



## SYNTHESIS AND STUDY OF A NOVEL HOMOLOGOUS SERIES 4 -(4'-N-ALKOXY BENZOYLOXY) B- PHENOXY ETHYL BENZOATES

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### Abstract:

*Novel homologous series 4 -(4'-n-alkoxy benzyloxy)  $\beta$ - Phenoxy Ethyl Benzoates consisted of eleven homologues. Methyloxy to propyloxy homologues do not show any mesomorphic behavior, while; the rest of the homologues show mesomorphic behavior. Octyloxy to tetradecyloxy homologues exhibit smectogenic and nematogenic characteristic, while butyloxy, pentyloxy, hexyloxy and hexadecyloxy homologue exhibit only nematogenic characteristics. Transition temperatures of homologues as observed and determined by hot stage polarizing microscope are proportional to number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group. Odd-even effect doesn't observe for smectic-nematic and nematic-isotropic transition curves showing phase behavior of a series. Smectic and nematic thermal stabilities are 187.2°C and 200.1°C respectively. Analytical data support the structures of the homologue molecules. A*

*texture of nematic mesophase is threaded or schlieren type and that of a smectic phase is of smectic-A type. Liquid crystal properties of a series are compared with another structurally similar isomeric homologous series. Smectic mesophase lengths vary from 4.0°C (C<sub>14</sub>) to 10.0°C (C<sub>10</sub>) and nematic mesophase lengths vary from 4.0°C (C<sub>4</sub>) to 14.0°C (C<sub>6</sub>) with middle ordered melting type.*

**Keywords:** Liquid crystal, Mesogen, Smectic, Nematic, Enantiotropy.

### Introduction :

Exhibition of an intermediate state of a matter between crystalline solid state and isotropic liquid state in addition to three well-known states of matter, termed as Liquid Crystal state. The resultant adhering intermolecular forces of attractions based upon molecular structure of a matter has direct relation with molecular rigidity and flexibility caused by rigid core and flexible core of a molecule. The present molecular structure of homologues of a

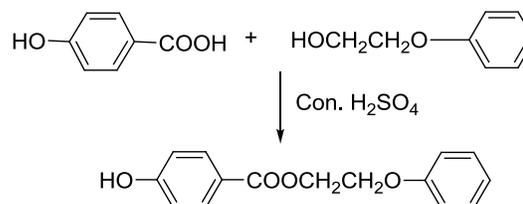
homologous series is constructed by linking three phenyl rings bridged through two central groups viz; -COO- and -COO-CH<sub>2</sub>-CH<sub>2</sub>-O- as rigid core and n-alkoxy -OR group which act as a flexible part of a molecule. Thus, present investigation is planned with a view to understand, establish and discuss a relation between molecular structure and liquid crystallinity of a substance as a consequence of resultant molecular rigidity and flexibility.

### MATERIALS AND METHODS

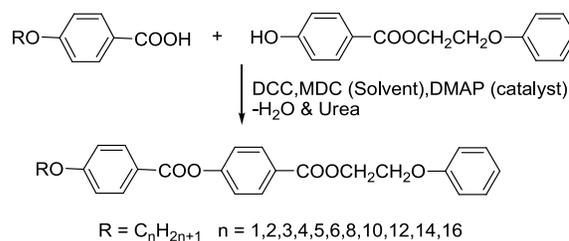
p-n-alkoxy benzoic acids were prepared by the method of Gray and Winsor [1,2], Vora and Dave [3,4], Vogel [5,6]. p-hydroxyβ-phenoxy ethyl benzoate is prepared by reacting p-hydroxy benzoic acid with corresponding freshly distilled 2-phenoxy ethyl alcohol in presence of concentrated sulphuric acid mixture. p-n-alkoxy benzoic acids dissolved in MDC with p-hydroxyβ-phenoxy ethyl benzoate is in portions with DCC & DMAP as catalyst by stirring reaction mixture. [7,8,9,10] Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy benzoic acid, alkyl halides (R-X), 2-phenoxy ethyl alcohol, KOH, 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**

#### (1) P-Hydroxy -β-Phenoxy Ethyl benzoate.



#### (2) p-(p'-n-alkoxy benzoyloxy) β-Phenoxy Ethyl Benzoates



**Scheme -1**

### Characterization

Some homologs as representative members of the series were selected for characterization of their structures by IR and <sup>1</sup>HNMR techniques. IR spectra were recorded on Perkin Elmer spectrum GX and NMR were recorded using CDCl<sub>3</sub> as solvent. Microanalysis was performed on Perkin Elmer PE 2400 CHN analyzer. Transition and melting temperatures and

liquid crystal properties were investigated by using optical polarizing microscopy.

#### Analytical Data

#### Spectral Data

NMR in ppm for Hexyloxy Derivative. 0.9 ( -CH<sub>3</sub> of -OC<sub>6</sub>H<sub>13</sub> group), 1.14 ( -CH<sub>2</sub>-)<sub>n</sub> polymethylene group of -OC<sub>6</sub>H<sub>13</sub>, 4.6 ( -OCH<sub>2</sub>CH<sub>2</sub> of -OC<sub>5</sub>H<sub>11</sub>), 3.5 ( -OCH<sub>3</sub>), 6.8 to 8.2 (mono and p-di-substituted phenyl ring).

NMR in ppm for Dodecyloxy Derivative. 0.94 ( -CH<sub>3</sub> of -OC<sub>12</sub>H<sub>25</sub> group), 1.12 ( -CH<sub>2</sub>-)<sub>n</sub> polymethylene group of -OC<sub>12</sub>H<sub>25</sub>, 4.5 ( -OCH<sub>2</sub>CH<sub>2</sub> of -OC<sub>12</sub>H<sub>25</sub>), 3.5 ( -OCH<sub>3</sub>) 6.8 to 7.2 (p substituted phenyl ring). The NMR data are consistent with the molecular structure.

IR in cm<sup>-1</sup> for Propyloxy Derivative. 770 polymethylene ( -CH<sub>2</sub>-)<sub>n</sub> group of -OC<sub>3</sub>H<sub>7</sub>, 850 p substituted phenyl ring, 1200, 1260 and 1685 ( -COO ester group), 1600, 1580 (phenyl ring). The IR data are consistent with the molecular structure.

IR in cm<sup>-1</sup> for Octyloxy Derivative. 780 (polymethylene ( -CH<sub>2</sub>-)<sub>n</sub> group of -OC<sub>8</sub>H<sub>17</sub>), 855 (p substituted phenyl ring), 1260 and 1605 ( -COO ester group), 1605, 1550 (phenyl ring).

IR in cm<sup>-1</sup> for Dodecyloxy Derivative. 740 (polymethylene ( -CH<sub>2</sub>-)<sub>n</sub> group of -OC<sub>12</sub>H<sub>25</sub>), 840 (p substituted phenyl ring),

1210, 1260 & 1600 ( -COO ester group.)

1580, 1480 (phenyl ring). The NMR data are consistent with the molecular structure.

**Table 1.**

Elemental analysis for some derivatives.

Sr. No.	R = n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1	Hexyl	C <sub>28</sub> H <sub>30</sub> O <sub>6</sub>	72.7	6.4	71.9	6.5
			2	9	1	0
2	Octyl	C <sub>30</sub> H <sub>34</sub> O <sub>6</sub>	73.4	6.9	72.2	6.9
			6	3	3	0

#### Result and Discussion:

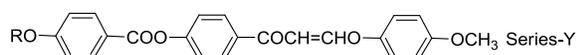
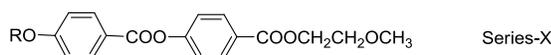
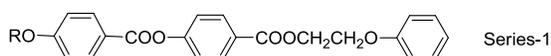
n-Alkoxy Benzoic acids and 4-Hydroxy-β-phenoxy ethyl benzoate are nonmesomorphic. However, on condensing the two nonmesomorphic components through DCC, the resultant homologous ester derivatives from Butyloxy to Hexadecyloxy give rise to mesomorphic behaviour. The methyl to propyl homologs are nonmesomorphic. The octyloxy, decyloxy, dodecyloxy, tetradecyloxy homologs are enantiotropically smectogenic in addition to nematogenic in character and the rest of the homologs are enantiotropic nematic only (**Table 2**). A phase diagram (**Fig. 1**) shows the phase behavior through a graph of the number of carbon atoms present

in the left *n*-alkoxy terminal end group versus the transition temperatures as determined from an optical polarizing microscope equipped with a heating stage.

**Table -2**

**Transition temperatures of series in 0C**

Sr. No	n-Alkyl Group	Transition Temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	204
2	Ethyl	-	-	205
3	Propyl	-	-	212
4	Butyl	-	203	207
5	Pentyl	-	192	204
6	Hexyl	-	188	202
7	Octyl	182	190	195
8	Decyl	175	185	192
9	Dodecyl	177	184	195
10	Tetradecyl	186	190	202
11	Hexadecyl	-	193	204



The phase diagram (**Fig. 1**) consists of three transition curves: (1) First is the solid-mesomorphic or isotropic transition curve, which adopts a zigzag path of falling and rising values with an overall descending tendency as the series is ascended and behaves in the normal established manner. (2) Second is the smectic–nematic transition curve, which initially falls, passes through maxima falling at the decyloxy homologue and then rise at the tetradecyloxy homologue with the not exhibition of an odd–even effect, and behaves in the usual manner. (3) Third is the nematic–isotropic transition curve, which follows a descending tendency as the series is ascended with a negligible falls of few degrees at the tetradecyloxy homologues and then rise till to hexadecyloxy homologues. Thus, all three transition curves behave in a normal established manner. The textures of the nematic phase are threaded or Schlieren and for the smectic phase of the type A or C. Variations in mesomorphic properties from homologue to homologue in the present series are observed. Smectic mesophase lengths vary from 4.0°C (C<sub>14</sub>) to 10.0°C (C<sub>10</sub>) and nematic mesophase lengths vary from 4.0°C (C<sub>4</sub>) to 14.0°C (C<sub>6</sub>) with middle ordered melting type. The smectic–nematic



and nematic–isotropic thermal stabilities are 187.2°C and 200.1°C, respectively. Thus, the present homologous series is predominantly nematogenic and partly smectogenic with a middle ordered melting type and a short range of liquid crystallinity. The mesomorphic properties of the novel homologous series are compared with known structurally similar homologous series. The spectral and analytical data confirm the molecular structure of the homologues concerned. The nonmesomorphic behavior of the methyl to butyl homologues is attributed to the high crystallizing tendency, which arises from the shorter, less flexible *n*-alkoxy terminal endgroup. The butyl to hexadecyl homologue derivatives are liquid crystalline because the molecules set themselves at an angle less than 90° and resist thermal vibrations exposed upon them between two temperatures with or without lamellar packing of molecules in their crystal lattices. All such molecules have an ordered two-dimensional array and exhibit either/both a smectogenic or/and a nematogenic mesophase. Thus, the molecules of the octyloxy to tetradecyloxy homologues have a layered molecular arrangement due to the lamellar molecular packing in their crystal lattices from the temperature  $t_1$  to higher

temperature  $t_2$  enantiotropically and on further continued heating up to a higher temperature  $t_3$ , with a statistically parallel orientational molecular two-dimensional order. Thus, the smectic mesophase formation between  $t_1$  and  $t_2$  and the nematic mesophase formation between  $t_2$  and  $t_3$  occurred. The octyl, decyl, dodecyl and tetradecyl homologue derivatives have an absence of lamellar packing of the molecules with only a statistically parallel orientational order between  $t_1$  and a higher temperature  $t_2$ , enantiotropically showing only a nematogenic mesophase without smectogenic mesophase formation. The exhibition of a variation of mesomorphic properties from homologue to homologue in the novel series is attributed to the sequentially added methylene unit to the *n*-alkoxy terminal end group. The overall mesomorphism induced from butyl to hexadecyloxy homologue derivatives is attributed to the suitable magnitudes of anisotropic intermolecular forces end to end and lateral adhesion as a result of varying favorable molecular rigidity and flexibility against exposed thermal vibrations. The mesomorphic properties of the present homologous series (1) are compared with other structurally similar homologous series X [11] and Y [12] as shown in the **Fig. 2**.

**Table-(3)**  
**Thermal stabilities in °C**

Novel homologous series-1, and y are identical with respect to three phenyl rings and central bridge linking first and middle phenyl ring but series-X having only two phenyl ring. Moreover left n-alkoxy flexible terminal end group  $C_nH_{2n+1}$  i.e. RO- are the same for the same homologue from series to series. But remaining part of each series differs with each other. i.e. series-1, X and Y differs with respect to central bridges linking middle and third phenyl rings as and i.e. molecular rigidity differs but molecular flexibility remains unaltered. Homologous series-1, X and series Y are identical with respect to central bridge linking middle and right terminal end groups as differs with respect to  $-COO-CH_2-CH_2-OPH$ ,  $-COOCH_2-CH_2-OCH_3$  and  $-CO-CH=CH-PH-OCH_3$  respectively for the same homologue from series to series i.e. molecular flexibility is altered keeping molecular rigidity unaltered for the same homologue from series to series. Thus, variations in mesogenic properties and the degree of mesomorphism observed, are depended upon the altering magnitudes of either molecular rigidity or the molecular flexibility among the

presently investigated series-1 and the homologous series - X and Y chosen for

Series	(1)	(X)	(Y)
Smectic-isotropic	187.2°C (C <sub>8</sub> - C <sub>10</sub> )	179.0 °C (C <sub>8</sub> - C <sub>10</sub> )	118.0 °C (C <sub>7</sub> - C <sub>14</sub> )
Commencement of Smectic phase	C <sub>8</sub>	C <sub>8</sub>	C <sub>7</sub>
Nematic-isotropic	200.1 °C (C <sub>4</sub> - C <sub>16</sub> )	196.28 °C (C <sub>5</sub> - C <sub>16</sub> )	157.0 °C (C <sub>5</sub> - C <sub>16</sub> )
Commencement of Nematic-phase	C <sub>4</sub>	C <sub>5</sub>	C <sub>5</sub>

comparative study. Following **Table-3** represents some mesogenic properties like average thermal stabilities, commencement of mesophase or mesophases, mesophase lengths etc. to indicate effect of molecular structure on liquid crystal properties in terms of or as a consequence of altering molecular rigidity or flexibility; as under.

From above table-3, it is clear that,

- Presently investigated novel series -1, X and Y all series are nematogenic & smectogenic



- Smectic property commences from C<sub>8</sub> homologue of a series -1 and Series-X, whereas, Series - Y smectic commences from C<sub>7</sub> homologue
- Nematic mesophase commences from C<sub>4</sub> homologue of series-1 whereas it commences from C<sub>5</sub> homologue of the series X and Y respectively.
- Total Mesophase length range of series-1 is relatively higher than series- X and Y.

Mesogenic characteristics difference of a substance varies with changing structural part of a molecules under comparison. The changing molecular structural part between series-1, X and Y is a -COO-CH<sub>2</sub>-CH<sub>2</sub>-OPH, -COOCH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub> and -CO-CH=CH-PH-OCH<sub>3</sub>. Such differences induces differences into molecular polarity and polarizability as a consequence of molecular rigidity, keeping molecular flexibility unchanged for the same homologue from series-1 to series -X, which causes difference in the suitable magnitudes of anisotropic forces of intermolecular end to end attractions, commencement of mesophase, thermal stability, mesophase length range and other mesogenic properties.

#### Conclusions:

A novel homologous series consisted of three phenyl rings and two ester central

bridges which acts as rigid core and two end groups contributing flexible core of the molecules, induces nematic type of mesomorphism with absence of smectic property by less than 50% homologues. series is middle ordered melting type with high thermal stability.

Group efficiency order derived on the basis of -

(i) thermal stability (ii) commencement of mesophase (iii) total mesophase length for smectic and nematic with reference to molecular rigidity/flexibility are as under

#### (i) Smectic:

Rigidity/Flexibility : -COO-CH<sub>2</sub>-CH<sub>2</sub>-OPH> -COOCH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub> - > -CO-CH=CH-PH-OCH<sub>3</sub>

#### Nematic

Rigidity/Flexibility : -COO-CH<sub>2</sub>-CH<sub>2</sub>-OPH> -COOCH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub>- > -CO-CH=CH-PH-OCH<sub>3</sub>

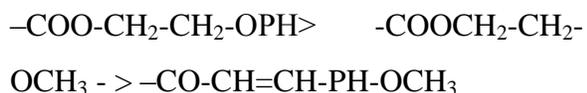
#### (ii) Smectic:

Rigidity/Flexibility : -COO-CH<sub>2</sub>-CH<sub>2</sub>-OPH> -COOCH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub> - > -CO-CH=CH-PH-OCH<sub>3</sub>

#### Nematic

Rigidity/Flexibility : -COO-CH<sub>2</sub>-CH<sub>2</sub>-OPH> -COOCH<sub>2</sub>-CH<sub>2</sub>-OCH<sub>3</sub> - > -CO-CH=CH-PH-OCH<sub>3</sub>

(iii) Total (Sm+N):- (Central group)



Series- 1

Series -X Series - Y

- Suitable magnitudes of combined effect through molecular rigidity and flexibility can induce mesomorphism.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Present novel ester compounds may be useful in the study of binary systems and agricultural field.
- Presence of vinyl group is predominantly nematogenic.

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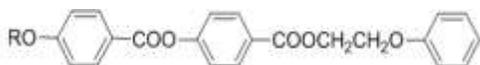
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Figure: 1 Phase Behavior of Series

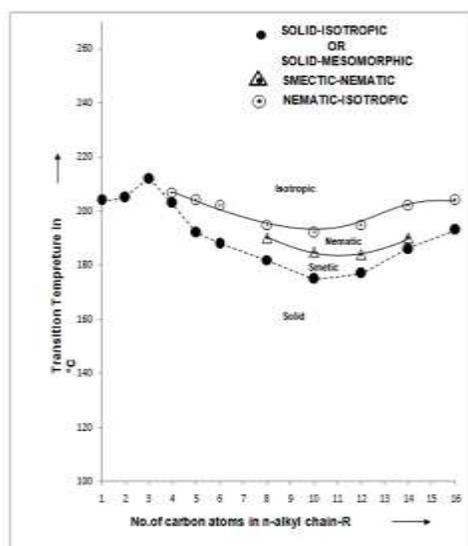


Figure: 1 Phase Behavior of Series