CHAPTER-3

RESULTS AND DISCUSSION:

Homologous series:

The following novel homologous series (1 to 8) have been synthesized and their characteristics have been determined.

Series-1

\[
\begin{align*}
\text{RO-} & \begin{array}{c}
\text{CH=CH-CO} \\
\text{CO-CH=CH-}
\end{array} \text{NO}_2 \\
\text{RO-} & \begin{array}{c}
\text{CH=CH-COO} \\
\text{CO-CH=CH-}
\end{array} \text{RO}
\end{align*}
\]

Series-2

\[
\begin{align*}
\text{RO-} & \begin{array}{c}
\text{CH=CH-CO} \\
\text{CO-CH=CH-}
\end{array} \text{OCH}_2 \\
\text{RO-} & \begin{array}{c}
\text{CH=CH-COO} \\
\text{CO-CH=CH-}
\end{array} \text{OCH}_3
\end{align*}
\]

Series-3

\[
\begin{align*}
\text{RO-} & \begin{array}{c}
\text{CH=CH-CO} \\
\text{CH=CH-CO-}
\end{array} \text{NO}_2 \\
\text{RO-} & \begin{array}{c}
\text{CH=CH-COO} \\
\text{CH=CH-CO-}
\end{array} \text{RO}
\end{align*}
\]

Series-4

\[
\begin{align*}
\text{RO-} & \begin{array}{c}
\text{CH=CH-CO} \\
\text{CH=CH-CO-}
\end{array} \text{NO}_2 \\
\text{RO-} & \begin{array}{c}
\text{CH=CH-COO} \\
\text{CH=CH-CO-}
\end{array} \text{RO}
\end{align*}
\]
Where, R stands for n-alkyl chain in alkoxy group from C\textsubscript{1} to C\textsubscript{8}, C\textsubscript{10}, C\textsubscript{12}, C\textsubscript{14}, C\textsubscript{16}.

The synthesis of above listed homologous series involves various steps as described in experimental part of this thesis. Enough care was taken for obtaining the compounds in pure form. The analytical data conformed with the calculated one and structural characterization is confirmed by IR and NMR spectra of some representative members of the homologous series.

During the course of the present investigation totally 90 new substances have been synthesized and 60 of them are found mesogenic in nature. The molecular geometry as designed for left alkyl chain of alkoxy group is that of normal linking and third benzene ring with substitution through CO-CH=CH- or –CH=CH-CO- group.

The molecular geometry of series (1) to (8) homologous series possess;
(i) Three phenyl rings

(ii) Two central bridges viz. –CH=CH-COO or –COO and –CO-CH=CH- or –CH=CH-CO-.

(iii) Terminal and lateral groups of varying polarity and,

(iv) An overall length to breadth ratio besides linearity.

These factors favor the exhibition of mesogenic property in the homologues of the above mentioned series.

These novel homologous series can be categorized into four different types.

Type: 1

(i) **Series-1**: α-4-[4’-n-Alkoxy-Cinnamoyloxy] Benzoyl-β-3” Nitro phenyl Ethylenes

![Series-1 Diagram]

(ii) **Series-2**: Series: α-4-[4’-n-Alkoxy Cinnamoyloxy] benzoyl β-3”,4”-dimethoxy Phenyl Ethylenes

![Series-2 Diagram]

Homologous series-(1) and (2) consists of three benzene rings bonded through –CH=CH-COO- and –CO-CH=CH- central groups act as rigid core of the molecules and the rest of the molecular part which includes terminal end groups and/or lateral group act as flexible core of the molecules. In present series of Type-1 the flexible molecular parts are Series-1 RO- and -NO₂

Series-2 RO- and -OCH₃(dimethoxy)

And the commonly present rigid core is
Type:2

(i) **Series-3:** \(\alpha-4'(4'-n-Alkoxy\text{ Cinnamoyloxy})\text{ phenyl} \beta-4''\text{- Nitrobenzoyl Ethylene.}\)

(ii) **Series-4:** Homologous Series: \(\alpha-3[4'-n-Alkoxy\text{ Cinnamoyloxy}]\text{ phenyl} \beta-4''\text{- Nitrobenzoyl Ethylene.}\)

Homologous series-(3) and (4) consists of three phenyl rings bonded through \(-\text{CH}=\text{CH-COO}-\) and \(-\text{CH}=\text{CH-CO}-\) central groups act as rigid core of the molecules and the rest of the molecular part which includes terminal end groups and/or lateral group act as flexible core of the molecules. In present series of Type-2 the flexible molecular parts are Series-3 \(\text{RO-}\) and \(-\text{NO}_2\) (Linear) and

Series-4 \(\text{RO-}\) and \(-\text{NO}_2\) (Non linear)

And the commonly present rigid core is

Type:3
(i) **Series-5**: $\alpha$-4-[4'-n-Alkoxybenzoyloxy] Benzoyl-$\beta$-3” Nitro phenyl Ethylenes.

(ii) **Series-6**: $\alpha$-4-[4'-n-Alkoxy benzoyloxy] benzoyl $\beta$-3”,4”-dimethoxy Phenyl Ethylenes.

Homologous series-(5) and (6) consists of three phenyl rings bonded through COO- and –CO-CH=CH- central groups act as rigid core of the molecules and the rest of the molecular part which includes terminal end groups and/or lateral group act as flexible core of the molecules. In present series of Type-3 the flexible molecular parts are

Series-5 RO- and -NO$_2$

Series-6 RO- and -OCH$_3$(dimethoxy)

And the commonly present rigid core is

**Type:4**
(i) **Series-7**: α – 4-[4’-n-Alkoxy benzoyloxy] phenyl- β-4’’-nitro benzoyl ethylenes

![Chemical structure of Series-7](image1)

(ii) **Series-8**: α – 3-[4’-n-Alkoxy benzoyloxy] phenyl- β-4’’-nitro benzoyl ethylenes

![Chemical structure of Series-8](image2)

Homologous series-(7) and (8) consists of three phenyl rings bonded through COO- and –CH=CH-CO- central groups act as rigid core of the molecules and the rest of the molecular part which includes terminal end groups and/or lateral group act as flexible core of the molecules. In present series of Type-4 the flexible molecular parts are

- **Series-7**: RO- and -NO₂ (linear)
- **Series-8**: RO- and -NO₂ (Non linear)

And the commonly present rigid core is

![Chemical structure of rigid core](image3)

3.1 **Mesogenic characteristics of the individual series:**

1. **Homologous series**: α-4-[4’- n-Alkoxy- Cinnamoyloxy] Benzoyl-β-3’’ Nitro phenyl Ethylenes
The title homologous series $\alpha$-$4'$-[4'-n-Alkoxy- cinnamoyloxy] benzoyl-$\beta$-3” nitro phenyl ethylenes is entirely mesogenic in character because mesomorphism is display by all the homologues of the series in enantiotropic condition except first four members of the series, i.e. First to fourth homologues of the series are nonmesomorphic, while Pentyl, hexyl, octyl and decyl homologues are enantiotropically smectogenic in combination with nematogenic character. Dodecyl, tetradecyl and hexadecyl homologues are only nematogenic without exhibition of any smectogenic character even in the monotropic condition. Transition temperatures (table-2 ) of the homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal as recorded in (table-2). The phase behavior of the series is discussed in figure-(9). Solid-isotropic or mesomorphic transition curve adopt a zigzag path of rising and falling and behaves in normal manner. Smectic-nematic transition curve gradually rises from n-pentyloxy to n-octyloxy derivatives of the series and then smoothly falls to the n-decyloxy derivative of the series. Thus smectic-nematic transition curve behaves in usual expected manner. Nematic-isotropic transition curve partly behaves in normal manner upto n-decyloxy derivative i.e. curve rises from n-pentyloxy derivative and then adopt descending tendency as series is ascended up to n-decyloxy homologue. But then curve abnormally behaves i.e. it rises instead of falling in case of dodecyloxy and tetra decyloxy derivatives. Odd-even effect is absent for Smectic-Nematic and Nematic-isotropic transition curves as mesophase commences from and beyond pentyloxy homologue. Smectic phase length and nematic phase length ranges from $6.0^0\text{C}$ to $21.0^0\text{C}$ and $8.0^0\text{C}$ to $23.0^0\text{C}$ respectively. Total mesophase length vary minimum $09.0^0\text{C}$ at hexadecyl derivatives to maximum of $36.0^0\text{C}$ at n-octyl and n-decyl derivatives. Series under discussion is predominantly nematogenic and partly smectogenic of middle ordered melting type and short phase length.


The title homologous series : $\alpha$-$4'$-[4'-n-Alkoxy Cinnamoyloxy] benzoyl $\beta$-3”,$4''$-dimethoxy Phenyl Ethylenes is mesomorphic in character. Methyl to butyl homologue derivatives are nonliquid crystal, while pentyl to hexadecyl homologue members of the series are enantiotropically liquid crystals with nematogenic character only without exhibition of
smectogenic property even in the monotropic condition. Thus, there are eight homologues, out of twelve homologues of a series are liquid crystal. Plot of a phase diagram drawn for transition temperatures (table-6) versus number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group, which consists of two transition curves (figure-10). Solid-isotropic or nematic transition curve adopt a zigzag path of rising and falling as series is ascended with overall descending tendency and behave in normal manner. Nematic-isotropic transition curve initially rises upto decyl homologue and then descended as series is ascended with exhibition of odd-even effect and negligible rise of few degree at the hexadecyl homologue derivative. Thus, N-I transition curve behaves in usual established manner. Nematic-isotropic transition curves for odd and even members of a series merge into each other at the nonyl homologue derivative of the series. The odd-even effect less as series is ascended for higher homologues because longer n-alkyl chain may coil, bend flex or couple to lie with the major axis of the core. The texture of the nematic mesophase is threaded or schlieren. The maximum nematogenic mesophase length 59°C at the octyl homologue and the minimum mesophase length is 24°C at the hexadecyl homologue derivative. Thermal stability for nematic mesophase is 163.1. Thus, presently investigated homologous series is entirely or predominantly nematogenic without exhibition of any smectogenic character and the middle ordered melting type. The mesomorphic (LC) properties vary from homologue to homologue in the same series.


The title homologous series: Series: α-4-[4’-n-Alkoxy Cinnamoyloxy] phenyl β-4” Nitrobenzoyl Ethylenes exhibited mesogenic nature from pentyl to decyl derivatives of the series. Rest of the members of the series are nonmesogenic in nature. Transition temperatures in °C (table-10) are plotted versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal and on joining the points related to each other, a phase diagram (figure-11) showed phase behavior of the series. It indicates that, solid-isotropic or smectic transition curve follows zigzag path of rising and falling with overall rising tendency as series is ascended. Smectic-nematic transition curve at the beginning rises and continue to rise up to decyloxy homologue with exhibition of odd-even effect. Mesomorphic property is absent from and beyond decyl derivative. Nematic-isotropic transition curve adopt a descending tendency as series is
ascended without exhibiting of odd-even effect. Nematic-isotropic transition curve is extrapolated for dodecyloxy, tetradecyloxy and hexadecyloxy homologues fitting the trend of the curve. The predicted probable latent transition temperatures (LTT) for dodecyl, tetradecyl and hexadecyl derivatives are 154\(^0\)C, 145\(^0\)C and 138\(^0\)C respectively in monotropic manner. The mesomorphic phase length minimum from 36\(^0\)C to a maximum 76\(^0\)C in pentyl and hexyl homologues respectively. Smectic and nematic mesophases commences from pentyl homologue of the series. The extent of mesomorphic property vary from homologue to homologue in the same series.

4. Homologous series: \(\alpha\text{-3-[4'}-n\text{-Alkoxy Cinnamoyloxy]}\) phenyl-\(\beta\text{-4''- Nitrobenzoyl Ethylenes.}\)

Homologous series: \(\alpha\text{-3-[4'}-n\text{-AlkoxyCinnamoyloxy]}\) phenyl-\(\beta\text{-4''- Nitrobenzoyl ethylenes}\) is mesomorphic in nature. However, mesomorphism induced in seven members of the series. Rest of the four members viz. methyl, ethyl, butyl and hexadecyl derivatives are nonmesomorphic. Mesomorphic homologues exhibit only enatiotropism nematogenic mesomorphism with absence of smectogenic character. A phase diagram (figure-12) showing phase behavior indicate that solid-isotropic or nematic transition curve rises and falls in zigzag manner with overall descending tendency. Nematic-isotropic transition curve gradually descend as series is ascended with exhibition of odd-even effect. Transition curves of a phase diagram drawn for number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group versus transition temperatures (table-14) of homologues. Mesomorphic phase length vary minimum by 30\(^0\)C at the pentyl derivative to maximum of 62\(^0\)C at the octyl derivative of the series. Nematic-isotropic transition curve is extrapolated [91] to nonmesomorphic homologues fourth and hexadecyl derivative to predict their probable latent transition temperatures (LTT) keeping in mind, the trend of the actual transition curve. The predicted LTT for nematic are monotropic 140\(^0\)C, 140\(^0\)C and 158 \(^0\)C for fourth and hexadecyl derivative respectively. Monotropic temperature 140\(^0\)C is not realizable because before it show nematic phase, it undergoes to solidify due to its high crystallizing tendency. LTT for nematic and solid-isotropic temperature co-insided to 158\(^0\)C. i.e. practically nematic phase length 158-158=0 zero or nematic phase disappear or not realizable for hexadecyl derivative. This homologous series is predominantly nematic without shown of smectic character.

The title homologous series: α-4(-4'-n-Alkoxy benzoyloxy) benzoyl β-3″-Nitro phenyl ethylenes exhibits mesogenic nature. Methoxy to pentyloxy homologues are nonliquid crystal and sharply melts at their melting point without showing liquid crystal mesophase. Hexyloxy to hexadecyloxy homologues are liquid crystal. Hexyloxy to dodecyloxy derivatives exhibit enantiotropically smectogenic property in addition to nematogenic property. Tetradecyloxy and hexadecyloxy derivatives exhibit enantiotropic nematogenic property without showing of smectogenic character. Phase diagram showing phase behavior is drawn for transition temperatures of homologues as determined using hot stage polarizing microscope (table-18) versus number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group is shown as in figure-13. Phase diagram (figure-13) indicate that, solid-isotropic or mesomorphic transition curve rises and falls in zigzag manner with overall falling tendency. Smectic-nematic transition curve initially falls from hexyloxy to octyloxy homologue and then behaves in normal manner by rising up to dodecyloxy derivative and then smectogenic mesophase disappears. Therefore, the curve is extrapolated [91] to tetradecyloxy homologue following the trend of the curve. Extrapolated curve merges and coincide to solid-nematic transition temperature 120°C i.e. Smectogenic phase length of tetradeoxy homologue must be 120-120=0 zero. Odd-even effect is absent for the smectic-nematic transition curve. Nematic-isotropic transition curve also adopts similar pattern of propagation as shown by smectic-nematic transition as series is ascended without showing of odd-even effect. i.e. initially falls at octyloxy derivative, then, rises and falls from decyloxy to hexadecyloxy homologue as series is ascended and behaves in normal manner. Thus, smectic-nematic and nematic-isotropic transition curves showed serpentine shape of their way of propagation as series is ascended. The mesomorphic phase length vary minimum of twelve degree centigrade at hexadecyloxy derivative to maximum of 63 degree centigrade at decyloxy derivatives. Smectogenic and nematogenic phase length vary from 13 to 30 °C and 12 to 47 °C. Thus, the present series under discussion is predominantly nematogenic and partly smectogenic with middle ordered melting type.

Homologous series: \( \alpha-4-[4'-n\text{-Alkoxy benzoyloxy}] \) benzoyl \( \beta-3'',4''\)-dimethoxy Phenyl ethylenes exhibits mesogenic characteristics. All the members of a novel series except first member are enantiotropically mesogenic in character. Hexyl to tetradecyl homologue derivatives exhibited smectogenic in addition to nematogenic property while ethoxy to pentyloxy and hexadecyloxy homologues exhibit only nematogenic property. Transition temperatures (table-22) of homologues as determined from an optical polarizing microscope equipped with a heating stage were plotted versus the number of carbon atoms in \( n\)-alkyl chain of left \( n\)-alkoxy terminal end group. Solid-smectic, smectic-nematic and nematic-isotropic transition curves were obtained showing the phase behavior of series are shown in phase diagram (figure-14). Solid-isotropic or mesomorphic transition curve follows a Zigzag path of rising and falling with overall descending tendency and behaves in usual manner. Smectic-nematic transition curve initially rises, passes through maxima and then descended in normal manner with exhibition of odd-even effect. Curve is extrapolated [91,93] to hexadecyloxy homologue which merges in solid-nematic transition temperature, indicating that, smectogenic mesophase ceases to appear at solid-nematic transition temperature, i.e. smectogenic phase length is zero for the hexadecyloxy homologue. Nematic-isotropic transition curve is descended as series is ascended with exhibition of odd-even effect; and behaved in normal established manner. Odd-even effect diminishes as series is ascended and curves for odd and even homologues merges into each other at the decyloxy homologue for smectic and/or nematic at the, octyloxy homologue in the curve. The smectic and nematic mesophase ranges from 07 to 28\(^\circ\)C and 07 to 52\(^\circ\)C respectively. Homologous series is predominantly nematogenic and partly smectogenic.

7. Homologous series: \( \alpha-4-[4'-n\text{-Alkoxy benzoyloxy}] \) phenyl-\( \beta-4''\)-nitro benzoyl ethylenes.

The title homologous series: \( \alpha-4-[4'-n\text{-Alkoxy benzoyloxy}] \) phenyl-\( \beta-4'' \) Nitro benzoyl ethylenes shows mesogenic characteristics. Methoxy and ethoxy derivatives are nonliquid crystals (NLC). Propyloxy to pentyloxy and hexadecyloxy homologues are enantiotropic nematonic. Hexyloxy to tetra decyloxy homologues are enantiotropic nematonic in addition to enantiotropic smectic property. Transition temperatures of homologues (table-26) are plotted versus the number of carbon atoms in \( n\)-alkyl chain of left \( n\)-alkoxy terminal end group. A phase diagram (figure-15) is obtained by linking like or related points forming; Solid-isotropic or
mesomorphic, smectic-nematic and nematic-isotropic transition curves. Solid-isotropic or mesomorphic transition curve rises and falls in zigzag manner with overall falling tendency. Smectic-nematic transition curve falls from hexyloxy homologue and then rises and passes through maxima at the dodecyloxy derivative and finally falls to the tetradecyloxy homologue. Curve is extrapolated [93] to both ends of it following trend of a curve up to butyloxy and hexadecyloxy derivatives to determine their latent transition temperatures of (LTT). LTT predicted for smectic-nematic transition of hexadecyloxy derivative is monotropic 99°C and that of butyloxy homologue is 140°C, which is actually a nematic-isotropic point of it. Thus, smectic-nematic phase length is 140-140=0 i.e. zero; means there should not exist smectic phase and practically there is no existence of smectic phase. The nematic-isotropic transition curve initially rises and then falls after passing through maxima and descended as series is ascended. Thus, it behaves in normal expected manner. Odd-even effect is observed for nematic-isotropic transition curve; and both curves (for odd and even) merge into each other at the hexyloxy homologue. Odd-even effect and variations in mesogenic properties from homologue to homologue in the same series is due to the sequentially added methylene unit in the n-alkyl chain of left n-alkoxy terminal end group. The nematogenic and smectogenic phase length vary between 14 to 50 and 19 to 35°C respectively. Total mesophase length vary between 18 to 73°C. Thus, homologous series is entirely nematogenic and partly smectogenic with middle ordered melting type.


Presently investigated novel mesogenic series consisted of eleven homologues. Methyl and ethyl homologue derivatives are nonliquid crystalline while, the rest of the homologues from propyl to hexadecyl homologue derivatives are enantiotropically nematogenic without exhibition of smectogenic character. Transition temperatures (table-30) were plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group. The phase diagram showing phase behavior of the series is shown in figure-16. Solid-isotropic or nematic transition curve rises and falls in zigzag manner is ascended with overall descending tendency. Nematic-isotropic transition curve initially rises and then gradually descended as series is ascended and behave in normal manner. Odd-even effect is observed with very narrow temperature difference. Curves for odd and even homologues merge into each other between
octyl and nonyl derivative of the series and the effect diminishes disappears from and beyond nonyl derivative of the series. Nematogenic phase length vary between 18°C to 57°C. Isotropic temperatures of LC homologue derivatives vary between 118°C to 188°C. Series is entirely nematogenic with N-I thermal stability 158.25°C and middle ordered melting type. Variation in mesomorphic properties observed from homologue to homologue.

3.2 Mutual comparison of homologous series:

The mutual comparison of homologous series under discussion can be grouped as under,
(A) Mutual comparison of homologous series (1) and (2).
(B) Mutual comparison of homologous series (3) and (4).
(C) Mutual comparison of homologous series (5) and (6).
(D) Mutual comparison of homologous series (7) and (8).

(A) Mutual comparison of homologous series (1) and (2).

The mesomorphic properties, mesophase length and thermal stability of the presently investigated novel homologous series-(1) is compared with the other structurally similar homologous series-(2) as mentioned below in figure-17.

Homologous series-(1) and (2) are similar in respect of three phenyl rings bridged through two identical central groups –CH=CH-COO- and -CO-CH=CH- as well as commonly substituted left n-alkoxy (RO-) terminal end group. However they differ in respect of terminal end group or groups substituted on third right handed phenyl ring. Therefore observed variations in their mesomorphic properties and the degree of mesomorphism can be attributed to the differing features of series (1) and (2) respectively.
Homologous series (1) and (2) differ in respect of their groups substituted on third phenyl ring, i.e. –C₆H₄NO₂ and –C₆H₅(OCH₃)₂. Therefore, the length to breadth ratio, intermolecular end to end and lateral attraction, molecular polarizability due to molecular width by laterally substituted –OCH₃ and –NO₂ group contributing to magnitudes of anisotropic forces of intermolecular adhesion considerably differ based on rigidity and flexibility. Thus, magnitudes of anisotropic forces of intermolecular adhesion differing by molecular width or intermolecular closeness, molecular polarity and polarizability as a consequences of resultant rigidity and flexibility related to thermodynamic quantity, enthalpy (ΔH) differs considerably.

Thus, mesogenic characteristics and degree of mesomorphism exhibited by homologues of the homologous series (1) and (2) under discussion can be assessed keeping in view of above effects and effects related to it.

The upper transition of the members of the series (1) and (2) under discussion are tabulated in table-33 as under.

**Table :33 Upper transition temperatures of mesogens**

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(1)</td>
</tr>
<tr>
<td>C₁</td>
<td>172.0</td>
</tr>
<tr>
<td>C₂</td>
<td>166.0</td>
</tr>
<tr>
<td>C₃</td>
<td>180.0</td>
</tr>
<tr>
<td>C₄</td>
<td>171.0</td>
</tr>
</tbody>
</table>
From table-34 it is seen that the upper transition of the homologues to homologues in the same series gradually decreases as series is ascended. Also the upper transitions of the corresponding homologues are relatively lower for series-(1) as compared to series (2). The ratio of the polarity to polarizability changing from –NO$_2$ to –OCH$_3$ affects the intermolecular attractions in a manner reverse than expected. Actually –OCH$_3$ terminal being more polar group and should increases the intermolecular attraction as compared to –NO$_2$ and value of upper transitions indicate that series-(1) have lower than homologous series (2) with few exception. Thus, polarity and hence the end to end attraction are affected by substituent groups –OCH$_3$(dimethoxy) and –NO$_2$.

The variation of smectic and nematic phase length from homologue to homologue in the same series and series to series are recorded in table-35.

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
<th>Series (1)</th>
<th>Series (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sm</td>
<td>Nm</td>
<td>Total</td>
</tr>
<tr>
<td>C$_1$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Looking to the phase length of homologues of two homologous series-(1) and (2) from the table-35, the homologous series-(1) is partly smectogenic and nematogenic while homologous series-(2) is predominately nematogenic. Maximum total mesophase length of series-(1) is 36.0°C and series (2) of 59.0°C respectively. Thus mesophase length of series (2) are relatively more than series-(1) under comparison of right terminal end group, series-(2) and series-(1) contains –OCH$_3$ methoxy group and one nitro group respectively.

The homologous series (1) and (2) are identical in all respect except in respect of their right-sided terminal end groups –NO$_2$ and –OCH$_3$(dimethoxy) groups bonded to the third phenyl ring. Thus, mesomorphic properties and degree of mesomorphism and mesophase length are differed due to the electro negativity of oxygen is greater than nitrogen. Hence series (2) is contained –OCH$_3$(dimethoxy) group right terminal end group. Therefore the Ph–NO$_2$ and Ph-(OCH$_3$)$_2$ bond polarities are difference. Moreover, the N-O bond polarity of –NO$_2$ and C-H bond polarity of –OCH$_3$ are also different.. Thus, the vector sum of all bond polarities differs considerably for series-(1) and (2) vary due to the variation in molecular flexibility [3,4,54,99], which cause mesophase length of series-(1) is lower than series -(2).

Looking to the table-36 for relatively average thermal stabilities for series (1) and (2).

### Table:-36 Average Thermal Stabilities

<table>
<thead>
<tr>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectic-isotropic or</td>
</tr>
<tr>
<td>Series-(1)</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Series-(2)</td>
</tr>
</tbody>
</table>
Table-36 indicates that homologous series-(1) and (2) selected for comparison are smectogenic in addition to nematogenic while series-(2) does not exhibit smectogenic character at all. The intermolecular closeness due to the varying molecular width plays an important roll to the net magnitudes of intermolecular anisotropic forces of attraction when molecular width increases, the intermolecular forces of attraction depend upon two opposing forces operating at a time. (i) As molecular width increases, the intermolecular distance diminishes. Now at the same time (ii) increased molecular width, raises molecular polarizability, which results into razing of intermolecular attractions [54]. The net resultant effects (i) and (ii) operating at a nonlinear series (2) while second (ii) effect predominates for nonlinear series-(1). Thus, suitable magnitudes of anisotropic forces of intermolecular attraction is favorable and sufficient to facilitate lamellar packing of molecules of series (1) in their crystal lattices but it is insufficient, unfavorable and unsuitable to facilitate lamellar packing of molecules in the crystal lattices of series-(2). Hence, the statistically parallel orientational order of molecules is maintained by end to end attractions but, the sliding layered arrangement of molecule is missing in floating condition for series-(2). Highest value of nematic thermal stability of series-(2) than series-(1) under comparison is obvious from the point of view of intermolecular closeness.

From the table-36, it is clear that average thermal stability for smectic is 141.0 while that of series (2) is 00.0. Series-(1) being nonlinear due to presence of electron widrawng group –NO₂ on position 3” with third phenyl ring which widraws electrons from third phenyl ring. Therefore molecular polarity and polarizability are strengthened as compared to-OCH₃ (3”,4”-dimethoxy)
of series-(2). Thus, thermal stability which depend upon enthalpy ($\Delta H$) and entropy value ($\Delta S$) of homologue as system at a given temperature.

Commencement of smectic mesophase depend upon the extent of noncoplsnarity caused by the molecule. The extent of noncoplanarity is relatively more of series-(1) in combination with higher magnitudes of intermolecular attractions as compared series-(2), due to presence of meta substituted $-\text{NO}_2$ group. increased molecular width, raises molecular polarizability, which results into razing of intermolecular attractions [54].

Therefore smectic mesophase commences from fifth homologue in series (1) while it does not occur till the last hexadecyloxy derivate of the series (2).

Thus, from the present investigation the smectic-nematic and nematic-isotropic group efficiency order derived on the basis of average thermal stability with respect to lateral substituent as under.

Group efficiency for smectic:

\[
\begin{align*}
\text{NO}_2 & > \text{OCH}_3 \\
\text{OCH}_3 & > \text{H}
\end{align*}
\]

Group efficiency for nematic:

\[
\begin{align*}
\text{OCH}_3 & > \text{OCH}_3 \\
\text{NO}_2 & > \text{H}
\end{align*}
\]

Group efficiency order derived on the basis of early commencement of mesophase.

Smectic : $-\text{C}_6\text{H}_4\text{NO}_2 > -\text{C}_6\text{H}_3(\text{OCH}_3)_2$

Nematic : $-\text{C}_6\text{H}_4\text{NO}_2 = -\text{C}_6\text{H}_3(\text{OCH}_3)_2$

(B) Mutual comparison of homologous series (3) and (4)

The LC properties of the novel series-(3) and (4), including upper transition temperature, average thermal stability and commencement of mesomorphism are compared with each other series-(3) and (4) as mentioned below.
The two homologous series (3) and (4) under comparison commonly contain three phenyl rings bridged through \(-\text{CH}=\text{CH}-\text{COO}\)- and \(-\text{CH}=\text{CH}-\text{CO}\)- central groups and an \(\text{n-alkoxy}\) terminal chain. However, they differ in their geometrical shape, size, linearity of molecules. Therefore, observed variations in their mesomorphic properties and degree stability are attributed to the differing magnitudes of molecular polarity, polarizability [54] molecular rigidity and flexibility [2-4] as well as inter molecular anisotropic forces of attraction.

The upper transition of the members of the series (3) and (4) under discussion are tabulated in table-37 as under.

**Table :-37 Upper transition temperatures of mesogens**

<table>
<thead>
<tr>
<th>No. of carbon atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(3)</td>
</tr>
<tr>
<td>C_1</td>
<td>152.0</td>
</tr>
<tr>
<td>C_2</td>
<td>170.0</td>
</tr>
<tr>
<td>C_3</td>
<td>150.0</td>
</tr>
<tr>
<td>C_4</td>
<td>165.0</td>
</tr>
<tr>
<td>C_5</td>
<td>176.0</td>
</tr>
<tr>
<td>C_6</td>
<td>178.0</td>
</tr>
<tr>
<td>C_8</td>
<td>168.0</td>
</tr>
</tbody>
</table>
From the table-37, the mesomorphic isotropic transition increases from series-(3) to series-(4). However, irregular trend of upper transition in case of second, sixth as well as twelfth, fourteenth and sixteenth member of the series is observed. In general it can be stated that intermolecular forces of attraction are weakened from series-(4) to (3).

The mesophase length of series (3) and (4) are recorded in table-38.

**Table :-38 Mesomorphic Phase length in °C**

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (3)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>8.0</td>
</tr>
<tr>
<td>C₆</td>
<td>20.0</td>
</tr>
<tr>
<td>C₈</td>
<td>15.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>16.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>-</td>
</tr>
<tr>
<td>C₁₄</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
</tr>
</tbody>
</table>
Looking to the phase length of homologues of two homologous series (3) and (4) from the table-38. Total mesophase range varies between $34.0^0\text{C}$ to $76.0^0\text{C}$ for series-(3). The homologous series (3) is partly smectogenic and nematogenic while homologus series (4) is entirely nematogenic and smectic mesophase totally absent. Total mesophase ranges varies between $30.0^0\text{C}$ to $62.0^0\text{C}$ for series-(4). Total phase length of series (3) is higher than series (4). This difference causes difference in their molecular length, length to breath ratio, molecular polarity and polarizability, steric hindrance, molecular size and hidden magnitudes of anisotropic forces of attractions, which are responsible to induce smectic and/or nematic mesophase formation in floating condition. Series-(3) being linear the intermolecular distance is smaller and hence the intermolecular anisotropic forces of attraction are relatively more than the isomeric series-(4). The absence of smectogenic character in series-(4) indicates the absence of lamellar packing due to intermolecular widening, which reduced intermolecular cohesive forces.

Looking to the the table-39 for average thermal stabilities for series-(3) and (4).

**Table :-39 Average Thermal Stabilities**

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in $^0\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(3)</td>
</tr>
<tr>
<td>Smectic-isotropic or</td>
<td>132.25</td>
</tr>
<tr>
<td>Smectic-nematic</td>
<td>($C_5$—$C_{10}$)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>$C_5$</td>
</tr>
<tr>
<td>Smectic phase</td>
<td></td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>171.5</td>
</tr>
<tr>
<td>($C_5$—$C_{10}$)</td>
<td>($C_3$—$C_{14}$)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>$C_5$</td>
</tr>
<tr>
<td>nematic phase</td>
<td></td>
</tr>
</tbody>
</table>
Table-39 indicates that the thermal stability of smectic-nematic for series (3) and (4) are 132.25°C and 00.0°C with the commencement of smectogenic mesophase formation from fifth member of series-(3), while absence of smectogenic mesophase in series (4) because series-(4) is nonlinear where as series-(3) is linear. i.e. is wider than series-(3). An increases of molecular width increases intermolecular distance, and hence reduces intermolecular attraction and molecular polarizability. Thus, on one hand intermolecular anisotropic forces of attraction are reduced due to increased molecular width, while on the other hand, increased molecular polarizability enhances intermolecular cohesive forces. Therefore, these two opposing effects are operating for series-(4). Series-(3) exhibits of smectogenic behavior from the pentyloxy to decyloxy homologues of the series-(3) is attributed to the presence of lamellar packing of molecules in their crystal lattices and the molecules disalign with plane of surface acquiring a statistically parallel orientational order of the molecules in a floating condition with maintenance of two-dimensional array and to cause smectogenic mesophase formation in series (3).

The nematic-isotropic thermal stability of homologous series-(3) and (4) are 171.5°C and 175.7 respectively with commencement of nematogenic phase early formation in series-(4). However, the observed 4.2°C difference in their nematic-isotropic thermal stabilities is attributed to the difference in molecular length and breadth (width) and size. Moreover, homologous series-(3) is linear while homologous series-(4) is nonlinear. Hence the molecular polarity of series-(4) is greater than that that of series-(3). There fore, the magnitudes of anisotropic forces of intermolecular adhesion of series-(4) exceed that of series-(3).

The group efficiency order derived for smectic and nematic on the basis of thermal stability are as under.

Nematic : \(-\text{NO}_2\) > \(-\text{NO}_2\)

(Non-linear) (linear)

Smectic : \(-\text{NO}_2\) > \(-\text{NO}_2\)

(linear) (Non-linear)
(C) **Mutual comparison of homologous series (5) and (6).**

The mesomorphic properties of homologous series-(5) is compared with other structurally similar homologous series-(6) as shown in figure-19.

![Series-5 and Series-6 structures](image)

**Figure :-19**

Homologous series-(5) and (6) are structurally identical in all respect except their right terminal end groups which are 4" –NO₂ and 3",4" –(–OCH₃)₂ dimethoxy groups. Three phenyl rings bonded through two central groups –COO- and –CO-CH=CH- contributing molecular rigidity and n-alkoxy (-OR) left terminal end group contributing molecular flexibility [2,3,4] are identically and commonly present to the series selected under comparison. However varying right handed flexible terminal end group causes variation in overall molecular rigidity and flexibility [2,3,4]. This variation enables the mutual difference in mesomorphic properties and the degree of mesomorphism.

The upper transition temperature of the homologous series-(5) and (6) showing mesogenic behavior are recorded in table-40.

From the table-40, the mesomorphic-isotropic transition decreases from homologue to homologue in same and series to series for same homologue depends upon varying the polarity.
of the n-alkoxy terminal chain (RO-) with ascended homologous series-(5) and (6). The odd-even effect in mesomorphic or isotropic transition curve is attributed to the progressive addition to n-alkyl chain of n-alkoxy terminal end group. The upper transition of series-(5) is higher than series-(6) due to increases width of series-6 because of lateral substituted methoxy-OCH$_3$ present with third phenyl, while lateral group absent in series-(5) and hence decreases intermolecular attractions as consequences of molecular rigidity and flexibility compits [2,3,4] each other.

Table :-40, Upper transition temperatures of mesogens

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(5)</td>
</tr>
<tr>
<td>C$_1$</td>
<td>183.0</td>
</tr>
<tr>
<td>C$_2$</td>
<td>160.0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>169.0</td>
</tr>
<tr>
<td>C$_4$</td>
<td>161.0</td>
</tr>
<tr>
<td>C$_5$</td>
<td>170.0</td>
</tr>
<tr>
<td>C$_6$</td>
<td>165.0</td>
</tr>
<tr>
<td>C$_7$</td>
<td>-</td>
</tr>
<tr>
<td>C$_8$</td>
<td>155.0</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>172.0</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>158.0</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>120.0</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>122.0</td>
</tr>
</tbody>
</table>

The variation of smectic and nematic phase length for homologous series-(5) and (6) are recorded in table-41.

Maximum total mesophase length of homologous-(5) is 63.0$^\circ$C and series-(6) is 67.0$^\circ$C respectively. Thus, mesophase length of homologous series (6) is relatively more than
homologous series-(5) under comparison of right terminal end group of two methoxy and one –NO$_2$ group contained by series-(5) and (6) respectively.

Table :-41, Mesomorphic Phase length in 0°C

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in 0°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sm</td>
<td>Nm</td>
<td>Total</td>
<td>Sm</td>
<td>Nm</td>
</tr>
<tr>
<td>C$_1$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>33.0</td>
<td>33.0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>C$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>24.0</td>
<td>24.0</td>
</tr>
<tr>
<td>C$_5$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>C$_6$</td>
<td>18.0</td>
<td>31.0</td>
<td>49.0</td>
<td>7.0</td>
<td>49.0</td>
<td>56.0</td>
</tr>
<tr>
<td>C$_7$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13.0</td>
<td>52.0</td>
<td>65.0</td>
</tr>
<tr>
<td>C$_8$</td>
<td>13.0</td>
<td>43.0</td>
<td>56.0</td>
<td>14.0</td>
<td>50.0</td>
<td>64.0</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>16.0</td>
<td>47.0</td>
<td>63.0</td>
<td>28.0</td>
<td>39.0</td>
<td>67.0</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>30.0</td>
<td>22.0</td>
<td>52.0</td>
<td>24.0</td>
<td>21.0</td>
<td>45.0</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>-</td>
<td>15.0</td>
<td>15.0</td>
<td>15.0</td>
<td>33.0</td>
<td>48.0</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>-</td>
<td>12.0</td>
<td>12.0</td>
<td>-</td>
<td>36.0</td>
<td>36.0</td>
</tr>
</tbody>
</table>

Total mesophase length different between homologous series-(6) and (5) as 4.0°C and difference in liquid crystal properties of series-(6) and (5) are attributed to the additional methoxy group substituted at the ortho position (3”-methoxy) to a right terminal (4”-methoxy) end group and more polar –OCH$_3$ group compared to –NO$_2$. Hence molecular polarities, anisotropic forces of intermolecular attractions as a consequence of molecular rigidity and flexibility [2,3,4,54] increases in series-(6) compared to series-(5). Net or predominance of
intermolecular attraction of homologous series-(6) are affected by molecular polarizability due to molecular length resulting from two opposing forces operating at a time. Thus, end to end attractions emerging statically parallel orientational order of molecules and the lamellar packing arrangement of molecules facilitating orientational order of molecules in floating condition. Hence mesomorphic properties and degree of mesomorphism are differed due to the electro negativity of oxygen is greater than nitrogen and homologous series-(6) is contained dimethoxy groups right terminal end group. Therefore the Ph-NO$_2$ and Ph-(OCH$_3$)$_2$ bond polarities are difference. Moreover the N-O bond polarity of -NO$_2$ and C-H bond polarity of - OCH$_3$ are also different. Thus, the vector sum of all bond polarities differ considerably for homologous series (5) and (6). Hence, molecular polarities of homologous series (5) and (6) vary due to the variation flexibility [2-4] which cause mesophase length of homologous series-(5) is lower than homologous series-(6).

Table-42 shows the relative thermal stability and commencement of the mesophase mentioned as below.

Table-42, Average Thermal Stabilities

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(5)</td>
</tr>
<tr>
<td>Smectic-isotropic or Smectic-nematic</td>
<td>126.7</td>
</tr>
<tr>
<td></td>
<td>(C$<em>6$—C$</em>{12}$)</td>
</tr>
<tr>
<td>Commencement of Smectic phase</td>
<td>C$_6$</td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>148.6</td>
</tr>
<tr>
<td></td>
<td>(C$<em>6$—C$</em>{16}$)</td>
</tr>
<tr>
<td>Commencement of nematic phase</td>
<td>C$_6$</td>
</tr>
</tbody>
</table>
Table-42 indicates that the relatively thermal stability of smectic-nematic for the homologous series (5) and (6) are 126.7°C and 115.6 respectively with the commencement of smectogenic mesophase formation from same hexaloxy homologue of both homologous series. The difference of thermal stability by 11.1°C is attributed to the difference of molecular flexibility caused by -NO₂ and dimethoxy(-OCH₃) terminal end groups of homologous series (5) and (6) respectively and the intermolecular closeness due to the varying molecular width plays an important roll to the net magnitudes of intermolecular anisotropic forces of attractions. Because laterally substituted -OCH₃ and -NO₂ groups increases molecular width for series-(5) and (6) under comparison. When molecular width increases, the intermolecular forces of attraction depend upon two opposing forces operating at a time. (i) as molecular width increases, the intermolecular distance increases or intermolecular closeness reduces. Consequently intermolecular attractions diminishes. Now at the same time (ii) increased molecular width, raises molecular polarizability, which results into raising of intermolecular attractions [2]. The net resultant effect of intermolecular attractions depends upon the predominating effect out of two opposing effects (i) and (ii) operating at a time. Thus, the (i) effect predominates for nonlinear series-(6) while; second (ii) effect predominates for nonlinear series X. The electro negativity of oxygen is grater than nitrogen, therefore Ph-(OCH₃)₂ bond more polar than Ph-NO₂ bond. Also series-(6) is contained two polar group (-OCH₃), while homologous series- (5) is contained only one -NO₂ polar group. Thus, the vector sum of all bond polarities differs considerably for homologous series (5) and (6). Hence more molecular polarities of homologous series-(5) and (6) vary due to the variation in molecular flexibility [2-4], which causes variation in the nematic-isotropic thermal stability 148.0°C and 156.6°C with the commencement of nematogenic mesophase formation from the hexyloxy and ethoxy homologue of the series-(5) and (6) respectively. The thermal stability for N-I of homologous series-(5) is lower than series (6). The difference of thermal stability by 4.0°C is attributed to the difference of molecular polarity and the molecular flexibility caused by -NO₂ and -OCH₃ dimethoxy terminal end groups of homologous series-(5) and (6) respectively.

The extent of non-coplanarity also contributes to the lamellar packing of molecules. In short, the molecular flexibility and the difference in arrangement in space of the -NO₂ and -OCH₃ cause a difference in non coplanarity of the molecules of homologous series (5) and (6). The net resultant effect of intermolecular attractions depends upon the predominating effect out of two
opposing effects (i) and (ii) operating at a time. Thus, the (i) effect predominates for nonlinear series-(6) while; second (ii) effect predominates for nonlinear series-(5), hence increased molecular width, raises molecular polarizability, which result into raising of intermolecular attractions [54] in series-(5). Thus smectic-nematic thermal stability of series-(5) is higher than series-(6).

Thus, from the present investigation the smectic-nematic and nematic-isotropic group efficiency order derived on the basis of average thermal stability as under.

<table>
<thead>
<tr>
<th>Smectic group</th>
<th>Efficiency order</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C₆H₄NO₂</td>
<td>&gt; -C₆H₃(OCH₃)₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nematic group</th>
<th>Efficiency order</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C₆H₃(OCH₃)₂</td>
<td>&gt; -C₆H₄NO₂</td>
</tr>
</tbody>
</table>

(D) Mutual comparison of homologous series (7) and (8).

The liquid crystal properties (LC) of the homologous series-(7) is compared with the other structurally similar homologous series-(8) in figure-20.

Homologous series-(7) and (8) (fig.24) under comparison commonly contain three phenyl rings bridged through –COO- and –CH=CH-CO- central groups and n-alkoxy terminal chain and right terminal end group –NO₂. However, they differ in their geometrical shape, size, linearity of molecules. Therefore, observed variations in their mesomorphic properties and degree of mesomorphism including upper transition temperature, thermal stability are attributed to the
differing magnitudes of molecular polarity, polarizability [54], molecular rigidity and flexibility [2-4] as well as intermolecular anisotropic of attraction.

The upper transition temperature of the homologous series-(7) and (8) under discussion are recorded in table-43.

### Table:-43, Upper transition temperatures of mesogens

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(7)</td>
</tr>
<tr>
<td>C₁</td>
<td>191.0</td>
</tr>
<tr>
<td>C₂</td>
<td>200.0</td>
</tr>
<tr>
<td>C₃</td>
<td>164.0</td>
</tr>
<tr>
<td>C₄</td>
<td>140.0</td>
</tr>
<tr>
<td>C₅</td>
<td>160.0</td>
</tr>
<tr>
<td>C₆</td>
<td>167.0</td>
</tr>
<tr>
<td>C₈</td>
<td>169.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>166.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>162.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>136.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>128.0</td>
</tr>
</tbody>
</table>

The upper transition temperature of homologous series-(8) is higher than homologous series- (7) due to homologous series-(7) is linear whereas homologous series (8) is non linear, i.e. homologous series-(8) is wider than homologous series-(7). An increases of molecular distance and hence reduces intermolecular attractions and increases molecular polarizability. Series- (7) being linear, the intermolecular distance is smaller and hence the intermolecular anisotropic forces of attractions are relatively more than the isomeric homologous series-(8). Thus difference between upper transition temperature of homologous series-(7) is lower than
homologous series-(8). However, irregular trend of upper transition temperature in ascending of series-(7) and (8).

Looking to the mesophase length of homologues of two homologous series- (7) and (8) from the table-44.

Table:-44, Mesomorphic Phase length in {0}C

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sm</td>
<td>Nm</td>
<td>Total</td>
<td>Sm</td>
<td>Nm</td>
<td>Total</td>
</tr>
<tr>
<td>Series (7)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
<td>-</td>
<td>16.0</td>
<td>16.0</td>
</tr>
<tr>
<td>C4</td>
<td>-</td>
<td>20.0</td>
<td>20.0</td>
<td>-</td>
<td>26.0</td>
<td>26.0</td>
</tr>
<tr>
<td>C5</td>
<td>-</td>
<td>50.0</td>
<td>50.0</td>
<td>-</td>
<td>48.0</td>
<td>48.0</td>
</tr>
<tr>
<td>C6</td>
<td>23.0</td>
<td>30.0</td>
<td>53.0</td>
<td>-</td>
<td>60.5</td>
<td>60.5</td>
</tr>
<tr>
<td>C8</td>
<td>24.0</td>
<td>49.0</td>
<td>73.0</td>
<td>-</td>
<td>57.0</td>
<td>57.0</td>
</tr>
<tr>
<td>C10</td>
<td>20.0</td>
<td>46.0</td>
<td>66.0</td>
<td>-</td>
<td>35.0</td>
<td>35.0</td>
</tr>
<tr>
<td>C12</td>
<td>35.0</td>
<td>33.0</td>
<td>68.0</td>
<td>-</td>
<td>26.0</td>
<td>26.0</td>
</tr>
<tr>
<td>C14</td>
<td>26.0</td>
<td>14.0</td>
<td>40.0</td>
<td>-</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>C16</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Series (8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
<td>-</td>
<td>16.0</td>
<td>16.0</td>
</tr>
<tr>
<td>C4</td>
<td>-</td>
<td>20.0</td>
<td>20.0</td>
<td>-</td>
<td>26.0</td>
<td>26.0</td>
</tr>
<tr>
<td>C5</td>
<td>-</td>
<td>50.0</td>
<td>50.0</td>
<td>-</td>
<td>48.0</td>
<td>48.0</td>
</tr>
<tr>
<td>C6</td>
<td>23.0</td>
<td>30.0</td>
<td>53.0</td>
<td>-</td>
<td>60.5</td>
<td>60.5</td>
</tr>
<tr>
<td>C8</td>
<td>24.0</td>
<td>49.0</td>
<td>73.0</td>
<td>-</td>
<td>57.0</td>
<td>57.0</td>
</tr>
<tr>
<td>C10</td>
<td>20.0</td>
<td>46.0</td>
<td>66.0</td>
<td>-</td>
<td>35.0</td>
<td>35.0</td>
</tr>
<tr>
<td>C12</td>
<td>35.0</td>
<td>33.0</td>
<td>68.0</td>
<td>-</td>
<td>26.0</td>
<td>26.0</td>
</tr>
<tr>
<td>C14</td>
<td>26.0</td>
<td>14.0</td>
<td>40.0</td>
<td>-</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>C16</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
</tr>
</tbody>
</table>

From table-44, it is seen that the nematogenic and smectogenic phase ranges for series- (7) and (8). Total mesophase ranges varies between 18.0{0}C to 73.0{0}C of series-(7). Homologous series-(7) is predominatly nematogenic and partly smectogenic with middle ordered melting type, while series-(8) is nematogenic middle order melting type.

Homologous series-(8) does not exhibit smectogenic character. The absence of smectogenic character is attributed to the absence of lamellar packing of molecules in their crystal lattice and a sliding layered arrangement of molecule does not occur in floating condition due to molecular width increases, hence the intermolecular distance increases. Consequently intermolecular
attraction diminishes in series-(8). Thus suitable magnitudes of anisotropic forces of intermolecular attractions is unfavorable, insufficient and unsuitable to facilitate lamellar packing of molecules in the crystal lattices of series-(8), hence absent smectic property in series-(8).

The molecular shape of a molecule of the series-(7) is linear lath like and the terminal end groups are sufficiently polar. Therefore, the length to breadth ratio and the molecular polarity to polarizability ratio satisfy the required environment to cause suitable magnitudes of anisotropic forces of intermolecular adhesion, which enables smectic and/or nematic mesophase formation within a defined range of temperature. While series (8) is nonlinear so does not exhibit smectogenic character due to not suitable lamellar packing and anisotropic attractions.

The thermal stability and commencement of mesophase for homologous series (7) and (8) are recorded in table-45.

**Table-45, Average Thermal Stabilities**

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(7)</td>
</tr>
<tr>
<td>Smectic-isotropic or</td>
<td>125.6 (C&lt;sub&gt;6&lt;/sub&gt;—C&lt;sub&gt;14&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Smectic-nematic</td>
<td></td>
</tr>
<tr>
<td>Commencement of</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td>Smectic phase</td>
<td></td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>154.6 (C&lt;sub&gt;3&lt;/sub&gt;—C&lt;sub&gt;16&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>nematic phase</td>
<td></td>
</tr>
</tbody>
</table>

The thermal stability of homologous series-(7) is less than homologous series (8), However, the observed difference in their thermal stability is attributed to the difference in molecular length and breadth (width) and size. Moreover, series-(7) is linear while series (8) is nonlinear.
Hence the molecular polarity of homologous series-(8) is greater than homologous series-(7). Therefore the magnitudes of anisotropic forces of intermolecular adhesion of series (8) exceed that of series-(7).

The smectogenic mesophase commences from the hexyloxy homologue for series- (7) while series-(8) does not exhibit smectogenic character. This indicates that lamellar the sixth member of the series for the molecules of series-(7), while lamellar packing is hindered in case of series-(8) due to the size of molecule which affects the extent of noncoplanarity.

Homologous series-(7) being linear, the intermolecular distance is smaller hence the intermolecular anisotropic forces of attraction are relatively more than the isomeric series (8) which causes lamellar packing of molecules in their crystal lattices and causes sliding layered arrangement of molecules in a floating condition under the influence of heat. The absence of smectogenic character in series-(8) indicates the absence of lamellar packing due to intermolecular widening, which reduced intermolecular cohesive forces. The commencement of the nematic mesophase earlier for third member of series-(8) while late for six member of series-(7) is due to the molecules of series-(7) and (8) differ in molecular length, molecular rigidity, molecular length to breadth ratio. Hence these differences cause a difference in the magnitudes of anisotropic intermolecular forces of attractions.

The group efficiency order derived for smectic and nematic on the basis of average thermal stability are as under.

<table>
<thead>
<tr>
<th>Nematic</th>
<th>–NO₂</th>
<th>&gt;</th>
<th>–NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Non-linear)</td>
<td>(linear)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Smectic</th>
<th>–NO₂</th>
<th>&gt;</th>
<th>–NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(linear)</td>
<td>(Non-linear)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.3 Comparison of other structural homologous series

3.3.1 Comparison of Homologous series (1) and (A) :
The homologous series-(1) and (A) are structurally similar, the molecules with common core structure excluding right terminal end group as shown in figure-21. the basic length due to three benzene rings linked central bridges, left and right terminal end groups, aromaticity of the molecules are the constant unchanging features and the forces on account of these factors will remain same but they differ from their linking groups –CO-CH=CH- or –CH=CH-CO- with third phenyl ring. Both series are isomeric in structurally.

![Figure:21](image)

Therefore, the variation in mesomorphic property and degree of mesomorphism have direct relation with difference in polarity and polarizability as well as resultant difference of intermolecular cohesive forces of attraction arising out of it and their rigidity and/or flexibility[9],[53,54],[101].

Firstly, Both the homologous series under comparison exhibit mesomorphism from pentyl to last hexadecyl homologue while rest of the homologue methyl to butyl are nonmesogenic.

The upper transition of the homologues of homologous series-(1) and (A) displaying mesomorphism and mesomorphic phase length are recorded in following table-46 and table-47 respectively.

From table-46, it is seen that the upper transition of homologous series (1) is higher than the homologous series-(A). Homologous series-(1) being >C=O group is linked directly with middle phenyl ring while it links with last phenyl ring in case of series-(A). Therefore present investigated series-(1) differs from series-(A) with respect to keeping molecular length unchanged, same substituted group with last phenyl ring on same position but positional variation of >C=O group in addition to differenced by varying inductive and steric effect of –NO₂. i.e. increased intermolecular separation due to >C=O group is linked directly last phenyl ring in homologous series-(A) while it links with directly middle phenyl ring in series-(1). Therefore increases intermolecular attraction or decreases intermolecular separation consequence molecular rigidity and flexibility with higher polarity and polarizability in series-
Hence, upper transition of series-(1) is higher than series-(A). Odd-even effect is absent in the phase diagram of the both series because the absence of mesophase formation by early member of the series (1) and (A).

Table:-46, Upper transition temperatures of mesogens

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(1)</td>
</tr>
<tr>
<td>C₁</td>
<td>172.0</td>
</tr>
<tr>
<td>C₂</td>
<td>166.0</td>
</tr>
<tr>
<td>C₃</td>
<td>180.0</td>
</tr>
<tr>
<td>C₄</td>
<td>171.0</td>
</tr>
<tr>
<td>C₅</td>
<td>144.0</td>
</tr>
<tr>
<td>C₆</td>
<td>158.0</td>
</tr>
<tr>
<td>C₈</td>
<td>166.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>152.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>156.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>162.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>154.0</td>
</tr>
</tbody>
</table>

Table-47 represents variation of mesophase length from homologue in the same series and series to series.

Looking from table-47, indicates mesophase length of homologous series (A) are relatively more than homologous series-(1) under comparison. Total mesophase length different between homologous series-(1) and (A) as 10.0°C is attributed molecular polarities, anisotropic forces of intermolecular attractions as a consequence of molecular rigidity and flexibility [2,3,4,54] each other.
Table : -47, Mesomorphic Phase length in °C

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (1)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>6.0</td>
</tr>
<tr>
<td>C₆</td>
<td>14.0</td>
</tr>
<tr>
<td>C₈</td>
<td>21.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>13.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>-</td>
</tr>
<tr>
<td>C₁₄</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
</tr>
</tbody>
</table>

Thermal stabilities of the homologous series-(1) and (A) under present discussion are recorded in table-48.

From the table-48, it is clear that, average thermal stability of homologous series (1) for smectic is 141.0 while that of series-(A) is 163.0. Therefore smectic thermal stability for series-(A) is higher than series-(A) under comparison. Secondly nematic thermal stability for series-(1) is higher than series-(A). Homologous series-(1) being >C=O group is linked directly with middle phenyl ring while it links with last phenyl ring in case of series-(A). Therefore present investigated series-(1) differs from series-(A) with respect to keeping molecular length unchanged, same substituted group with last phenyl ring on same position but positional variation of >C=O group in addition to differenced by varying inductive and steric effect of –NO₂. Thus, variation in thermal stabilities as well as other related mesogenic or thermodynamic
properties under go variation. Smectic mesophase shows pentyl to decyl homologue for series-(1) while series-(A) exhibits pentyl to octyl derivative.

**Table-48, Average Thermal Stabilities**

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(1)</td>
</tr>
<tr>
<td>Smectic-isotropic or</td>
<td>141.0</td>
</tr>
<tr>
<td>Smectic-nematic</td>
<td>(C₅—C₁₀)</td>
</tr>
<tr>
<td></td>
<td>Series-(A)</td>
</tr>
<tr>
<td></td>
<td>163.8</td>
</tr>
<tr>
<td></td>
<td>(C₅-C₁₆)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C₅</td>
</tr>
<tr>
<td>Smectic phase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₅</td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>156.0</td>
</tr>
<tr>
<td></td>
<td>(C₅—C₁₆)</td>
</tr>
<tr>
<td></td>
<td>154.6</td>
</tr>
<tr>
<td></td>
<td>(C₅-C₈)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C₅</td>
</tr>
<tr>
<td>nematic phase</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₅</td>
</tr>
</tbody>
</table>

Variation in mesogenic properties can be brought about by varying molecular rigidity and flexibility. The group efficiency order derived on the basis of thermal stability for smectic and nematic with respect to lateral substituent as under.
3.3.2 Comparison of Homologous series (4) and (8):

The mesogenic properties, thermal stability and commencement of smectic and nematic etc of the presently investigated homologous series-(4) are compared with the other structurally similar homologous series-(8) as mentioned below in figure-22.

Homologous series-(4) and (8) consist of three phenyl ring and two central bridges – CH=CH-CO- as common and-COO and –CH=CH-COO- as other central bridge that contribute to the overall molecular rigidity and n-alkoxy(-OR) and –NO\textsubscript{2} end groups that contribute to the molecular flexibility without any laterally substituted flexible group. Both of the series have their identical geometrical shape, but their molecular length and central group differs. The homologous series-(4) and (8) are identical in all respects, except with respect to their central bridge linking first and middle phenyl ring, that is, –COO- and –CH=CH-COO- respectively.

The upper transition of the members of the series-(4) and (8) under discussion are tabulated in table-49 as under.
From table-49, it is seen that the upper transition of the homologues to homologues in the same series gradually decreases as series is ascended, in irregular manner. Also the upper transition of the corresponding homologues are relatively lower for series-(4) as compared to series-(8) due to central bridge –COO- is sorter than –CH=CH-COO-, and hence decrease molecular length, thus the magnitudes of anisotropic intermolecular forces of attractions more of series-(8) compared to series-(4). The odd-even effect diminishes in the phase diagram as the series-(4) and (8) are ascended because n-alkoxy chain of higher homologues may coil, bend, flex or couple to lie with major axis of the core.

**Table:-49, Upper transition temperatures of mesogens**

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(4)</td>
</tr>
<tr>
<td>C_1</td>
<td>185.0</td>
</tr>
<tr>
<td>C_2</td>
<td>161.0</td>
</tr>
<tr>
<td>C_3</td>
<td>215.0</td>
</tr>
<tr>
<td>C_4</td>
<td>192.0</td>
</tr>
<tr>
<td>C_5</td>
<td>182.0</td>
</tr>
<tr>
<td>C_6</td>
<td>175.0</td>
</tr>
<tr>
<td>C_8</td>
<td>182.0</td>
</tr>
<tr>
<td>C_10</td>
<td>163.0</td>
</tr>
<tr>
<td>C_12</td>
<td>155.0</td>
</tr>
<tr>
<td>C_14</td>
<td>158.0</td>
</tr>
<tr>
<td>C_16</td>
<td>158.0</td>
</tr>
</tbody>
</table>

The variation of smectic and nematic phase length from homologue to homologue in the same series and series to series are recorded in table-50.

Looking to the phase length of homologues of two homologous series (4) and (8) from the table-50. Total mesophase ranges varies between16.0°C to 60.5°C for series-(8). Total phase
length of series-(4) is higher than series-(8). Thus, the difference of total mesophase length is attributed molecular length, molecular rigidity, molecular length to breadth ratio and hence these difference causes a difference in the magnitudes of anisotropic intermolecular forces of attractions by difference central groups –CH=CH-COO- and -COO- of series-(4) and (8), respectively.

Table:-50, Mesomorphic Phase length in ⁰C

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in ⁰C</th>
<th>Series (4)</th>
<th>Series (8)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sm</td>
<td>Nm</td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
<td>51.0</td>
<td>51.0</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>-</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>C₆</td>
<td>-</td>
<td>51.0</td>
<td>51.0</td>
</tr>
<tr>
<td>C₇</td>
<td>-</td>
<td>62.0</td>
<td>62.0</td>
</tr>
<tr>
<td>C₈</td>
<td>-</td>
<td>54.0</td>
<td>54.0</td>
</tr>
<tr>
<td>C₉</td>
<td>-</td>
<td>41.0</td>
<td>41.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
</tr>
<tr>
<td>C₁₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table-51 shows the relative thermal stability and commencement of the mesophase mentioned as below.

The N-I thermal stability of series (4) is 175.7⁰C, while the N-I thermal stability of series (8) is 158.25⁰C. The difference of thermal stability by 20.45⁰C is attributed to the difference molecular rigidity and flexibility caused by difference central groups –CH=CH-COO- and -COO- of series-(4) and (8), respectively. Smectogenic mesophase formation is absent in all
homologues of series(4) and (8) due to the absence of lamellar packing in crystal lattice of the molecules of series-(4) and (8) and also contributes the extent of noncoplanarity due to both series are non linear.

Table:-51, Average Thermal Stabilities

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(4)</td>
</tr>
<tr>
<td>Smectic-isotropic or Smectic-nematic</td>
<td>-</td>
</tr>
<tr>
<td>Commencement of Smectic phase</td>
<td>-</td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>175.7</td>
</tr>
<tr>
<td>(C₃—C₁₄)</td>
<td></td>
</tr>
<tr>
<td>Commencement of nematic phase</td>
<td>C₃</td>
</tr>
</tbody>
</table>

Now on comparing the LC properties of series-(4) and (8), geometrical shape is identical but they differ with only central groups –CH=CH-COO- and –COO-. Thus, the molecules of series-(4) and (8) differ in molecular length, molecular rigidity, molecular length to breadth ratio, negligible magnitudes of molecular polarizability and hence these differences causes more or less difference in the magnitudes of anisotropic forces of intermolecular attractions. As discussed above, presently investigated homologous series-(4) and (8) resemble each other except the central bridge which is –CH=CH-COO- and –COO-in case of homologous series-(8) under discussion, these two series under comparison are closely similar to each other. Both these central bridges are comparable though the vinyl carboxylate –CH=CH-COO- has greater length and causes more noncoplanarity due to the twist obtained as the oxygen atoms of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic
phenyl rings. On account of the enhanced length of the vinyl carboxy \(-\text{CH}=\text{CH}-\text{COO}\)- central bridge, increased conjugation by \(-\text{CH}=\text{CH}\)- unit and length which increases the rigidity of the molecule and lateral attractions and hence the, magnitudes of anisotropic forces of intermolecular attractions [54] which increases; while in case of \(-\text{COO}\)- central bridge, relative length is shorter and it do not link the phenyl rings through at least one multiple bond or hydrogen bonded ring system. Consequently the stereochemistry of the molecule does however, preserve the linearity of the molecule but results in less thermally stable mesophase. Hence the molecules of series-(4) under comparison tend to pack efficiently with higher thermal stability 175.7\(^{\circ}\)C and that of series-(8) tend to pack little bit less efficiently with lower thermal stability 158.25\(^{\circ}\)C. Commencement of nematogenic mesophase takes place from third (C\(_3\)) member of the series which very well match to all the series under comparison. The variation in mesomorphic properties from homologue to homologue in the same series and for the same homologue from series to series are due to the sequentially added methylene (-\text{CH}_2-) unit in the n-alkyl chain of left n-alkoxy terminal end group and due to right sided terminal end group or/and laterally substituted or central group which remain intact throughout the series respectively. Thus, present investigation verywell supports earlier views [102].

The group efficiency order derived on the basis of thermal stability for nematic mesophase formation is as mentioned below.

\[
\begin{align*}
\text{Nematic:} & \quad -\text{NO}_2 & > & -\text{NO}_2 \\
& \quad \text{with} & \quad \text{with} \\
& \quad -\text{CH}=\text{CH}-\text{COO} & \quad -\text{COO} \\
& \quad \text{central bridge} & \quad \text{central bridge}
\end{align*}
\]

3.3.3 Comparison of Homologous series (5) and (1) :

The mesomorphic properties like phase length or degree of mesomorphism, commencement of mesophases, predominancy of mesophase including average thermal stability etc. of present series-(5) is compared with the structurally similar homologous series-(1) as shown in figure-23.
Although series-(5) and (1) are structurally similar but, they differ from their central bridge. Therefore their rigidity and/or flexibility [2,3,4] vary to more or less extent and hence variation in mesomorphic properties and degree of mesomorphism accordingly. Series-(5) and (1) identical with respect to aromaticity due to three phenyl rings and central group -CO-CH=CH- and substituted -NO₂ and –OR group but they differ with respect to a central groups linking first and middle phenyl ring by –COO- and –CH=CH-COO- respectively. Therefore for molecular length due to –CH=CH- unit of series-(1) is longer than series-(5). Hence, length to breadth ratio vary accordingly causing difference of molecular rigidity and flexibility, such that, magnitudes of anisotropic forces of intermolecular attractions and hence the presence or absence of lamellar packing in their crystal lattices and disalignment of molecules at an angle less than ninety degree on the plane of surface to vary end to end intermolecular adhesion to form mesophase (smectic/nematic) varied. Therefore they differ in molecular breadth and hence the difference is reflected to cause variations in molecular polarity and polarizability due to differ in liquid crystal properties of series-(5) and (1).

The upper transition temperature of the homologous series-(5) and (1) showing mesogenic behavior are recorded in table-52.

The upper transition temperature of series-(5) is higher than series-(1) due to series-(5) and (1) contains central groups linking first and middle phenyl ring by –COO- and –CH=CH-COO- respectively. Therefore for molecular length due to –CH=CH- unit of series-(1) is longer than series-(5). Hence, length to breadth ratio vary accordingly causing difference of molecular rigidity and flexibility, such that, magnitudes of anisotropic forces of intermolecular attractions more of series-(5) is compared to series-(1).

**Table:-52, Upper transition temperatures of mesogens**
<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(5)</td>
</tr>
<tr>
<td>C₁</td>
<td>183.0</td>
</tr>
<tr>
<td>C₂</td>
<td>160.0</td>
</tr>
<tr>
<td>C₃</td>
<td>169.0</td>
</tr>
<tr>
<td>C₄</td>
<td>161.0</td>
</tr>
<tr>
<td>C₅</td>
<td>170.0</td>
</tr>
<tr>
<td>C₆</td>
<td>165.0</td>
</tr>
<tr>
<td>C₈</td>
<td>155.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>172.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>158.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>120.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>122.0</td>
</tr>
</tbody>
</table>

From table-52 it is seen that the upper transition of homologues to homologues in the series-(5) and (1) varies in irregular manner. Molecules of first five homologues are unable to resist thermal vibrations exposed upon them from external source of thermodynamic surroundings. Therefore, neither the statically parallel orientational order nor the sliding layered order of molecules occur in floating condition, which results into absence of the formation of either nematic or smectic mesophase and concerned homologues sharply transform into isotropic state from solid crystalline state.

The variation of smectic and nematic phase length from homologue to homologue in the same series and series to series are recorded in table-53.

Looking to the phase length of homologues of both homologous series from the table-53. The homologous series-(5) and (1) is predominantly nematogenic and partly smectogenic. Total
mesophase difference is 27.0°C. It is attributed to more magnitude anisotropic attractions of series-(5) due to series-(5) contains shorter -COO- central bridge linking first and second phenyl ring, while series-(1) contains longer –CH=CH-COO, and hence, decreases length of the molecules, length to breadth ratio and more polarity and polarizability of series-(5).

Table:-53, Mesomorphic Phase length in °C

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
<th>Series (5)</th>
<th>Series (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sm</td>
<td>Nm</td>
<td>Total</td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₆</td>
<td>18.0</td>
<td>31.0</td>
<td>49.0</td>
</tr>
<tr>
<td>C₈</td>
<td>13.0</td>
<td>43.0</td>
<td>56.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>16.0</td>
<td>47.0</td>
<td>63.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>30.0</td>
<td>22.0</td>
<td>52.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>-</td>
<td>15.0</td>
<td>15.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
<td>12.0</td>
<td>12.0</td>
</tr>
</tbody>
</table>

Table-54 shows the relative thermal stability and commencement of the mesophase of homologous series-(5) and (1) mentioned as below.

Table:-54, Average Thermal Stabilities

<table>
<thead>
<tr>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series-(5)</td>
</tr>
</tbody>
</table>

Table-54 represents that smectic and nematic thermal stability for series-(5) is lower than series-(1). Molecules of series-(5) and (1) are identical in all other respects except the central bridge which is –COO- and –CH=CH-COO- respectively under comparison. Both these central bridges are comparable though the –COO- has shorter length by –CH=CH- unit than the –CH=CH-COO- central bridge. Therefore greater length of vinyl carboxylate -CH=CH-COO- has greater length and causes more noncoplanarity due to a twist obtained as the oxygen atoms of vinyl carboxylate group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings. Moreover increased molecular length increases length to breadth ratio, enhancing end to end intermolecular anisotropic forces of attractions. On account of these differences the smectic-nematic and nematic-isotropic thermal stabilities are general way lower for the series-(5) than the corresponding homologous series- (1). Lamellar packing of molecules commences from sixth and fifth member of the series-(5) and (1) respectively because smectogenic mesophase formation commences from sixth and fifth homologues.

The group efficiency order derived on the basis of thermal stability for nematic mesophase formation is as mentioned below.

\[
\text{Nematic : } -\text{NO}_2 > -\text{NO}_2 \\
\text{with } -\text{COO-}
\]
3.3.4 Comparison of Homologous series (6) and (2):

The mesomorphic properties like phase length or degree of mesomorphism, commencement of mesophases, predominance of mesophase including average thermal stability etc. of present series-(6) is compared with the structurally similar homologous series-(2) as shown in figure-24.

Homologous series-(6) and (2) are structurally similar but, they differ from their central bridge or bridges at the phenyl ring. Therefore their rigidity and/or flexibility [2,3,4] vary to more or less extent and hence variation in mesomorphic properties and degree of mesomorphism accordingly. Series-(6) and (2) identical with respect to aromaticity due to three phenyl rings and central group –CO-CH=CH- and substituted3”,4”-dimethoxy(-OCH₃) and -OR group but they differ with respect to a central groups linking first and middle phenyl ring by –COO- and –CH=CH-COO- respectively. There for molecular length due to –CH=CH- unit of series-(2) is longer than series-(6). Hence, length to breadth ratio vary accordingly causing difference of molecular rigidity and flexibility, such that, magnitudes of anisotropic forces of intermolecular attractions and hence the presence or absence of lamellar packing in their crystal lattices and disalignment of molecules at an angle less than ninety degree on the plane of surface to vary end to end intermolecular adhesion to form mesophase (smectic/nematic) varied. Therefore they
differ in molecular breadth and hence the difference is reflected to cause variations in molecular polarity and polarizability due to differ in liquid crystal properties of series-(6) and (2).

The upper transition of the members of the series-(6) and (2) under discussion are tabulated in table-55 as under.

From table-55, it is seen that the upper transition of homologues to homologues in the series-(6) and (2) varies in irregular manner. The odd-even effect in mesomorphic or isotropic (Sm-Nm or Nm-I) transition curve is attributed to the progressive addition of odd and even numbers of carbon to n-alkyl chain of left n-alkoxy terminal end group in phase diagram of series-(6), while nematic-isotropic transition curve initially rises up to decyl homologue and then descended as series is ascended with exhibition of odd-even effect of series-(2).

The upper transition temperature of homologous series-(2) is highest compared to series-(6) because molecular length due to –CH=CH- unit of series-(2) is longer than series-(6). Hence, length to breadth ratio vary accordingly causing difference of molecular rigidity and flexibility, such that, magnitudes of anisotropic forces of intermolecular attractions increases in series-(2) than series-(6).

The variation of smectic and nematic phase length for homologous series (6) and (2) are recorded in table-56.

Table:-55, Upper transition temperatures of mesogens

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(6)</td>
</tr>
<tr>
<td>C₁</td>
<td>169.0</td>
</tr>
<tr>
<td>C₂</td>
<td>167.0</td>
</tr>
<tr>
<td>C₃</td>
<td>160.0</td>
</tr>
</tbody>
</table>
From table-56, indicates that the smectic and nematic mesophase ranges from 07 to 28\(^{\circ}\)C and 07 to 52\(^{\circ}\)C respectively of the homologous series-(6). Thus, the mesomorphic properties from homologue to homologue in the same series varies with number of carbon atoms present in n-alkyl group of left n-alkoxy terminal end group. Nematic mesophase commences from third member and smectic mesophase commences from seventh member of the series-(6), while The maximum nematogenic mesophase length 59\(^{\circ}\)C at the octyl homologue and the minimum mesophase length is 24\(^{\circ}\)C at the hexadecyl homologue derivative of the homologous series-(2). Absence of smectogenic character of a series-(2) indicates, absence of lamellar packing of molecules in their crystal lattices due to longer central bridge-CH=CH-COO-, which reduced intermolecular cohesive forces.

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in (^{\circ})C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (6)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C(_1)</td>
<td>-</td>
</tr>
<tr>
<td>C(_2)</td>
<td>-</td>
</tr>
</tbody>
</table>

Table:-56, Mesomorphic Phase length in \(^{\circ}\)C
The commencement of smectic and/or nematic mesophase, thermal stabilities, smectogenic and nematogenic character from homologue to homologue for the same series and series to series etc are given in table-57 as under for series under comparison.

On comparing the presently homologous series-(6) and series-(2), the thermal stability for nematic of series-(6) is less by 6.5 respectively. Secondly smectic mesophase commences from hexyloxy and the nematic mesophase commences earliest from ethoxy homologue of series-(6) which commences late from pentyloxy homologue in case of series-(2). Smectogenic mesophase formation is absent for series-(2); which is present in series-(6). Absence of smectogenic property of series-(2) indicates absence of lamellar packing of their crystal lattices. More over early commencement of nematic phase of homologous series-(6) is attributed to the extent of molecular noncoplanarity caused due to greater length of vinyl carboxylate -CH=CH-COO- has greater length and causes more noncoplanarity due to a twist obtained as the oxygen atoms of vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings. Moreover increased molecular length increases length to breadth ratio, enhancing end to end intermolecular anisotropic forces of attractions. On account of nematic-isotropic thermal stabilities are general way lower for the series-(6) than the corresponding homologous series- (2).

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C_3</td>
<td>-</td>
<td>7.0</td>
<td>7.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C_4</td>
<td>-</td>
<td>24.0</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C_5</td>
<td>-</td>
<td>13.0</td>
<td>13.0</td>
<td>-</td>
<td>38.0</td>
<td>38.0</td>
</tr>
<tr>
<td>C_6</td>
<td>7.0</td>
<td>49.0</td>
<td>56.0</td>
<td>-</td>
<td>36.0</td>
<td>36.0</td>
</tr>
<tr>
<td>C_7</td>
<td>13.0</td>
<td>52.0</td>
<td>65.0</td>
<td>-</td>
<td>41.0</td>
<td>41.0</td>
</tr>
<tr>
<td>C_8</td>
<td>14.0</td>
<td>50.0</td>
<td>64.0</td>
<td>-</td>
<td>59.0</td>
<td>59.0</td>
</tr>
<tr>
<td>C_{10}</td>
<td>28.0</td>
<td>39.0</td>
<td>67.0</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
</tr>
<tr>
<td>C_{12}</td>
<td>24.0</td>
<td>21.0</td>
<td>45.0</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
</tr>
<tr>
<td>C_{14}</td>
<td>15.0</td>
<td>33.0</td>
<td>48.0</td>
<td>-</td>
<td>27.0</td>
<td>27.0</td>
</tr>
<tr>
<td>C_{16}</td>
<td>-</td>
<td>36.0</td>
<td>36.0</td>
<td>-</td>
<td>24.0</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Table:-57,Average Thermal Stabilities

<table>
<thead>
<tr>
<th>Average transition temperature in °C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(6)</td>
<td>Series-(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>------------</td>
<td>------------</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smectic-isotropic or</td>
<td>115.6</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smectic-nematic</td>
<td>(C(<em>6)–C(</em>{14}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commencement of</td>
<td>C(_6)</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smectic phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>156.6</td>
<td>163.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C(<em>2)–C(</em>{16}))</td>
<td>(C(<em>5)–C(</em>{16}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commencement of</td>
<td>C(_2)</td>
<td>C(_5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nematic phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The group efficiency order derived on the basis of thermal stability for nematic mesophase formation is as mentioned below.

Smectic : \((-\text{OCH}_3)_2\) with \(-\text{COO}\) > \((-\text{OCH}_3)_2\) - with \(-\text{CH}=\text{CH}-\text{COO}-\)

Nematic : \((-\text{OCH}_3)_2\) with \(-\text{CH}=\text{CH}-\text{COO}-\) > \((-\text{OCH}_3)_2\) with \(-\text{COO}\)

3.3.5 Comparison of Homologous series (8) and (E):

The mesomorphic properties like phase length or degree of mesomorphism, commencement of mesophases, predominancy of mesophase including average thermal stability etc. of present series-(8) is compared with the structurally similar homologous series-(E) [103] as shown in figure-25.

Homologous series-(8) and (E), the geometrical shape is identical, but they differ only through the central bridge linking first and middle phenyl ring, that is \(-\text{COO}\) and \(-\text{CH}=\text{CH}-\text{COO}-\) respectively and position of right terminal end group \(-\text{NO}_2\) on last phenyl ring (i.e 4” and 3”-position) Thus, mesomorphic properties and degree of mesomorphism are differed due to their differing features as describe above. Therefore, the molecules of series-(8) and (E) differ in molecular length, molecular rigidity, molecular length to breadth ratio, and hence these difference causes a difference in the magnitudes of anisotropic intermolecular forces of
attractions and their rigidity and/or flexibility [2,3,4] vary to more or less extent and hence variation in mesomorphic properties and degree of mesomorphism accordingly.

Figure:-25
The upper transition of the members of the series-(8) and (E) under discussion are tabulated in table-58 as under.

From table-58, it is seen that the upper transition of the homologues to homologues in the same series gradually decreases as series is ascended, but in irregular manner. Also the upper transition of the corresponding homologues are relatively higher for series-(8) as compared to series-(E) except third, fourth, eighth, tenth and last members of homologous series. Due to the central bridge vinyl carboxylate –CH=CH-COO- has a greater length compared to central bridge –COO- hence increased conjugation by the –CH=CH- unit the rigidity of the molecule and lateral attractions increase, and hence the magnitudes of anisotropic intermolecular forces of attractions[2,3,4] increase of homologues for series-(8).

Table:-58, Upper transition temperatures of mesogens

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(8)</td>
</tr>
<tr>
<td>C₁</td>
<td>202.0</td>
</tr>
<tr>
<td>C₂</td>
<td>203.0</td>
</tr>
<tr>
<td>C₃</td>
<td>184.0</td>
</tr>
</tbody>
</table>
In homologous series-(8) and (E), odd-even effect and variation of mesomorphic properties of series from homologue to homologue is attributed to the sequentially added methylene unit [2,3,4] in an n-alkyl chain of left alkoxy end group.

Table-59 represents variation of mesophase length from homologue to homologue in the same series and series to series.

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (8)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C_4</td>
<td>-</td>
</tr>
<tr>
<td>C_5</td>
<td>-</td>
</tr>
<tr>
<td>C_6</td>
<td>-</td>
</tr>
<tr>
<td>C_8</td>
<td>-</td>
</tr>
<tr>
<td>C_10</td>
<td>-</td>
</tr>
<tr>
<td>C_12</td>
<td>-</td>
</tr>
<tr>
<td>C_14</td>
<td>-</td>
</tr>
<tr>
<td>C_16</td>
<td>-</td>
</tr>
</tbody>
</table>

In homologous series-(8) and (E), odd-even effect and variation of mesomorphic properties of series from homologue to homologue is attributed to the sequentially added methylene unit [2,3,4] in an n-alkyl chain of left alkoxy end group.

Table-59 represents variation of mesophase length from homologue to homologue in the same series and series to series.
From table-59, it is seen that the nematogenic phase ranges vary between 18.0°C to 60.5°C for a series-(8). Homologous series-(8) does not exhibit smectogenic character. The absence of smectogenic character is attributed to the absence of lamellar packing of molecules in their crystal lattice and a sliding layered arrangement of molecule does not occur in floating condition is due to position of right terminal end group on last phenyl ring. In series-(8) it is present on pera position while meta position in series-(E). The extent of noncoplanarity is relatively more of series-(E) in combination with higher magnitude of intermolecular attraction as compared to series-(8) due to meta substituted-NO₂ group. hence length decreases of molecule or breadth increases therefore net molecular closeness increases in series-(E) compared to series-(8), hence homologous series-(8) is nematogenic middle order melting type, while series-(E) is nematogenic and partly smectogenic middle order melting type series.

The average thermal stabilities and commencement of mesophases of homologous series-(8) and (E) are recorded in table-60.

**Table :-60, Average Thermal Stabilities**

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(8)</td>
</tr>
<tr>
<td>Smectic-isotropic or Smectic-nematic</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Commencement of Smectic phase</td>
<td>-</td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>158.25</td>
</tr>
</tbody>
</table>
Looking in from table-60. that N-I thermal stability of the series-(8) is 158.25 while smectic-
nematic and nematic-isotropic thermal stability of the series-(E) is 140.5 and 164.8 respectively. Hence, the thermal stability of the series-(8) is lower than series-(E) because series (8) and (E), geometrical shape is identical but they differ with only central groups –COO- and –CH=CH-COO- and position of terminal end group with last phenyl ring.

Thus, the molecules of series-(8) and (E) differ in molecular length, molecular rigidity, molecular length to breadth ratio, negligible magnitudes of molecular polarizability and hence these differences causes more or less difference in the magnitudes of anisotropic forces of intermolecular attractions. As discussed above, presently investigated homologous series–(8) and (E) resemble each other except the central bridge which is –COO- and –CH=CH-COO- in case of homologous series-(E) under discussion, these two series under comparison are closely similar to each other. Both these central bridges are comparable though the vinyl carboxylate –CH=CH-COO- has greater length and causes more noncoplanarity due to the twist obtained as the oxygen atoms of the vinyl carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic phenyl rings. On account of the enhanced length of the vinyl carboxy –CH=CH-COO- central bridge, increased conjugation by –CH=CH- unit and length which increases the rigidity of the molecule and lateral attractions and hence the, magnitudes of anisotropic forces of intermolecular attractions [4] which increases; while in case of –COO- central bridge, relative length is shorter and it do not link the phenyl rings through at least one multiple bond or hydrogen bonded ring system. Consequently the stereochemistry of the molecule does however, preserve the linearity of the molecule but results in less thermally stable mesophase. Commencement of nematogenic mesophase takes place from third (C_3) member of the series-(8) which late in the series-(E) under comparison. In series-(8) absence of smectogenic character is attributed to the absence of lamellar packing of molecules in their crystal lattices, without which sliding layered arrangement of molecule does not occur in floating condition while smectogenic
commencement from C$_2$ homologue of the series-(E). The variation in mesomorphic properties from homologue to homologue in the same series and for the same homologue from series to series are due to the sequentially added methylene (-CH$_2$-) unit in the n-alkyl chain of left n-alkoxy terminal end group and due to right sided terminal end group or/and laterally substituted or central group which remain intact throughout the series respectively. Thus, present investigation very well supports earlier views [54,102].

The group efficiency order derived on the basis of thermal stability for nematic and smectic mesophase formation is as mentioned below.

(a) Nematic: \(-\text{NO}_2\) > \(-\text{NO}_2\)

with \(-\text{CH}=\text{CH}-\text{COO}-\) with \(-\text{COO}-\) central bridge

(b) Smectic: \(-\text{NO}_2\) > \(-\text{NO}_2\)

with \(-\text{CH}=\text{CH}-\text{COO}-\) with \(-\text{COO}-\) central bridge

3.3.6 Comparison of Homologous series (7) and (F):

The mesomorphic properties like phase length or degree of mesomorphism, commencement of mesophases, predominancy of mesophase including average thermal stability etc. of present series-(7) is compared with the structurally similar homologous series-(F) [104] as shown in figure-26.

The molecular geometry of the homologous series-(7) and (F) is common with respect to three phenyl rings, central bridge-\text{COO-} linking first and middle phenyl ring and left n-alkoxy terminal, while they differ in second central bridges-\text{CH}=\text{CH}-\text{CO} and \text{=N=N} linking middle and last phenyl ring and right terminal end group \text{NO}_2 and \text{H} respectively.

Therefore, the variation in mesomorphic property and degree of mesomorphism have direct relation with difference in polarity and polarizability as well as resultant difference of
intermolecular cohesive forces of attractions arising out of it and molecular rigidity and flexibility due to second central bridge linking middle and last benzene ring –CH=CH–CO and –N=N and right terminal end group -NO$_2$ and –H. But effect of right terminal end group-NO$_2$ and –H on mesomorphic property and degree of mesomorphism is negligible.

Firstly, The homologous series under comparison exhibit mesomorphism from second to the last homologue, while series-(F) exhibit richer mesomorphism from third to the last homologue. The nematic or/and smectic property is exhibited by the members of both series enantiotropically or in few cases monotropically. Alternation in transition temperature due to odd-even effect is displayed in both homologous series.

The upper transition of the homologues displaying mesomorphism and mesomorphic phase length are recorded in following table-61 and 62 respectively.

**Table:-61, Upper transition temperatures of mesogens**

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(7)</td>
</tr>
<tr>
<td>C$_1$</td>
<td>191.0</td>
</tr>
<tr>
<td>C$_2$</td>
<td>200.0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>164.0</td>
</tr>
<tr>
<td>C$_4$</td>
<td>140.0</td>
</tr>
<tr>
<td>C$_5$</td>
<td>160.0</td>
</tr>
<tr>
<td>C$_6$</td>
<td>167.0</td>
</tr>
<tr>
<td>C$_7$</td>
<td>-</td>
</tr>
<tr>
<td>C$_8$</td>
<td>169.0</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>166.0</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>162.0</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>136.0</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>128.0</td>
</tr>
</tbody>
</table>
Looking from table-62, it is seen that the upper transition of the corresponding homologues in presently reported homologous series to series increases (series-(7)). The upper transition temperature of homologous series-(7) is higher than the series-(F). The end to end attractions in case of series-(F) are stronger than series-(7) because length of the molecules of series-(F) shorter than the molecules of series-(7) due to difference central group linking second and last phenyl ring is –CH=CH-CO- and –N=N- respectively. Thus, increased intermolecular attractions and closeness. But, molecular polarity and polarizability increase consequence with molecular flexibility and rigidity of series-(7) because of series-(7) contains –CH=CH-CO central bridge and more polar right terminal end group-NO$_2$ compared to –H, therefore upper transition temperature of series-(7) is higher than series-(F).

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (7)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C$_1$</td>
<td>-</td>
</tr>
<tr>
<td>C$_2$</td>
<td>-</td>
</tr>
<tr>
<td>C$_3$</td>
<td>-</td>
</tr>
<tr>
<td>C$_4$</td>
<td>-</td>
</tr>
<tr>
<td>C$_5$</td>
<td>-</td>
</tr>
<tr>
<td>C$_6$</td>
<td>23.0</td>
</tr>
<tr>
<td>C$_7$</td>
<td>-</td>
</tr>
<tr>
<td>C$_8$</td>
<td>24.0</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>20.0</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>35.0</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>26.0</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>-</td>
</tr>
</tbody>
</table>

From the table-62 indicates that the nematogenic and smectogenic phase length of series-(7) and series-(F). Total mesophase length vary between 18 to 73 °C of series-(7), while total
mesophase length vary between 16 to 38 °C of series-(F). The total mesophase length of homologous series-(7) is higher than homologous series-(F) due to central group-CH=CH-CO compared to –N=N longer and hence higher length-to-breadth ratio, polarities, a higher ratio of the molecular polarity to polarizability, more molecular rigidity of series-(7), therefore intermolecular attractions of series-(7) is higher than series-(F).

Thermal stabilities of the homologous series under present discussion are recorded in table-63.

Table-63 indicates that the smectic-nematic and nematic-isotropic stabilities of series-(7) under comparison are higher than series-(F). This, suggests that intermolecular anisotropic forces of attraction due to end to end and lateral cohesion which are relatively higher for series-(7) as compared to series-(F). The electronagativity of nitrogen is more than the carbon but presence of only one double bond between two nitrogen i.e. –N=N- while series-(7) involve one –CH=CH- units in a molecules. Therefore molecular rigidity of series-(7) due to one vinyl linkages surpasses the rigidity possessed by series (F) because of electronic interactions.

**Table-63, Average Thermal Stabilities**

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(7)</td>
</tr>
<tr>
<td>Smectic-isotropic or</td>
<td>125.6</td>
</tr>
<tr>
<td>Smectic-nematic</td>
<td>(C₆—C₁₄)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C₆</td>
</tr>
<tr>
<td>Smectic phase</td>
<td></td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>154.6</td>
</tr>
<tr>
<td>(C₃—C₁₆)</td>
<td>(C₁—C₈)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C₃</td>
</tr>
<tr>
<td>nematic phase</td>
<td></td>
</tr>
</tbody>
</table>
The nematic commencement early i.e from first member of the series-(F) enantiotropically while it is late i.e. from third member of series-(7). The end to end attractions in case of series-(F) are stronger than series-(7) because of length of the molecules of series-(F) shorter than molecules of series-(7) due to central group \(-N=N-\) and \(-CH=CH-CO-\) respectively. Therefore increased intermolecular attraction, closeness, polarity and polarizability and hence statistically parallel orientations stabilizes less in series-(7) as compared to series-(F). Thus first and second member of the series-(7) are nonmesomorphic acquiring high crystallizing tendency.

The early or late commencement of a smectic mesophase depend upon extent of noncoplanarity [105] caused by the molecule. Less extent of noncoplanarity causes early commencement of smectic mesophase. The noncoplanarity of the molecule is reduced to some extent in case of series (7) involving \(-CH=CH-CO\) as central bridge and noncoplanarity extended by the molecules of series-(F) involving \(-N=N-\) as central bridge. The \(-COO-\) and \(-N=N-\) central bridge present in the molecules of homologous series-(F), which causes[104] bumping of the oxygen atom into the nonbonded sides of the adjacent hydrogen of the aromatic ring which in turn causes considerable strain on the molecule. Consequently, a twist occurs around C-O bond forcing the benzing ring out of the plane of the molecule. Thus the co-planarity of the molecule is reduced to some extent making it thick. But, noncoplanarity of series-(7) less compared to series-(F) due to series-(7) contains longer central group compared to \(-N=N-\) central bridge and hence increased molecular rigidity, polarity and polarizabiltiy, which reduce molecular noncoplanarity enable earlier (i.e. from sixth homologue) lamellar packing and commencement of smectic phase.

Moreover SP\(^2\) carbon of third phenyl ring is linked directly with \(-C-\) part of the molecule in case of series-(7) while SP\(^2\) carbon of third phenyl ring in series(F) is linked with \(-N=N-\), in which electronegativity of nitrogen is more than a carbon. On account of these differences, smectic mesophase commences from decyl homologue of the series-(F) but it does not commence to appear till the hexadecyl homologue of the series-(7), as the molecules of a series-(7) involve one \(-CH=CH-\) unit while series-(F) involve \(-N=N-\) unit under comparison.

Both the series under discussion are predominantly nematogenic and partly smecogenic.
Thus, group efficiency order derived on the basis of thermal stability for smectic and nematic are as under.

### 3.3.7 Comparison of Homologous series (2) and (B):

The liquid crystal properties of the presently investigated homologous series-(2) are compared with the other structurally similar homologous series-(B) [106] as mentioned below in figure-27.

Homologous series-(2) and (B) are similar in respect of three phenyl rings bridged through two identical central groups –CH=CH-COO- and –CO-CH=CH- as well as commonly substituted left n-alkoxy (-OR) terminal end group. However, they differ in respect of terminal end group or groups substituted on third right hand phenyl ring. Therefore, observed variations in their mesomorphic properties and the degree of mesomorphism can be attributed to the differing features of series-(2) and (B) respectively. Homologous series-(2) and (B) differ in respect of only one of the –OCH$_3$ group at lateral position (3”) i.e. two –OCH$_3$ groups present on 3”,4”-position of series (2) and one –OCH$_3$ group present on 4”-position of series-(B); or 3” –OCH$_3$ group is missing in series-(B) which result to possess linear shape to series (B) and nonlinear shape to the series-(2). The variation in liquid crystallinity and degree of crystallinity exhibited can be attributed to the lateral substitution of –OCH$_3$ group present on 3”-position with third phenyl ring in series-(2).
The upper transition of the members of the series-(2) and (B) under discussion are tabulated in table-64 as under.

**Table:-64, Upper transition temperatures of mesogens**

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(2)</td>
</tr>
<tr>
<td>C₁</td>
<td>200.0</td>
</tr>
<tr>
<td>C₂</td>
<td>206.0</td>
</tr>
<tr>
<td>C₃</td>
<td>190.0</td>
</tr>
<tr>
<td>C₄</td>
<td>201.0</td>
</tr>
<tr>
<td>C₅</td>
<td>170.0</td>
</tr>
<tr>
<td>C₆</td>
<td>160.0</td>
</tr>
<tr>
<td>C₇</td>
<td>174.0</td>
</tr>
<tr>
<td>C₈</td>
<td>169.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>178.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>166.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>152.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>156.0</td>
</tr>
</tbody>
</table>
From table-64, it is seen that upper transition temperature of series- (B) are relatively lower than the corresponding homologue of the series-(2) because lateral –OCH₃ group present on 3”-position with last phenyl ring for series -(2), hence series-(2) is nonlinear, while series- (B) is linear. Therefore increases the width of the molecules as compared to series-(B). Hence intermolecular attraction are diminished of series-(2), Thus present of –OCH₃ lateral substituent group keeps the breadth of the of the molecule almost unlatered more over length of the molecule is also almost equivalent. Therefore, length to breadth ratio and hence overall polarizability of the molecule do not play much role on mesomorphic characteristics and upper transition temperature also. However the polarity of laterally substituted functional group and hence its effect on overall polarisability of the molecule effected directly hence more polar –OCH₃ lateral substituent group present in series-(2) which is related with the exhibition of higher upper transition temperature compared to series-(B).

Odd-even effect and the difference in mesomorphic properties from homologue to homologue in the same series is due to the sequentially added methylene unit at the n-alkyl chain of the left n-alkoxy terminal end group [2-4] for series -(2).

The nonmesomorphic property displayed by first to fourth and last homologue derivatives is attributed to the high crystallizing tendency arising due to unfit magnitudes of anisotropic forces of intermolecular attraction resulted from unfavorable molecular rigidity and flexibility [2,3,4] for series-(B).

The variation of smectic and nematic phase length from homologue to homologue in the same series and series to series are recorded in table-65.

Looking to the table-65, mesomorphic phase length varies in irregular manner but decreases as series is ascended for homologous series- (2). This indicates decrease in intermolecular forces of attractions as series is ascended from octyl homologue.

Difference between total phase length 13.0°C is attributed to the homologus series-(2) is nonlinear while series-(B) is nonlinear. Homologous series-(2) is contained two methoxy group while series-(B) contains only one metoxy group with last phenyl ring. Thus, magnitudes of anisotropic forces of intermolecular adhesion increases in series-(2) by molecular width or intermolecular closeness, rigidity and flexibility.
Table:-65, Mesomorphic Phase length in °C

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Sm</th>
<th>Nm</th>
<th>Total</th>
<th>Sm</th>
<th>Nm</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>-</td>
<td>38.0</td>
<td>38.0</td>
<td>10.0</td>
<td>23.0</td>
<td>33.0</td>
</tr>
<tr>
<td>C₆</td>
<td>-</td>
<td>36.0</td>
<td>36.0</td>
<td>24.0</td>
<td>21.0</td>
<td>45.0</td>
</tr>
<tr>
<td>C₇</td>
<td>-</td>
<td>41.0</td>
<td>41.0</td>
<td>21.0</td>
<td>15.0</td>
<td>36.0</td>
</tr>
<tr>
<td>C₈</td>
<td>-</td>
<td>59.0</td>
<td>59.0</td>
<td>19.0</td>
<td>17.0</td>
<td>36.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
<td>-</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>-</td>
<td>27.0</td>
<td>27.0</td>
<td>-</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
<td>24.0</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Series (B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>-</td>
<td>38.0</td>
<td>38.0</td>
<td>10.0</td>
<td>23.0</td>
<td>33.0</td>
</tr>
<tr>
<td>C₆</td>
<td>-</td>
<td>36.0</td>
<td>36.0</td>
<td>24.0</td>
<td>21.0</td>
<td>45.0</td>
</tr>
<tr>
<td>C₇</td>
<td>-</td>
<td>41.0</td>
<td>41.0</td>
<td>21.0</td>
<td>15.0</td>
<td>36.0</td>
</tr>
<tr>
<td>C₈</td>
<td>-</td>
<td>59.0</td>
<td>59.0</td>
<td>19.0</td>
<td>17.0</td>
<td>36.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>-</td>
<td>46.0</td>
<td>46.0</td>
<td>-</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>C₁₄</td>
<td>-</td>
<td>27.0</td>
<td>27.0</td>
<td>-</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
<td>24.0</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Looking to the table-66 for average thermal stabilities of mesophase, commencement of for series (3) and (4).

Table-66, indicate that nematic thermal stability is 163.1 for series-(2) while N-I thermal stability is 174.1. Smectic-nematic thermal stability is 00.0 for series-(2) while 159.7 is for series-(B). Homologous series-(B) is smectogenic in addition to nematogenic while present investigated series does not exhibit smectogenic character at all. The intermolecular closeness due to the varying molecular width plays an important role to the net magnitudes of intermolecular anisotropic forces of attractions. Because laterally substituted –OCH₃ increases molecular width as compared to series-(B) when molecular width increases, the intermolecular forces of attraction depend upon two opposing forces operating at a time. (i) as molecular width
increases, the intermolecular distance diminishes. Now at the same time (ii) increased molecular width, raises molecular polarizability, which results into rising of intermolecular attractions [54]. The net resultant effects (i) and (ii) operating at a nonlinear series (2) while second (ii) effect predominates for linear series-(B). Thus, suitable magnitudes of anisotropic forces of intermolecular attraction is favorable and sufficient to facilitate lamellar packing of molecules of series-(B) in their crystal lattices but it is insufficient, unfavorable and unsuitable to facilitate lamellar packing of molecules in the crystal lattices of series-(2). Hence, the statistically parallel orientational order of molecules is maintained by end to end attractions, but the sliding layered arrangement of molecule is missing in floating condition for presently investigated series-(2).

**Table:-66, Average Thermal Stabilities**

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Series-(2)</strong></td>
</tr>
<tr>
<td>Smectic-isotropic or</td>
<td>-</td>
</tr>
<tr>
<td>Smectic-nematic</td>
<td></td>
</tr>
<tr>
<td>Commencement of</td>
<td>-</td>
</tr>
<tr>
<td>Smectic phase</td>
<td></td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>163.1</td>
</tr>
<tr>
<td>(C₅—C₁₆)</td>
<td>(C₅—C₁₄)</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C₅</td>
</tr>
<tr>
<td>nematic phase</td>
<td></td>
</tr>
</tbody>
</table>

Homologous series-(B) being linear, induces highest intermolecular closeness to exhibit smectic and nematic mesophase formation. The nematic-isotropic thermal stability of series-(B) are higher than series-(2) because, series-(2) contain two highly polar groups -OCH₃ while series-(B) contain only one polar group -OCH₃. Nematic mesophases commences from fifth homologue of both the series-(2) and (B) but smectic phase does not occur or commence till the last hexadecyloxy homologue. However, smectic mesophase formation commences from fifth
member of the series-(B). This difference of behavior is attributed to the different magnitudes of extent of noncoplanarity caused by the molecules of series-(2) and (B) under comparison. The absence of smectic property of a present investigated series-(2) because absence of lamellar packing of molecules in their crystal lattice due to series-(2) is non leaner, induces lowest intermolecular closeness because of molecular breadth increases i.e. present of meta substituted (lateral group)-OCH₃ present in series-(2) while it is absent in series-(B). Homologous series-(B) exhibits of smectic property in pentyl to octyl homologues in addition to nematic property is attributed to simultaneously the intermolecular forces are strengthened due to increase in molecular polarizability and molecular dipolarity.

Thus, the variations in mesomorphic properties for the same homologue from series to series is attributed to the unchanging lateral and/or terminal end group throughout the same series. Thus presently investigated homologous series-(2) is predominantly or entirely nematogenic without exhibition of smectogenic character and with middle ordered melting type, while series-(B) is partly smectogenic and predominantly nematogenic.

The smectic-nematic and nematic-isotropic group efficiency order derived on the basis of average thermal stability with respect to lateral substituent as under.

Group efficiency for smectic:

\[
\begin{align*}
\text{Group efficiency for smectic:} \\
\text{OCH}_3 & > \text{OCH}_3 \\
\end{align*}
\]

Group efficiency for nematic:

\[
\begin{align*}
\text{Group efficiency for nematic:} \\
\text{OCH}_3 & > \text{OCH}_3 \\
\end{align*}
\]

Group efficiency order derived on the basis of early commencement of mesophase.

\[
\begin{align*}
\text{Smectic:} & \quad -\text{C}_6\text{H}_4\text{OCH}_3 > -\text{C}_6\text{H}_3(\text{OCH}_3)_2 \\
\text{Nematic:} & \quad -\text{C}_6\text{H}_4\text{OCH}_3 = -\text{C}_6\text{H}_3(\text{OCH}_3)_2
\end{align*}
\]

3.3.8 Comparison of Homologous series (3) and (C):

\[
\begin{align*}
\text{Group efficiency order derived on the basis of early commencement of mesophase.} \\
\text{Smectic:} & \quad -\text{C}_6\text{H}_4\text{OCH}_3 > -\text{C}_6\text{H}_3(\text{OCH}_3)_2 \\
\text{Nematic:} & \quad -\text{C}_6\text{H}_4\text{OCH}_3 = -\text{C}_6\text{H}_3(\text{OCH}_3)_2
\end{align*}
\]
The mesomorphic properties, mesophase length and thermal stability of the presently investigated homologous series-(3) are compared with the other structurally similar homologous series (C) [107] as mentioned below in figure-28.

Homologous series-(3) and (C) possess three benzene rings linked through –CH=CH-COO- and –CH=CH-CO- central bridges, left n-alkoxy terminal group at pera as common identical moiety. But both series differ in right terminal end group viz., -NO$_2$ and -OCH$_3$ respectively.

Series-3: \[ RO-CH=CH-COO-CH=CH-CO-NO_2 \]

Series-C: \[ RO-CH=CH-COO-CH=CH-CO-OCH_3 \] [107]

Figure:-28

Therefore molecular length and hence length to breadth ratio, molecular polarity and polarizability, molecular rigidity and flexibility vary only with right terminal placed end groups -NO$_2$ and -OCH$_3$ without change molecular aromaticity and central groups. Therefore, intermolecular adhesion anisotropic forces of attraction and suitable magnitude of end to end molecular adhesion as a consequence of molecular rigidity and flexibility are responsible to cause or induce mesomorphic properties like thermal stability occurrence or commencement of mesophase and type of mesophase etc. which vary only with presence of varying -OCH$_3$ and –NO$_2$. The observed variation in liquid crystallinity and degree of mesomorphic properties from homologue to homologue in same series and in the same homologue from series to series are thus, attributed to the sequentially added methylene unit in left n-alkoxy terminal and varying right terminal end groups –NO$_2$ and –CH$_3$ respectively.

The upper transitions of the members of the homologous series-(3) and (C) under present discussion are recorded in following table-67.

Table:-67, Upper transition temperatures of mesogens

<table>
<thead>
<tr>
<th>No. of carbon Atom in</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
</table>

From the table-67, it is seen that upper transition temperature of homologous series-(3) lower than homologous series-(C). The observed variation upper transition from homologue to homologue in same series and in the same homologue from series to series are thus, attributed to the sequentially added methylene unit in left n-alkoxy terminal and varying right terminal end groups respectively. The alternation of upper transition temperature due to the odd-even effect is clearly seen in the phase diagram of the homologous series-(3) and (C). Thus, end to end forces of intermolecular attractions in the molecules of series-(3) and (6) are strong enough to alternate the upper transition temperatures. The upper transition temperature of series-(C) is higher than series-(3) due to more polar right terminal end group –OCH$_3$ present in series-(C). Electro negativity of oxygen is more than nitrogen; therefore, the bond polarity of –OCH$_3$ group is more than that of the –NO$_2$ group. Hence, the molecular polarity of series-(C) is greater than that of series-(3). Therefore, the magnitudes of anisotropic forces of intermolecular adhesion of series-(C) exceed that of series-(3). The inter molecular closeness of series-(3) and (C) are almost the same, but the intermolecular adhesion differs due to different polarities of terminal end groups.

Table-68 represents variation of mesophase length from homologue to homologue in the same series and series to series.

**Table:-68, Mesomorphic Phase length in °C**

<table>
<thead>
<tr>
<th>n-alkyl chain</th>
<th>Series-(3)</th>
<th>Series-(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_1$</td>
<td>152.0</td>
<td>195.0</td>
</tr>
<tr>
<td>C$_2$</td>
<td>170.0</td>
<td>200.0</td>
</tr>
<tr>
<td>C$_3$</td>
<td>150.0</td>
<td>189.0</td>
</tr>
<tr>
<td>C$_4$</td>
<td>165.0</td>
<td>205.0</td>
</tr>
<tr>
<td>C$_5$</td>
<td>176.0</td>
<td>166.0</td>
</tr>
<tr>
<td>C$_6$</td>
<td>178.0</td>
<td>160.0</td>
</tr>
<tr>
<td>C$_8$</td>
<td>168.0</td>
<td>168.0</td>
</tr>
<tr>
<td>C$_{10}$</td>
<td>164.0</td>
<td>170.0</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>172.0</td>
<td>164.0</td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>186.0</td>
<td>160.0</td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>180.0</td>
<td>170.0</td>
</tr>
</tbody>
</table>
Looking to the phase length of homologues of two homologous series (3) and (C) from the table-68. The homologous series (3) is partly smectogenic and nematogenic while homologous series (C) is entirely nematogenic and smectic mesophase totally absent. Total phase length of series (3) is higher than series (C). This difference and causes difference in their molecular length, length to breath ratio, molecular polarity and polarizability, steric hindrance, molecular size and hidden magnitudes of anisotropic forces of attractions, due polarity of right terminal end group which are responsible to induce smectic and/or nematic mesophase formation in floating condition.

Average thermal stabilities of the homologous series-(3) and (C) under present discussion are recorded in table-69.

**Table-69, Average Thermal Stabilities**

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (3)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>8.0</td>
</tr>
<tr>
<td>C₆</td>
<td>20.0</td>
</tr>
<tr>
<td>C₈</td>
<td>15.0</td>
</tr>
<tr>
<td>C₁₀</td>
<td>16.0</td>
</tr>
<tr>
<td>C₁₂</td>
<td>-</td>
</tr>
<tr>
<td>C₁₄</td>
<td>-</td>
</tr>
<tr>
<td>C₁₆</td>
<td>-</td>
</tr>
</tbody>
</table>
Table-69 indicate that smectic and nematic thermal stability of homologous series-(3) are higher than series-(C) under comparison. Such behavior is attributed to the higher polarity of –OCH₃ terminal end group as compared to –NO₂ group of series-(3); which causes relatively higher magnitudes of intermolecular end to end terminal attraction and sliding layered formation from lamellar packing in case of series-(C) while sliding layered arrangement in series-(3) fails to form due to absence of lamellar packing of molecules. Moreover extent of molecular noncoplanarity difference due to more electron withdrawing group –NO₂ present in series-(3) causes early commencement of smectic phase which does not appear till the last hexadecyl homologue of series. Thus, present series-(3) is equiprapotionally smectogenic and nematogenic with high melting type. Electro negativity of oxygen is more than nitrogen; therefore, the bond polarity of –OCH₃ group is more than that of the –NO₂ group. Hence, the molecular polarity of series-(C) is greater than that of series-(3). Therefore, the magnitudes of anisotropic forces of intermolecular adhesion of series-(C) exceed that of series-(3). The intermolecular closeness of series-(3) and (C) are almost the same, but the intermolecular adhesion differs due to different polarities of terminal end groups. The lowest value of thermal stabilities of series (C) under comparison with series-(3) can also be linked with weakest inductive effect, which reflects in molecular rigidity and flexibility to cause lowering thermal stability values 00.0°C and 166.6°C for smectic and nematic respectively. The smectogenic mesophase commences from the
pentyloxy homologue for series-(3), while smectogenic character absence in series-(C) because
the extent of noncoplanarity due to –OCH₃ group inductive effect and electron releasing group.

The group efficiency order derived for smectic and nematic on the basis of average thermal stability are as under.

Nematic : –NO₂ > –OCH₃
Smectic : –NO₂ > –OCH₃

3.3.9 Comparison of Homologous series (7) and (D):

Liquid crystal properties of the present homologous series-(7) are compared with structurally similar homologous series-(D) [108] (Fig:-29) and comparison their thermal stabilities and commencement of mesophases.

![Chemical structures](image-url)

Figure:-29

Homologous series-(7) and (D) are identical in size, shape, with their rigidity caused by three benzene ring and molecular aromaticity, central groups and left n-alkoxy terminal groups but they differ with reference to their magnitudes of flexibility due to the varying of right terminal end group –NO₂ and-H. This variation causes difference in their molecular length, length to breadth ratio, molecular polarity and polarizability, steric hindrance, molecular size and hidden magnitudes of anisotropic intermolecular forces of attraction, which are responsible to induce smectic and/or nematic mesophase in floating condition.

Therefore molecular aromaticity, intermolecular closeness etc. remains almost same. But the molecular length due to -NO₂ and- H groups of different polarities, and hence the length to breadth ratio, ratio of the molecular polarity to polarizability, induced electron-electron interactions, steric hindrance by Z= -NO₂, -H group and phenyl ring –Z bond polarity due to different electro negativity of N, and H and extent of molecular coplanarity etc. will differ. Hence, unidentical features will cause differences in liquid crystallinity properties and the degree of mesomorphism of series-(7) and (D) under comparison.
The upper transition of the members of the series-(7) and (D) under discussion are tabulated in table-70 as under.

From table-70, it is seen that the upper transition of the homologues to homologues in the same series gradually decreases as series is ascended, but in irregular manner. Also the upper transition of the corresponding homologues is relatively higher for series-(7) as compared to series-(D) due to the higher polarity of –NO₂ terminal end group as compared to –H of series-(D); which causes relatively higher magnitudes of intermolecular terminal attraction. Odd-even effect and variations in mesogenic properties from homologue to homologue in the same series is due to the sequentially added methylene unit in the n-alkyl chain of left n-alkoxy terminal end group in phase diagram for series-(7)

The variation of smectic and nematic phase length from homologue to homologue in the same series and series to series are recorded in table-71.

From the table-71, indicates that the nematogenic and smectogenic phase length of homologous series-(7) and (D). Total mesophase length vary between 18 to 73 °C of series-(7). Thus presently investigated homologous series-(7) is predominantly nematogenic and partly smectogenic with middle ordered melting type, while Total mesophase length vary between 32 to 46 °C of series-(D). Thus, homologous series-(D) is predominantly nematogenic and partly smectogenic with middle ordered melting type. The total mesophase length of homologous series-(7) is higher than homologous series-(D). Such manners is ascribed to the more polarity and highly electron withdrawing group of –NO₂ terminal end group as compared to –H of series-(D); which cause relatively higher magnitude of intermolecular attraction with consequences more molecular flexibility and rigidity and higher polarity and molecular polarizability.

<table>
<thead>
<tr>
<th>No. of carbon Atom in n-alkyl chain</th>
<th>Upper transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series-(7)</td>
<td>Series-(D)</td>
</tr>
</tbody>
</table>

Table:-70, Upper transition temperatures of mesogens
<table>
<thead>
<tr>
<th>No. of carbon atom in n-alkyl chain</th>
<th>Temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series (7)</td>
</tr>
<tr>
<td></td>
<td>Sm</td>
</tr>
<tr>
<td>C₁</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>-</td>
</tr>
<tr>
<td>C₃</td>
<td>-</td>
</tr>
<tr>
<td>C₄</td>
<td>-</td>
</tr>
<tr>
<td>C₅</td>
<td>-</td>
</tr>
<tr>
<td>C₆</td>
<td>23.0</td>
</tr>
</tbody>
</table>

Table: -71, Mesomorphic Phase length in °C
The thermal stabilities and commencement of mesophases of homologous series-(7) and (D) are recorded in table-72.

From the table-72 of average thermal stabilities it is observed that thermal stability of a homologous series-(7) is more than the series-(D). Both homologous series under comparison exhibit smectogenic and nematogenic character within certain range of temperatures. However observed difference in their thermal stabilities is attributed to the difference in the polarities of terminally substituted end groups viz. -NO$_2$ and –H and the difference in molecular length.

<table>
<thead>
<tr>
<th></th>
<th>C$_8$</th>
<th>24.0</th>
<th>49.0</th>
<th>73.0</th>
<th>-</th>
<th>-</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{10}$</td>
<td>20.0</td>
<td>46.0</td>
<td>66.0</td>
<td>17.0</td>
<td>15.0</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>35.0</td>
<td>33.0</td>
<td>68.0</td>
<td>21.0</td>
<td>25.0</td>
<td>46.0</td>
<td></td>
</tr>
<tr>
<td>C$_{14}$</td>
<td>26.0</td>
<td>14.0</td>
<td>40.0</td>
<td>16.0</td>
<td>27.0</td>
<td>43.0</td>
<td></td>
</tr>
<tr>
<td>C$_{16}$</td>
<td>-</td>
<td>18.0</td>
<td>18.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table :-72, Average Thermal Stabilities

<table>
<thead>
<tr>
<th></th>
<th>Average transition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series-(7)</td>
</tr>
<tr>
<td>Smectic-isotropic or Smectic-nematic</td>
<td>125.6</td>
</tr>
<tr>
<td></td>
<td>( C$<em>6$—C$</em>{14}$ )</td>
</tr>
<tr>
<td></td>
<td>( C$<em>{10}$—C$</em>{16}$ )</td>
</tr>
<tr>
<td>Commencement of Smectic phase</td>
<td>C$_6$</td>
</tr>
<tr>
<td>Nematic-isotropic</td>
<td>154.6</td>
</tr>
<tr>
<td></td>
<td>( C$<em>3$—C$</em>{16}$ )</td>
</tr>
<tr>
<td></td>
<td>( C$<em>8$—C$</em>{16}$ )</td>
</tr>
<tr>
<td>Commencement of</td>
<td>C$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
On comparing the present series-(7) with series-(D), whose smectic and nematic thermal stabilities are more than a series-(D), the -NO₂ end group being more polar and polarizable than -H contributes to such observed effect. Hence molecular polarity of series-(7) is more than a series-(D). Therefore, magnitudes of anisotropic forces of intermolecular adhesion of series-(7) exceeds the same of series-(D). The intermolecular closeness of series-(7) and (D) are almost the same but intermolecular adhesion differs due to different polarities of terminal end groups which causes difference in end to end attractions for nematic mesophase formation and lamellar packing of molecules from series to series; which results in the molecular stabilization energy (ΔH) at room temperature, reflecting higher (series-(7)) and lower (series-(D)) values of thermal stability directly and molecular rigidity and flexibility indirectly. The lowest values of thermal stabilities of series-(D) amongst the series under comparison can also be linked with its shortest molecular length and weakest inductive effect (H=0) whose C-H bond polarity is lower than C-N polarities which reflects in molecular rigidity and flexibility to cause lowering of thermal stability values 106.6 and 119.8 for smectic and nematic respectively. The smectogenic mesophase occurrence from hexyloxy homologue for series-(7) while it occurrence late from decyloxy homologue in series-(D). It indicates that lamellar packing of molecules commences early from the sixth member of the series for the molecules of series-(7) while lamellar packing is hindered in case of series-(D) due to the weakly polar end group-H or absence of terminal end group which affects the extent of noncoplanarity [54,101] caused by a molecule. -NO₂ group are being more polar and polarizable reduces molecular coplanarity and enables to facilitate earlier (i.e. from sixth homologue) lamellar packing and commencement of smectic phase. Early and late nematic mesophase formation by -NO₂ can be linked to the difference in the steric hindrance caused by triatomic -NO₂ group and poor extent of polar nature of -H for series-(7) and (D) respectively. The difference in mesomorphic properties for the same homologue from series to series is attributed to the different polarities of a terminal end group -NO₂, and -H of the series-(7) and (D) of fixed polarity for each series under comparison.

(1) The smectic and nematic group efficiency order derived on the basis of thermal stabilities are;

\[
\text{Smectic:} \quad -\text{NO}_2 > -\text{H}
\]
(2) Group efficiency order derived on the basis of early commencement of smectic and nematic mesophase are:

**Smectic:** -NO$_2$ > -H

**Nematic:** -NO$_2$ > -H.