Liquid crystals are special materials in terms of their unique combination of factors namely flow properties of liquids and anisotropic properties of solids. This aspect of liquid crystals makes them intrinsically interesting and ripe for technical applications. The ever widening liquid crystal 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 and for different application oriented studies.

Keeping this in view, fifteen homologous series, each comprising of twelve compounds, with special structural features have been synthesized to study the effect of structural variations on liquid crystalline properties of the mesogenic systems. The influence of different aromatic rings, central linkages, lateral and terminal substitutions has been investigated. Characterization of some of the homologues by elemental analysis, IR, NMR, Mass, UV-visible and DSC has been carried out. Transition temperatures and the textures of the mesophases are studied using Leitz Laborlux 12 POL polarizing microscope fitted with a Kofler heating stage.

**Mesogenic homologous series having terminal fluoro group**

A number of homologous series with ester and azo central linkages have been synthesized having different terminal groups. Introduction of lateral substitution makes molecules broad and plays an effective role in variation in mesogenic properties of mesogenic compounds. Similarly introduction of naphthalene ring in mesogenic homologues also makes molecules broad and plays an important role in variation in their mesomorphic properties.

Five homologous series having ester and azo central linkages with different lateral substituents and one series having central naphthalene moiety with terminal fluoro group are synthesized to investigate the effect of lateral substituents and central naphthalene moiety on fluoro liquid crystalline compounds (figure 1).
Where, \( R = C_nH_{2n+1}, \quad n = 1 \) to 8, 10, 12, 14, 16

<table>
<thead>
<tr>
<th>Series</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td></td>
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<td></td>
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</tbody>
</table>

**Figure 1**

- I: 4-(4′-n-alkoxybenzoyloxy)phenylazo-4′′-fluorobenzenes
- II: 4-(4′-n-alkoxybenzoyloxy)3-chlorophenylazo-4′′-fluorobenzenes
- III: 4-(4′-n-alkoxybenzoyloxy)3-methylphenylazo-4′′-fluorobenzenes
- IV: 4-(4′-n-alkoxybenzoyloxy)2-chlorophenylazo-4′′-fluorobenzenes
- V: 4-(4′-n-alkoxybenzoyloxy)2-methylphenylazo-4′′-fluorobenzenes
- VI: 4-(4′-n-alkoxybenzoyloxy)naphthylazo-4′′-fluorobenzenes

All the twelve homologues of each of these series are mesogenic in nature. Series I to IV show both smectic C and nematic phase while series V and VI show only nematic phase. Smectic phase of series I to IV shows schlieren texture of the smectic C variety. Nematic phase of series I to V shows marble texture whereas that of series VI shows schlieren texture.

**Mesogens having heterocyclic furfural moiety and chalcone as one of the central linkages**

It has been observed that chalcone central linkage is comparatively less conductive to mesomorphism as compared to azomethine, azo and ester central linkages due to the non linearity and angle strain arising from the keto group; however, when chalcone linkage is present with other central linkages it becomes conductive to mesomorphism. Liquid crystalline derivatives having heterocyclic moieties with chalcone as one of the central linkages are comparatively less explored. In view of this four homologous series (VII to X) are synthesized consisting of furfural moiety and chalcone as one of the central linkages along with other central linkages. Molecular structures of the homologous series (VII to X) are given in figure 2.
General molecular structure of series VII

```
RO-CH=N-\text{COCH}=CH-
```

Where, \(R = \text{C}_n\text{H}_{2n+1}, \quad n = 1 \text{ to } 8, 10, 12, 14, 16\)

General molecular structure of series VIII, IX, X

```
RO-\text{COO}---Y-\text{CO}||\text{CH}=
```

Where, \(R = \text{C}_n\text{H}_{2n+1}, \quad n = 1 \text{ to } 8, 10, 12, 14, 16\)

<table>
<thead>
<tr>
<th>Series</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>VIII</td>
<td>(-\text{H})</td>
<td>(-\text{CH}=\text{N})</td>
</tr>
<tr>
<td>IX</td>
<td>(-\text{OCH}_3)</td>
<td>(-\text{CH}=\text{N})</td>
</tr>
<tr>
<td>X</td>
<td>(-\text{H})</td>
<td>(\text{CH}_2\text{N}--)</td>
</tr>
</tbody>
</table>

**Figure 2**

**VII** 1-(4-(4’-n-alkoxybenzylideneamino)phenyl)-3-(furan-2-yl)-prop-2-en-1-ones  
**VIII** 1-(4-(4’-(4’’-n-alkoxybenzoyloxy)benzylideneamino)phenyl)-3-(furan-2-yl)-prop-2-en-1-ones  
**IX** 1-(4-(4’-(4’’-n-alkoxybenzoyloxy)2’-methoxybenzylideneamino)phenyl)-3-(furan-2-yl)-prop-2-en-1-ones  
**X** 1-(4-(4’-(4’’-n-alkoxybenzoyloxy)phenylethylideneamino)phenyl)-3-(furan-2-yl)-prop-2-en-1-ones

First three members of series VII are non-mesogenic in nature whereas \(C_4\) to \(C_{16}\) members are monotropic nematogens. All the twelve homologues of series VIII and IX are mesogens. Series VIII shows both nematic and smectic mesophases while series IX exhibits only nematic mesophase. First three members of series X are non-mesogens, \(C_4\) to \(C_5\) members are monotropic nematogens whereas \(C_6\) to \(C_{16}\) members are nematogens. Nematic phase of series shows threaded/ marble texture whereas smectic mesophase of series shows schlierene texture of smectic C variety.
Mesogenic homologous series having ester and ethylideneamino central linkages

Liquid crystalline compounds with different central linkages and terminal groups are known; however, mesogens having ethylideneamino central linkage are comparatively less explored. Three new homologous series (XI-XIII) with ester and ethylideneamino central linkages and fluoro, chloro and methyl terminal groups respectively are synthesised (figure 3) and their mesomorphic properties are studied.

General molecular structure of series XI-XIII

\[
\begin{array}{c}
\text{RO} \quad \text{COO} \quad \text{C} = \text{N} \quad \text{X} \\
\text{CH}_3
\end{array}
\]

Where, \( R = C_nH_{2n+1} \), \( n = 1 \) to \( 8, 10, 12, 14, 16 \) \( X = -F, -Cl, -CH_3 \)

**Figure 3**

- **XI** 4-(4’-n-alkoxybenzoyloxy)phenylethylidene-4”-fluoroanilines
- **XII** 4-(4’-n-alkoxybenzoyloxy)phenylethylidene-4”-chloroanilines
- **XIII** 4-(4’-n-alkoxybenzoyloxy)phenylethylidene-4”-toluidines

All the twelve homologues of each of the series are mesogenic in nature. Series XI and XII show both the smectic and nematic phase, whereas all the derivatives of series XIII are nematogenic in nature. The nematic phase of all the series show threaded texture, whereas smectic phase shows focal conic fan shaped texture of smectic A variety.

**Bent-shaped mesogens derived from Diphenylether moiety**

Since chemical structure has been understood to have most significant effect on the mesophase formed by liquid crystalline compounds. It is observed that a molecule which possesses a linear structure along with two or more phenyl rings linked via stable central linkages seems to have an advantage in the formation of mesophases. However, quite a good number of novel compounds with non-linear structures having bent core have been found exhibiting liquid crystalline behavior. In view of this two new homologous series with bent core are synthesized and their mesomorphic properties are studied (figure 4).
Where, R is C\textsubscript{n}H\textsubscript{2n+1}, \quad n = 1 to 8, 10, 12, 14, 16

<table>
<thead>
<tr>
<th>Series</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIV</td>
<td>-OCH\textsubscript{3}</td>
<td>-CH=N-</td>
</tr>
<tr>
<td>XV</td>
<td>-H</td>
<td></td>
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</tbody>
</table>

**Figure 4**

**XIV** 4,4’-Bis-[4”-(4”’-n-alkoxybenzoyloxy)3”-methoxybenzyldieneamino]-diphenylethers  
**XV** 4,4’-Bis-[4”-(4”’-n-alkoxybenzoyloxy)phenylethylideneamino]-diphenylethers

All the twelve homologues of both the series (XIV and XV) are mesogenic in nature and exhibit only nematic mesophase. Nematic phase of the series shows marble texture. The effects of lateral methoxy group and central linkages on mesomorphism are studied.

**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. In the present investigation, ten binary systems of structurally dissimilar components are studied (figure 5) to evaluate the effect on mixed mesomorphism due to the variations in the structural characteristics of the components.

The components of the binary systems taken are:

- **A1** 4-(4’-n-butoxybenzoyloxy)benzaldehyde (BBB)
- **A2** 4-methoxybenzyldene-4’-chloroaniline (MBCA)
- **A3** 4-methoxybenzyldene-4’-toludine (MBT)
- **A4** 4-(4’-n-dodecyloxybenzoyloxy)napthylazo-4”-fluorobenzene (DNFB)
B1 4-(4’-n-butyloxybenzoyloxy)phenylazo-4”-fluorobenzene (BPFB)
B2 4-(4’-n-butyloxybenzoyloxy)benzylidene-4”-fluoroaniline (BBFA)
B3 4-(4’-n-heptyloxybenzoyloxy)phenylazo-4”-fluorobenzene (HPFB)
B4 4-(4’-methoxybenzoyloxy)benzylidene-2”-aminopyridine (MBAP)

General molecular structure of component A1 to A3

![Molecular structure](image-url)

Where, R is CₙH₂n+1

A1 : BBB;  n=4, X= -COO-, Y= -CHO
A2 : MBCA;  n=1, X= -CH=N-, Y= -Cl
A3 : MBT;  n=1, X= -CH=N-, Y= -CH₃

Molecular structure of component A4

![Molecular structure](image-url)

A4 : DNFB

General molecular structure of component B1 to B4

![Molecular structure](image-url)

Where, R is CₙH₂n+1

B1 : BPFB;  n=4, X= -N=N-
B2 : BBFA;  n=4, X= -CH=N-
B3 : HPFB;  n=7, X= -N=N-

Molecular structure of component B4

![Molecular structure](image-url)

B4 : MBAP

**Figure 5**

The binary systems studied are:

**Type 1**

<table>
<thead>
<tr>
<th>Binary System</th>
<th>First Component</th>
<th>Second Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A1 (BBB)</td>
<td>B1 (BPFB)</td>
</tr>
<tr>
<td>II</td>
<td>A1 (BBB)</td>
<td>B2 (BBFA)</td>
</tr>
<tr>
<td>III</td>
<td>A2 (MBCA)</td>
<td>B2 (BBFA)</td>
</tr>
<tr>
<td>IV</td>
<td>A2 (MBCA)</td>
<td>B3 (HPFB)</td>
</tr>
<tr>
<td>V</td>
<td>A3 (MBT)</td>
<td>B2 (BBFA)</td>
</tr>
<tr>
<td>VI</td>
<td>A3 (MBT)</td>
<td>B3 (HPFB)</td>
</tr>
</tbody>
</table>
Summary

Type 2

<table>
<thead>
<tr>
<th>Binary System</th>
<th>First Component</th>
<th>Second Component</th>
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</thead>
<tbody>
<tr>
<td>VII</td>
<td>A4 (DIFB)</td>
<td>B1 (BPFB)</td>
</tr>
<tr>
<td>VIII</td>
<td>A4 (DIFB)</td>
<td>B2 (BBFA)</td>
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</tbody>
</table>

Type 3

<table>
<thead>
<tr>
<th>Binary System</th>
<th>First Component</th>
<th>Second Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>A2 (MBCA)</td>
<td>B4 (MBAP)</td>
</tr>
<tr>
<td>X</td>
<td>A3 (MBT)</td>
<td>B4 (MBAP)</td>
</tr>
</tbody>
</table>

As the molecular geometry of the components in the mixtures differ, the N-I transition curves deviate from the linear nature. In the binary systems with the non-mesogen as one of the components, the nematic phase emerges either in monotropic or enantiotropic form with the addition of as low as 10 to 20 mole% of the non-mesogenic component in the mixture. It is observed that all the binary mixtures exhibit good mixed mesophase range which is more than the mesophase range of individual components. Some of the mixtures show supercooling below 45° C.

The present studies have provided host of novel liquid crystalline compounds with different molecular structures and vast variations in their mesomorphic properties. The study of binary mixtures with structurally dissimilar mesogens also throws immense light on mixed mesomorphism and their potential for applications in nonlinear optics and electro-optic display devices.