Summary

Liquid Crystals are special materials in terms of their unique combination of factors namely flow properties of liquids and anisotropic properties of solids. These aspects of liquid crystals make them intrinsically interesting and ripe for technical applications. The ever widening liquid crystals activity has given rise to wider vista of new thinking, in turn creating a necessity of continued efforts for their basic study. Consequently, drive in search of new compounds have encouraged chemists to explore structural variations in liquid crystalline compounds, both, to understand the effect of chemical constitution on mesomorphic properties and for different application oriented studies.

The present work incorporates synthesis of thirteen new homologous series exhibiting mesomorphism over a range of temperature. In all one hundred and fifty six new compounds have been synthesized. Out of one hundred and fifty six new compounds one hundred and thirty eight compounds are mesogenic in nature, the rest eighteen compounds are non-mesogenic in nature; all the rest are mesomorphic in character. It is this variation between two extremes that has made the newly synthesized homologous series to acquire importance and significance. All the series with special structural features have been synthesized to study the effect of structural changes on liquid crystalline properties of the mesogenic systems. The influence of different aromatic rings, central linkages, terminal and lateral substituents have been investigated. Characterization of some of the homologues by elemental analysis, IR, NMR spectra, Mass spectra and DSC has been carried out. The textures of the mesophases were studied through Leitz Laborlux 12 POL optical polarizing microscope, fitted with kofler heating stage.

Chapter I of the thesis deals with the general introduction of liquid crystalline materials, history of LCs, Classification of LCs, effect of structural features on mesomorphism, banana shaped mesogens and its structural property relationship, classification of banana phases, liquid crystalline polymers, metallomesogens, mixed mesomorphism and applications of liquid crystalline compounds.

Chapter II deals with aims and objectives of this investigation work.

Chapter III deals with synthesis and mesomorphic characterization of new seven mesogenic homologous series having ester and azo central linkages, these seven homologous series are sub-classified in to Part I and Part II.

Part I consists of three new homologous series which reveals the study the effect of lateral substituents viz. –H (series I), $-CH_3$ (series II) and –Cl (series III) in ortho position of ester central linkage at central benzene ring on mesomorphism. Series I consists of twelve homologues which have three benzene rings, –COO– and –N=N– central linkages, $–CH_3$ methyl group as terminal substituent as well as $–CH_3$ methyl group lateral substituent at terminal benzene ring. Series II and III have similar structural features except that series II has $–CH_3$ methyl group in lateral position (ortho) to –COO– group and series III has –Cl group in lateral position (ortho) to –COO– group.

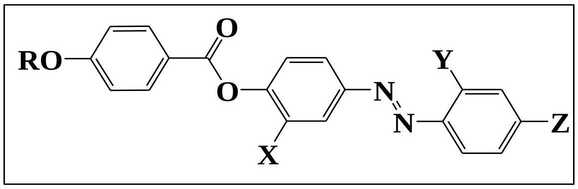
Part II contains four new homologous series with –CH=CH–COO– and –N=N– central linkages. Series IV & V are mesogenic positional isomers; they differ only in their position of lateral substituent. Series IV has $–CH_3$ group as lateral substituent in ortho position to –N=N– central linkage at terminal benzene ring while series V has $–CH_3$ group in ortho position to –CH=CH–COO– central linkage at central benzene ring. Series VI & VII have difference in only in their terminal substitution Viz $–CH_3$ group (Series VI) and $–NO_2$ group (Series VII).

Figure 1 shows general molecular structure of the series I to VII.

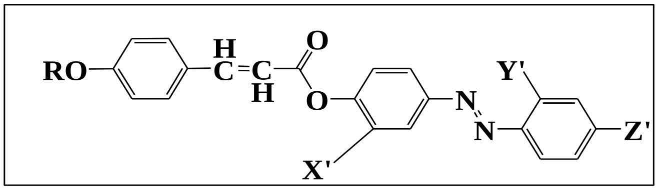
Series I	4-(4’-*n*-alkyloxybenzoyloxy)-phenylazo-2’’, 4’’-dimethylbenzenes.
Series II	4-(4’-*n*-alkyloxybenzoyloxy)-3-methylphenyl azo-2’’, 4’’-dimethylbenzenes.
Series III	4-(4’-*n*-alkyloxybenzoyloxy)-3-chlorolphenyl azo-2’’, 4’’-dimethylbenzenes.
Series IV	*trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzenes.
Series V	*trans*-4-(4’-*n*-alkyloxycinnamoyloxy)-3-methylphenylazo-4”-methylbenzenes.
Series VI	*trans*-(4’-*n*-alkoxycinnamoyloxy)-phenylazo-4’’-methylbenzenes.
Series VII	*trans*-4-(4’-*n*-alkoxycinnamoyloxy)-phenylazo-4’’-nitrobenzenes.

All the members of series I are nematogenic in nature; the last C16 homologue exhibits SmC mesophase alongwith nematic mesophase. Series II and III are purely nematogenic in nature. In series IV nematic mesophase commences from the very first member and remains upto the last C16 homologue synthesized; Smectic A mesophase in monotropic behavior commences from C10 homologue which becomes enantiotropic at C12 homologue and continues to be exhibited alongwith nematic mesophase. Series V exhibits nematic behavior from C1 to C16 homologue; C14 member shows SmC mesophase which becomes enantiotropic at C16 alongwith nematic mesophase. Series VI shows nematic mesophase from C1 to C16; SmC mesophase commences from C10 homologue and continues to be exhibited upto the last C16 homologue alongwith nematic mesophase. Series VII exhibits nematic mesophase from C1 to C8 and SmC mesophase commences from C7 member and continues upto the last C16 homologue synthesized. C7 and C8 members show SmC mesophase alongwith nematic mesophase whereas C10 to C16 members show purely smectogenic behavior. All of these series show marble/Schileren texture of nematic mesophase, Schileren texture of smectic C mesophase and focal conic fan shaped texture of smectic A mesophase.

All the homologous series exhibit good mesophase range with good thermal stabilities of smectic as well as nematic mesophases.



For series (I- III)



For Series (IV-VII)

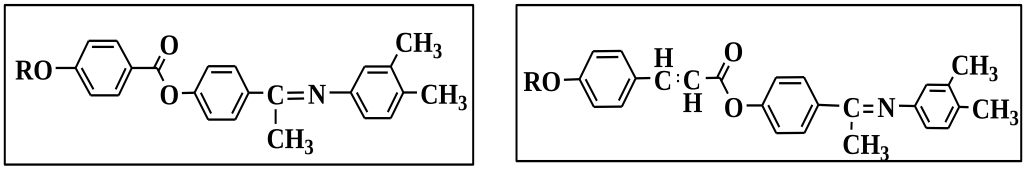
Where, R is C_nH_{2n+1} , n = 1 to 8, 10,12,14,16

Series	**Substituent**		
	X	**Y**	**Z**
I	-H	- CH_3	- CH_3
II	- CH_3	- CH_3	- CH_3
III	-Cl	- CH_3	- CH_3
Series	**Substituent**		
	X’	**Y’**	**Z’**
IV	-H	- CH_3	- CH_3
V	- CH_3	-H	- CH_3
VI	-H	-H	- CH_3
VII	-H	-H	-NO_2

Figure 1: General molecular structures of homologous series I to VII.

Chapter IV deals with synthesis and mesomorphic characterization of two new homologous series of ester and ethylideneamino central linkages with three benzene rings. Series VIII is composed of the three benzene rings, ester and ethylideneamino central linkages, methyl group as terminal substituent as well as –CH_3 group in lateral position i.e., in meta position to ethylideneamino central linkage at terminal benzene ring. Series VIII and IX have similar structural features except that series VIII has –COO– central linkage whereas series IX has –CH=CH–COO– central linkage.
Figure 2 shows general molecular structure of the series VIII to IX.

Series VIII 4-(4’-*n*-alkoxybenzoyloxy)-phenylethylidene-3”, 4”-dimethylanilines.
Series IX *trans*-4-(4’-*n*-alkoxycinnamoyloxy)-phenylethylidene-3”, 4”-dimethylanilines.



For Series VIII

For Series IX

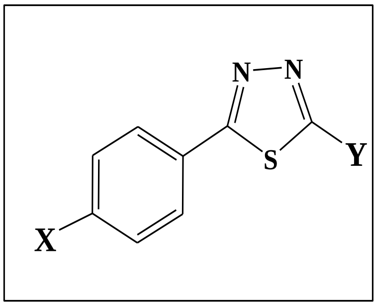
Where, R is C_nH_{2n+1}, n = 1 to 8, 10,12,14,16.

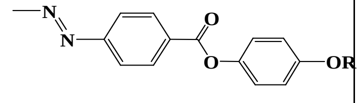
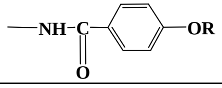
Figure 2: General molecular structures of homologous series VIII to IX.

All of these series show marble / Schileren texture of nematic mesophase and focal conic fan shaped texture of smectic A mesophase. All the homologous series exhibit lower mesophase range than those of series I – VII and thermal stabilities of smectic as well as nematic mesophases which can be due to ethylideneamino as one of the central linkages.

Chapter V deals with synthesis and mesomorphic characterization of heterocyclic bent shaped mesogens having 1, 3, 4-thiadiazole bent core; series X consists of heterocyclic bent core mesogens with 1, 3, 4-thiadiazole bent core and three benzene rings which is connected through –COO– and –N=N– bridging linkages and methyl group as terminal substituent whereas Series XI is composed of 1, 3, 4-thiadiazole bent core, two benzene rings and –CONH– bridging linkage and $–NO_2$ group as terminal substituent. These homologous series can display molecular forces arising from the dipolar nature, polarizability and inter molecular hydrogen bonding through bridging linkage which can explain their mesomorphic behavior and thermal stabilities smectic and nematic mesophases. Figure 3 shows general molecular structure of the series VIII to IX.

Series X 5-methylphenyl-2-(4”-n-alkoxybenzoyloxy)-phenylazo-1, 3, 4-thiadiazoles
Series XI 4-n-alkoxy-N-(5-(4’’-nitrophenyl)-1’, 3’, 4’-thiadiazol-2-yl)-benzamides



Series	substituent	
	X	Y
X	$-CH_3$	
XI	$-NO_2$	

Where, R is C_nH_{2n+1}, n = 1 to 8, 10,12,14,16

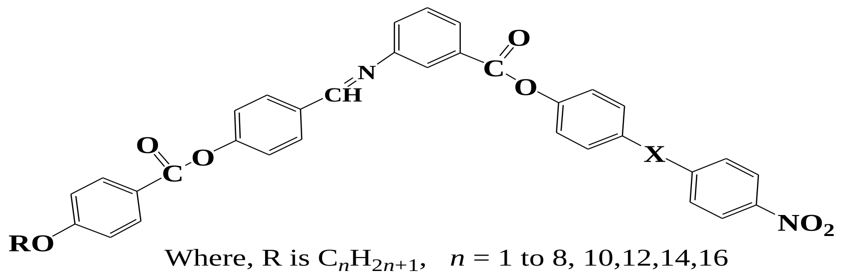
Figure 3: General molecular structure of the series X and XI.

Series X shows nematic mesophase from C3 to C16 homologue; smectic C mesophase commences alongwith nematic mesophase from C10 continues upto the last C16 homologue synthesized. Series XI exhibits only smectic C mesophase from C4 homologue to C16 homologue. All of these series show marble / Schileren texture of nematic mesophase, schileren texture of smectic C mesophase and focal conic fan shaped texture of smectic A mesophase. All the homologous series exhibit lower mesophase range than series I – VII but higher than series VIII and IX, with good thermal stabilities of smectic and nematic mesophases.

Chapter VI deals with the synthesis and mesomorphic characterization of asymmetric banana shaped mesogens. Series XII composed of asymmetric banana shaped mesogens which consists of five benzene rings, two –COO-, one -CH=N- and one –N=N- bridging linkages, –NO_2 group as terminal substituent. Series XIII has similar structural features as those in series XII except that it has –N=N– azo bridging linkage in place of –CH=N– bridging linkage.
Figure 4 shows general molecular structure of the series VIII to IX.

Series X: 3-[(4’”’-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneaminomethyl]-4’’-nitrophenyl-4’-azophenylbenzoates.

Series XI: 3-[(4’”’-*n*-alkyloxybenzoyloxy)-4’’’-benzilideneaminomethyl]-4’’-nitrophenylimino-4’-benzoates.



Where, R is C_nH_{2n+1}, n = 1 to 8, 10,12,14,16

Series	Bridging linkage X
XII	-N=N-
XIII	-CH=N-

Figure 4: General molecular structure of the homologous series XII and XIII.

All the compounds of series XII are mesomorphic in nature. Nematic mesophase commences from C1 homologue and continues to be exhibited upto the C10 homologue. The B7 phase commences from C7 homologue and continues to be exhibited upto the C16 homologue thus C12 to C16 members exhibit only B7 mesophase. Series XIII shows mesomorphic behavior from C4 homologue in the form of nematic mesophase which continues upto the C6 homologue; Smectic A mesophase commences alongwith nematic mesophase from C6 homologue and continues to be exhibited upto the last C16 homologue synthesized. All of these series show marble / Schileren texture of nematic mesophase, helical texture of B7 mesophase and focal conic fan shaped texture of smectic A mesophase. Both of the homologous series exhibit good mesophase range with good thermal stabilities.

Chapter VII deals with the study of mixed mesomorphism. Binary mixtures are necessary to lower the transition temperatures, broaden the available temperature range of mesophases and tailor the physical properties to find their possible applications especially in opto-electronic display devices [18-20]. In the present investigation, mesomorphic comprising ten binary systems are studied; out of which four binary systems comprising of structurally dissimilar components Type-I (Figure 5.1) and the rest six binary systems have chiral dopant as one of the components of the mixtures Type-II (Figure 5.2). Their mesomorphic properties are studied to evaluate the effect on mixed mesomorphism as well as depression in transition temperatures due to the variations in the structural changes of components.

Type I consists of four binary systems of structurally dissimilar components (Figure 5.1), all the four binary systems consist of mixtures of mesogenic azo-esters and non-mesogenic/mesogenic carboxy ester components. In all the four binary systems, nematic mesophase emerges in enantiotropic nematic form with the addition of less than 9 mole % of azo-ester mesogenic components. In all the four binary systems N-I curve deviates from linearity. All mixtures show a lower Cr – M transition temperatures with a good mesomorphic range as well as good supercooling tendency about 35 ˚C; which can thus be as potential binary mixtures for the opto-electronic display applications. All the prepared binary systems show marble/ schileren texture of nematic mesophase.

Type II consists of six binary systems which have chiral dopant exhibiting chiral nematic phase as one of the components of the binary mixtures (Figure 5.2). In all binary systems, cholesteric mesophase emerges in enantiotropic chiral nematic form with the addition of less than 24 mole % of cholesteric chiral dopant component. In all the six binary systems N* – I curve deviates from linearity. The above study of binary mixtures of chiral dopant with different achiral components reveals that the chiral dopant component induces chiral N* mesophase in the binary systems. In some binary mixtures chiral smectic mesophase is induced by adding chiral dopant to achiral nematogens.

Binary systems

Type 1: Components

A1 = 4-(4’-*n*-butoxybenzoyloxy) 3-methylphenyl azo-2’’, 4’’-dimethylbenzene **[BBMPAD]**

A2 = 4-(4’-*n*-hexyloxybenzoyloxy) 3-methylphenyl azo-2’’, 4’’-dimethylbenzene **[HBMPAD]**

B1 = 4-nitrophenyl-4_-*n*-butoxybenzoate **[NPBB]**

B2 = 4-nitrophenyl-4_-*n*-hexyloxybenzoate **[NPHB]**

Type 2: Components

X1 = 4-(4’-n-octyloxycinnamoyloxy)-phenylazo-2”, 4”-dimethylbenzene **[8CiXYP]**

X2 = 1-methoxy-4-[(4-methoxyphenyl)-NNO-azoxy] benzene (p-azoxyanisole) **[PAA]**

X3 = N-(4-methoxybenzylidene)-4-nitrobenzenamine **[MSN]**

X4 = 4-butoxybenzoic acid **[4ABA]**

X5 = 3-(4-butoxyphenyl)-propenoicacid **[4ACA]**

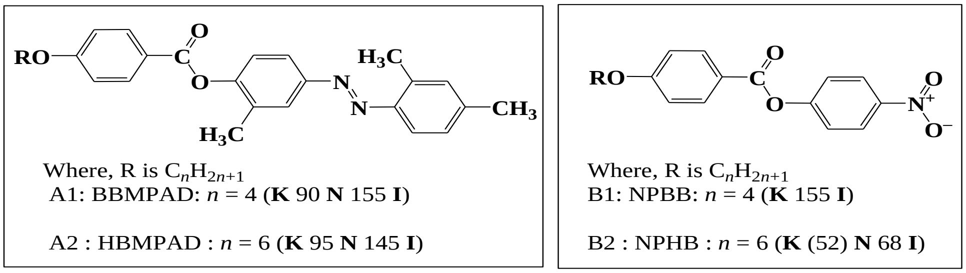
X6 = 4’-n-heptyloxy quinolin-8-yl-benzoate **[7HQE]**

Y = Cholesteryl-4-nitrobenzoate **[CHOLN]**

The binary systems studied are as follows:

Binary Systems	First Component	Second Component
Type : 1		
I	BBMPAD	NPBB
II	HBMPAD	NPBB
III	BBMPAD	NPHB
IV	HBMPAD	NPHB
Type : 2		
V	8CIXYP	CHOLN
VI	PAA	CHOLN
VII	MSN	CHOLN
VIII	4ABA	CHOLN
IX	4ACA	CHOLN
X	7HQE	CHOLN

Type I: General chemical structure of structurally dissimilar components.



Where, R is C_nH_{2n+1}

A1: BBMPAD: $n = 4$ (**K** 90 **N** 155 **I**)

A2 : HBMPAD : $n = 6$ (**K** 95 **N** 145 **I**)

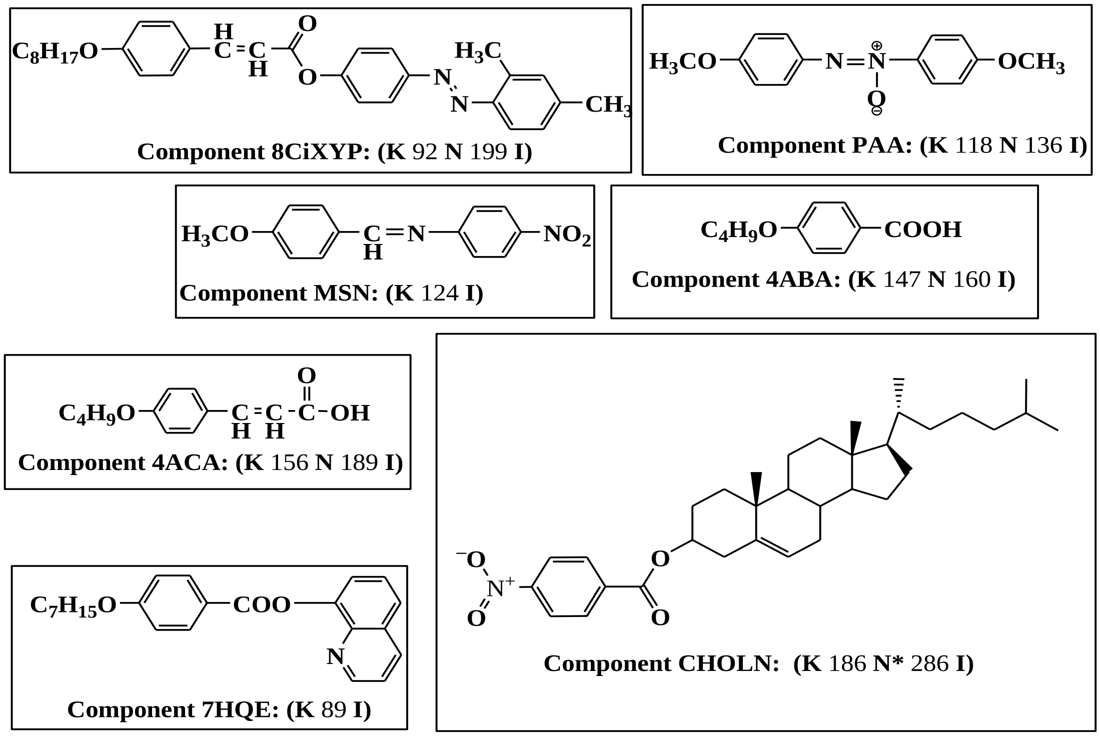
Where, R is C_nH_{2n+1}

B1: NPBB: $n = 4$ (**K** 155 **I**)

B2 : NPHB : $n = 6$ (**K** (52) **N** 68 **I**)

Figure 5.1: General chemical structure of structurally dissimilar components

Type II: General chemical structure for chiral dopant mixtures.



Component 8CiXYP: (K 92 **N** 199 **I)**

Component PAA: (K 118 **N** 136 **I)**

Component MSN: (K 124 **I)**

Component 4ABA: (K 147 **N** 160 **I)**

Component 4ACA: (K 156 **N** 189 **I)**

Component 7HQE: (K 89 **I)**

Component CHOLN: (K 186 **N*** 286 **I)**

Figure 5.2: General chemical structure for cholesterol dopant mixtures.

The present studies have provided host of novel liquid crystalline molecules with different molecular geometries and vast variations in their mesomorphic properties. The study of binary mixtures with structurally dissimilar mesogens as well as chiral dopant mixtures with chiral dopant also throws an immense light on the study of mixed mesomorphism and their potential applications in nonlinear optics and opto-electronic display applications in a wider vista.