Synthesis and study of new ester homologous series of Mesomorphs: 4-Ethoxy phenyl-4’-n-alkoxy benzoates

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ABSTRACT
The titled homologous series was synthesized by condensing n-alkoxy benzoyl chloride with 4-Hydroxy phenol in pyridine and studied with a view to understand effect of molecular structure on mesomorphic properties. All the nine members of the series except ethoxy derivative, are mesomorphic monotropically or enatiotropically with or without smectogenic property, in addition to nematic property. Odd-even effect is missing in a phase diagram plotted for number of carbon atoms in left n-alkyl chain of alkoxy terminal versus transition temperatures as observed from hot stage polarizing microscope. Series is predominantly nematogenic and partly smectogenic with mesophase length $10^6$ C to $38^6$ C. Mesomorphic properties are compared with structurally similar homologous series.

Keywords: Enatiotropy, Nematic, Smectic, Mesomorphic.

INTRODUCTION
Number of mesomorphic homologous series with two or three phenyl rings with different central bridges are reported earlier. In continuation of the same, an attempt is made to synthesize presently a series by varying flexible part n-alkoxy terminal group keeping right terminal end group intact. Thereby effect of varying flexible molecular part on mesomorphic properties are determined. Thus, effect of structure on mesomorphic properties is studied.
MATERIALS AND METHODS

Experimental Characterization:
Representative homologues of the series were selected for characterization of structure by elemental analysis, IR technique. Microanalysis was performed on Perkin Element PE2400 CHN analyzer. IR spectra were recorded on Perkin Elmer spectra GX. Enthalpy-Entropy concept discussed qualitative without performance on DSC scan. Mesomorphic properties were investigated using hot stage polarizing microscope.

Synthesis:
4-Ethoxy phenol, 4-hydroxy benzoic acid, n-alkyl halides, thionyl chloride, pyridine were used as received. The synthetic route to the present series is outlined in scheme-1.

\[
\text{R} = \text{C}_{2n+1}H, \quad n = 1 \text{ to } 6, 8, 10, 12.
\]

SCHEME-1: Synthetic route to the series.
4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by the modified method of Dave and Vora [3]. The nine esters of the series were synthesized by condensing equimolar proportion of 4-n-alkoxy benzoyl chlorides with 4-ethoxy phenol in pyridine. Ester homologues were purified from alcohol till constant transition temperatures obtained.

Analytical data.
IR spectra in cm\(^{-1}\) for propyl derivatives.

RESULTS AND DISCUSSION
Nine homologues of the series 4- Ethoxy phenyl 4′-n- alkoxy benzoates were synthesized and their mesomorphic properties were evaluated presently. The transition temperatures of the series are recorded in table-2. All the homologues except second member of the series showed threaded or schlieren texture on heating crystals or cooling the, isotropic liquid when viewed under a hot stage polarizing microscope. Methyloxy to pentyloxy excluding ethoxy homologue exhibited nematogenic mesophase monotropically while, enatiotropic nematogenic mesophase continued to appear from octyloxy to decyloxy homologue. Enatiotropic smectic mesophase commences from octyloxy derivative and continue upto dodecyloxy homologue. Figure-1 shows the
dependence of the transition temperatures on the number of the carbon atoms in left terminal substituent.

**TABLE-1 Elemental analysis for methoxy, butyloxy, octyloxy and dodecyloxy derivatives**

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>Elements % found ( % calculate)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>C_{16}H_{16}O_{2}</td>
<td>70.50</td>
</tr>
<tr>
<td>C_{19}H_{22}O_{2}</td>
<td>72.51</td>
</tr>
<tr>
<td>C_{23}H_{30}O_{2}</td>
<td>74.50</td>
</tr>
<tr>
<td>C_{27}H_{38}O_{2}</td>
<td>76.0</td>
</tr>
</tbody>
</table>

The solid mesomorphic or isotropic transition curve follows a zigzag path of rising and falling tendency as series is ascended.

**FIGURE-1 Phase behavior of the series**
**TABLE-2 Transition temperatures in °C of the series**

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R=CnH2n+1 [n]</th>
<th>Sm</th>
<th>Nm</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-</td>
<td>73.0</td>
<td>85.0</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>-</td>
<td></td>
<td>139.0</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>-</td>
<td>(127.0)</td>
<td>136.0</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>-</td>
<td>(130.0)</td>
<td>136.0</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>-</td>
<td>(128.0)</td>
<td>133.0</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>-</td>
<td>103.0</td>
<td>141.0</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>100.0</td>
<td>107.0</td>
<td>137.0</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>106.0</td>
<td>121.0</td>
<td>127.0</td>
</tr>
<tr>
<td>9</td>
<td>12</td>
<td>110.0</td>
<td>-</td>
<td>125.0</td>
</tr>
</tbody>
</table>

( ) Indicate monotropy

The phase diagram shows absence of odd-even effect in nematic-isotropic (or vice versa) transition curve. Initially it rises up to pentyloxy–hexyloxy homologue and then it declines from and beyond hexyloxy derivative to dodecyloxy derivative. Smectic-nematic or smectic-isotropic transition curve rises from octyloxy to dodecyloxy derivative. Nematic isotropic and smectic nematic or isotropic transition curve merges into each other between decyloxy and dodecyloxy derivatives indicating that, higher homologues beyond dodecyloxy derivatives should be smectogenic only. Table-3 summerizes average thermal stabilities and molecular structure of the present series and other structurally related series-A [5] and series-B [4] chosen for comparative study as shown in figure-2.

The molecular geometry of all the homologues of the series under comparison consist of two phenyl rings bridged through –COO- linkage with varying n-alkoxy group at the left terminal keeping intact right terminal end groups –OC₂H₅, -Cl and –COOC₂H₅ for series -1, A and B respectively. The variation in the mesomorphic characteristics for the same homologue from series to series can be attributed to the presence of different right terminal groups of varying polarity and polarizability to form mesophase. The variation in mesomorphic tendency of different homologues in the same series is attributed to the presence of left n-alkyl terminal end groups, varying in number of methylene unit or units keeping polarity of right terminal end group unchanged.

On comparing the mesomorphic characteristics of series-1 with series-A, it is observed that, the homologues of the entire series (except second homologue) are monotropic or enatiotropic nematogenic and / or smectogenic, while in the case of series-A, the members of the series exhibit smectogenic mesophase monotropically or enatiotropically. Molecules of the series -1
and A differ only in the polarity of the right terminal end groups. Similarly series-B is entirely smectogenic without exhibition of nematogenic property. In general, highly polar and polarizable \(-\text{OC}_3\text{H}_5\) right terminal of series-1, hinders a little bit more, the formation of layered structure as compared to shorter –Cl or longer \(-\text{COOC}_2\text{H}_5\) terminal to facilitate lamellar packing required for the formation of the smectic mesophase. Introduction of highly polar ethoxy group at the right terminal position in series -1 enables considerable and significant anisotropic attractions which serves to stabilize thermodynamically, parallel orientational order of molecules by end to end intermolecular attractions, depending upon enthalpy \(\Delta H\) and entropy \(\Delta S\) values [7], conducive to nematogenic mesophase formation in the floating condition. The nematic thermal stability of series-1 being higher than series A and B is understandable because of the difference in the magnitude of anisotropic forces of terminal attractions having relatively higher value of \(\Delta H\) arising due to highly polar and polarizable ethoxy group. Early or late commencement of smectic mesophase [1] is attributed to the extent of non-coplanarity caused by the molecule. Less extent of noncoplanarity causes early commencement of smectic mesophase as observed in series-B. Thus, variation in mesomorphic properties of same homologue from series to series is attributed to the varying right terminal end groups of different polarity and polarizibility.

### CONCLUSION

Present study of homologous series, 4-Ethoxy phenyl-4’-n-alkoxy benzoates suggest that, highly polar and polarizable ethoxy terminal end group does favorably induce nematogenic character more than a smectogenic character in a substance with such geometry which gives rise to exhibition of nematogenic mesophase. Present study very well support the conclusions drawn earlier [1].

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