the relationship between molecular structure and associated mesophases. The influence of substituents on the mesophase behaviour of the four ring containing liquid crystals for better understanding of the structure property relation of banana shaped molecules shall also be carried out. The emissive properties of these bent core compounds shall also be studied for their application potential.

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