A NOVEL MESOMORPHIC HOMOLOGOUS SERIES OF ESTER
DERIVATIVES P (P’-N-ALKOXY BENZOYLOXY) N-HEPTYL
BENZOATES

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ABSTRACT
A new homologous series of non amphiphilic liquid crystals p(p’-n-alkoxy Benzoyloxy) n-Heptyl Benzoates with configuration is synthesized and studied with a view to understand the effect of molecular structure on mesomorphic properties of substances which may be useful to the various fields of applications. Methyl to Pentyl homologues are nonmesomorphic but hexyl octyl, decyl, dodecyl, tetradecyl and hexadecyl homologues are mesomorphic i.e. nematogenic in character without exhibition of any smectic character. A phase diagram is drawn from the transition temperatures as determined from hot stage polarizing microscope of homologues against the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group. Solid-isotropic or solid nematic transition temperature curve follows a zigzag path of rising and falling throughout the series as series is ascended in normal manner. Nematic isotropic transition curve initially rises and then, shows descending tendency as series is ascended. Thus, it follows usual established trend as expected. Not shown odd-even effect for nematic-isotropic transition curve. Analytical data support the structures of molecules. The enantiotropic nematic mesophase appeared for all the homologues, is of threaded type as determined from miscibility method. Thermal stability for nematic is 143.6 °C and mesomorphic range is short which varies from 8.0 °C to 20.0 °C. mesomorphic properties of titled homologous series are compared with structurally similar homologous series.

KEYWORDS: Liquid Crystal, Smectic, Nematic, Mesogen, Thermotropic, Mesomorphic.
INTRODUCTION
Several homologous series of mesogens are reported earlier. The present homologous series is planned to synthesize new liquid crystal materials which may be useful from point of view of their utility in various fields of application like, medical field, manufacture of conventional and nonconventional display devices, analytical tool of drugs and chemical etc. and to understand the relations between structure of molecules and liquid crystal properties.\textsuperscript{[1,4]}

MATERIAL AND METHODS
Experimental
A reaction mixture containing equimolar proportion of p-Hydroxy benzoic acid and absolute n-Heptenol are refluxed for about three and half hours. The content is decomposed in excess of ice cold water to get the product. Next day the product p-Hydroxy n-Heptyl Benzoate was filtered, washed, dried and crystallized from alcohol yield 62.68 %.\textsuperscript{[5]}

(ii). Synthesis of P-n-alkoxy Benzoic acid.
P-Hydroxy Benzoic acid was alkylated by corresponding alkyl halide in suitable proportion by the modified method of Vora and Dave.\textsuperscript{[6]} P-n-alkoxy Benzoic acid formed.

(iii) Synthesis of p(p’-n-Alkoxy Benzoyloxy) n-Heptyl Benzoates.
P-n-alkoxy Benzoic acid were directly condensed with the P-Hydroxy n-Heptyl Benzoates dissolved in MDC in portions with DCC & DMAP as catalyst by stirring reaction mixture.\textsuperscript{[7]} Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. 4-Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH, 4-Hydroxy Benzoic acid, n-Heptyl Alcohol, con. H\textsubscript{2}SO\textsubscript{4}, DCC, DMAP, MDC etc. required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below in Scheme -1.

(iv) Transition temperatures are observed through a polarizing microscope with heating stage as recorded in Table-1. Analytical data of some selected representative homologues viz; elemental analysis, IR and \textsuperscript{1}HNMR data support the structure of molecules. Textures of homologues are confirmed by miscibility method. Enthalpy (\(\Delta H\)), entropy (\(\Delta S\)) concept discussed qualitatively due to inadequate facility available to the source, otherwise quantitatively \(\Delta H\) and \(\Delta S\) values would have been determined from the peak value temperature of D.S.C. scans.\textsuperscript{[8,13]}
P- Hydroxy n-heptyl benzoate

\[
\text{HO-} \text{C}=\text{O} + \text{C}_6\text{H}_{15}\text{OH}(n) \xrightarrow{\text{H}_2\text{SO}_4} \text{HO-} \text{C}=\text{O}_\text{C}_6\text{H}_{15}(n)
\]

P-(P’-n-alkoxy benzoyloxy) – n-heptyl Benzoate

\[
\text{HO-} \text{C}=\text{O} + \text{HO-} \text{C}=\text{O}_\text{C}_6\text{H}_{15}(n) \xrightarrow{\text{DCC}} \text{HO-} \text{C}=\text{O}_\text{C}_6\text{H}_{15}(n)
\]

R = \text{C}_n\text{H}_{2n+1} \quad n = 1,2,3,4,5,6,8,10,12,14,16

Scheme-1 Synthetic route to the series.

Characterization

Table 1: Elemental analysis for methylxy, ethyloxy and propyloxy derivatives.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Molecular Formula</th>
<th>Elements % Found (% Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1.</td>
<td>\text{C}<em>22\text{H}</em>{26}\text{O}_5</td>
<td>71.35 % (71%)</td>
</tr>
<tr>
<td>2.</td>
<td>\text{C}<em>23\text{H}</em>{28}\text{O}_5</td>
<td>71.87% (72%)</td>
</tr>
<tr>
<td>3.</td>
<td>\text{C}<em>24\text{H}</em>{30}\text{O}_5</td>
<td>72.36% (73%)</td>
</tr>
</tbody>
</table>

Spectral Data

\(^1\text{H NMR in ppm}\) for the Decyloxy derivatives: 1.2,1.3,1.5,1.6 (alkyl chain H), 3.8,3.6,4.08 (-OCH\_2 of – OC\_7H\_15), 7.3 8.1, 6.9 (p-di substituted benzene ring).

\(^1\text{H NMR in ppm}\) for the Tetradecyloxy derivatives: 0.88, 1.3,1.5,1.6,2.0 (alkyl chain H) 3.9, 4.0,4.06,(-OCH\_2 of -OC\_14H\_29 and –OC\_7H\_15),6.8,7.2,,7.34 (p-di substituted benzene ring and mono substituted benzene ring).

\text{IR in cm}^{-1}\) for Decyloxy derivatives: 891 & 844 cm\(^{-1}\) pera di substituted phenyl ring 1087,1045, 1244, cm\(^{-1}\) ether linkage, 1456,1512,1608 cm\(^{-1}\) aromatic ring,1728 cm\(^{-1}\) ester present, 2855, 2950 long chain alkane present.
IR in cm$^{-1}$ for Octyloxy derivatives: 893 & 842 cm$^{-1}$ para di substituted phenyl ring 1008, 1207, 1271 cm$^{-1}$ ether linkage, 1442,1608 cm$^{-1}$ aromatic ring, 1690 cm$^{-1}$ ester present, 2866, 2941 long chain alkane present.

Texture: by miscibility method;
Threaded nematic C$_8$
Schlieren nematic - C$_{10}$

Table-2

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>n-alkyl group</th>
<th>Transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Smectic</td>
</tr>
<tr>
<td>1</td>
<td>Methyl</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Ethyl</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Propyl</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Butyl</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>Pentyl</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Hexyl</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>Octyl</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Decyl</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Dodecyl</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Tetradecyl</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Hexadecyl</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 1: Phase Behavior of Series.
RESULTS AND DISCUSSION

p-Hydroxy n-Heptyl Benzoate is nonmesomorphic substance but on linking it with dimerized p-n-alkoxy Benzoic acids through p-n-alkoxy acid chlorides give rise to corresponding p-(p’-n-alkoxy benzyloxy) n-Heptyl Benzoate esters with spatial configuration. Six, out of eleven homologues are mesomorphic and remaining five viz; methyl to n-Pentyl homologues is nonmesomorphic. i.e. n-octyl, n-decyl, n-dodecyl, n-tetradecyl and n-hexadecyl homologues are not smectogenic even in the monotropic condition. All the six mesomorphic homologues are only and entirely nematogenic in enantiotropic manner. Transition temperatures are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group. Like points are joined to obtain solid-isotropic or solid-nematogenic transition curve and nematic-isotropic transition curve. The resulted phase diagram obtained is shown in the figure-I from table -1. Solid -nematic/isotropic transition curve rise from methyl to ethyl and Falls from n-propyl to n-hexyl homologue and then rises to n-octyl by ten degree and again falls up to decyl homologue. Finally it falls by ten to two degrees to hexadecyl homologue through tetradecyl homologue. Thus, it follows zigzag path of rising and falling as series is ascended in normal manner. Nematic-isotropic transition curve follows rise tendency from n-hexyl to n-octyl homologue in normal manner, then it passes through minima\(^{14 \text{ to } 21}\) at decyl homologue and falls abnormally from decyl to hexadecyl homologue as series is ascended. Odd-even effect is not observed for nematic isotropic transition curve. Mesomorphic properties like average thermal stability, commencement of mesophase, mesophase length, degree of mesomorphism etc. are compared with structurally similar homologous series. p-n-Alkoxy benzoic acids are dimeric, in which two phenyl rings are bonded through hydrogen bonding. Hydrogen bonding breaks on esterification and resulted esters consist of two phenyl rings bridged through carboxyl \(-\text{COO}^-\) unit with right terminal end group \(-\text{COOC}_2\text{H}_{15}(n)\). Thus, a molecule of homologue is long linear lath like or rod like. Spectroscopic data confirmed cis configuration of homologue. Texture of the homologues is of threaded type as determined by miscibility method. Methyl to Pentyl homologues is nonmesomorphic due to their high crystallizing tendency. High crystallizing tendency arises from stronger intermolecular adhesion due to end to end and lateral intermolecular attractions. According to third law of thermodynamics, “entropy of perfectly crystalline substance is zero at absolute zero degree Kelvin [-273.0°C]”. Thus, when a substance is formed, energy \((\Delta H)\) is released from system (crystalline solid) to surrounding (Rest of world other than system) at constant pressure. Thus, a system is a crystalline solid to be thermodynamically stable. Now on heating the thermodynamically stable un-layered crystalline solid state of a substance, the
heat energy (ΔH) supplied from surrounding to system which causes to destabilize the system i.e. solid crystalline state of a sample homologue tend to acquire less stable state of more entropy or randomness or disorder. Thus, as temperature increases (enthalpy ΔH increases), supplied heat from surrounding to system act against intermolecular attractions to break or to disrupt the structure of molecule till it either passes to higher state of existence, which may be an intermediate state between crystalline solid and isotropic liquid called liquid crystalline state, or, it may directly pass into a isotropic liquid without passing through liquid crystal or mesomorphic state of existence. Thus, rise of temperature increases entropy or randomness or high order of molecular disorder. Under this situation, the molecules of methyl to n-Pentyl homologues under vibrational motion are unable to resist thermal vibrations imposed upon them from surroundings. Hence imposed heat energy (ΔH) weakens the intermolecular forces of attractions to such an extent that, molecules of nonmesomorphic homologues are disable to maintain molecular alignment, i.e. molecules are individually linear lath like but randomly orient in all possible directions without any regular order or arrangement. Thus, intermolecular adhesion forces are neither anisotropic, nor of suitable magnitude to maintain molecular alignment at a given temperature at constant pressure. This type of molecular arrangement restricts the statically parallel orientational order of molecule which can cause two dimensional array in floating condition. Hence disaligned molecules do not form nematogenic or any other short of mesophase. However, the molecules of hexyl to hexadecyl homologues under above discussed situation, able to resist thermal vibrations imposed upon them and maintain molecular alignment as a consequence of intermolecular forces occurring due to their molecular rigidity and flexibility. Thus, intermolecular forces operating are anisotropic and of suitable magnitude to cause and maintain only statically parallel orientational order of molecules in floating condition. Hence, only nematogenic mesophase formation occur within definite range of temperature at constant pressure. Absence of originally lamellar packing of molecules in interlinked crystal lattices are unable to cause sliding layered arrangement of molecule in floating condition Therefore absence of smectogenic behavior is observed for any of the homologues under discussion. Odd-even effect is absent in nematic-isotropic transition curve because, nematogenic mesophase commences from even numbered hexyl homologue and continue up to the last homologue of the series. Abnormal behavior of nematic-isotropic transition curve from octyl to hexadecyl homologue is attributed to the effects due to the presence of highly polarizable carboxyl unit, present at the central and terminal end group, contributing to the molecular rigidity and restricting molecular bending. Mesomorphic range varies minimum of 8.0º C at the
hexadecyl homologue to maximum 20.0° C at the octyl homologue of series under discussion. Thus, titled homologous series is entirely nematogenic with short range of liquid crystallinity. Mesomorphic properties of titled homologous series is compared with structurally similar homologous series-A \(^{22}\) and B \(^{23}\) as shown in figure-II.

![Diagram of molecules]

**Series - A**

**Series - B**

**Figure - II**

Average thermal stability and stage of commencement of mesophase formation are recorded in.

<table>
<thead>
<tr>
<th>Series</th>
<th>Series - 1 -COO-C(<em>7)H(</em>{15})</th>
<th>Series - A -COO-C(<em>6)H(</em>{13})</th>
<th>Series - B -CH=CH-COO-C(<em>6)H(</em>{15})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smectic - isotropic Or Smectic- nematic Commencement of smectic phase</td>
<td>-</td>
<td>-</td>
<td>179.4 (C(<em>7)-C(</em>{14}))</td>
</tr>
<tr>
<td>Nematic - isotropic Commencement of nematic Phase</td>
<td>143.6 (C(<em>6)-C(</em>{16})) C(_6)</td>
<td>166.6 (C(<em>6)-C(</em>{16})) C(_6)</td>
<td>190.9 (C(<em>6)-C(</em>{14})) C(_6)</td>
</tr>
<tr>
<td>Total mesophase length in °C ( Nm-Iso)</td>
<td>8 – 20 C(_{16}) C(_8)</td>
<td>9 - 36 C(<em>6) C(</em>{16})</td>
<td>10 - 60 C(<em>6) C(</em>{14})</td>
</tr>
</tbody>
</table>
All the homologous series under comparison [Figure - II] possess commonly two phenyl rings bridged through carboxyl unit. Therefore Aromativity of molecules and effects due to two phenyl rings, central bridge remains unaltered. The changing part is right terminal end groups. The variation in mesomorphic properties and degree of mesomorphism depends upon the changing left n-alkyl unit by sequentially added methylene unit from homologue to homologue in the same series, keeping right terminal end group intact. The variation in mesomorphic properties and degree of mesomorphism from series to series is arise due to varying right terminal end group of different polarity keeping remaining part of the molecules unchanged for the same homologue. Therefore varying molecular polarity and polarizability to changing molecular length molecular rigidity and flexibility play an important role in variation of intermolecular end to end and lateral attractions, which reflect to the mesomorphic properties like thermal stability, commencement of mesophase and degree of mesomorphism. Careful investigation of table-3 indicates that, titled homologous series (1) is entirely nematogenic while series (B) is partly nematogenic and partly smectogenic. On comparing average thermal stability for nematic, the lowest value of titled homologous series is due to absence of occurrence of smectogenic mesophase. Thus, nematic mesophase formation take place at the cost of smectic mesophase. The cis configuration of homologues of titled homologous series (1) did not allow the originally absent lamellar packing of molecules in the interlinked layered lattices which restricts sliding layered arrangement of molecule in floating condition under the influence of imposed thermal vibrations at a given temperature. Series-1 and Series –A both have nearly equally thermal stability because both have same structure different only CH₂ left unit. Highering of average thermal stability of series (B) is attributed to the presence of -CH=CH-COO- unit at the terminal end group, which is less polarizable than highly polarizable vinyl carboxyl –CH=CHCOO- unit at the same position of series (1) and Series -A. According to Dave and Kurian (12) early commencement of the smectic phase is related with less non co-planarity of the molecule. Molecules of series (1), (A) and (B) are almost equally non-coplanar due to molecular moiety other than right terminal end group. Right terminal end groups of series (1), (A) and (B) are -COO-C₇H₁₅, -COO-C₆H₁₃ and CH=CH-COO-C₆H₁₃ respectively, the vinyl carboxyl containing terminal is longer than carboxy group by –CH=CH- unit which causes more non-co-planarity due to a twist obtained as the oxygen atoms of relatively longer vinyl carboxy – CH=CH-COO- group bump into the non-bonded adjacent hydrogen atoms of the aromatic phenyl rings. This, result to induce more noncoplanarity in the molecule as compared to similar effect caused by shorter –COO- group. On account of this difference, a smectic
mesophase commences earlier in series (B) but it does not commence till the last homologue of series (1) and Series-(A).

Thus, smectic and nematic group efficiency order derived on the basis of thermal stability for terminal end group are as under.

Nematic Group Efficiency:
- COO-C_7H_{15} < -COO-C_6H_{13} < -CH=CH-COO-C_6H_{13}

Smectic Group Efficiency:
Only -CH=CH-COO-C_6H_{13} Group.

CONCLUSION
Titled homologous series is entirely nematogenic with short range of liquid crystallinity without exhibition of smectic phase. Present investigation support the earlier view and raises credibility to the established views derived earlier.

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