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# Mesomorphism dependence on central bridge (-COO-CH $_2$ -) and terminal end group (-Br)

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#### ABSTRACT

A novel series of liquid crystalline (LC) ester materials has been synthesized and studied with a view to understanding the effects of molecular structure on LC behavior. The homologous series of eleven members is entirely enantiotropically smectogenic without exhibition of a nematic phase. Transition temperatures and the texture of smectic phase was determined by an optical polarizing microscope equipped with a heating stage (POM). Transition curves (Cr-Sm and Sm-I) showing phase behavior in a phase diagram behave in a normal manner. Textures of smectic phase are focal conic fan shaped of the type Smectic-A or Smectic-C. An odd-even effect is exhibited by the Sm-I transition curve. The average thermal stability for smectic is 91.2°C and the mesogenic phase length ranges between 3.6°C and 39.3°C. Thus, the novel smectogenic homologous series is a middle-ordered melting type whose LC phase is relatively middle ordered. The LC properties of the present series are compared with a structurally similar homologous series. Analytical and spectral data support the molecular structures.

#### **KEYWORDS**

Enantiotropy; liquid crystals; mesomorphism; nematic; smectic

# Introduction

Liquid crystalline state (LC) is popular among scientific and technological community since 1888 [1] for the combination of liquidity and anisotropic properties. Thus, thermotropic and lyotropic LCs are well known for their applicability in various fields of research and for applications such as display devices and for biological or microbiological activity [2–10]. A critical survey of the literature about LC studies [11–15] reveals much interest in the effect of molecular structures on LC properties. Based on literature survey of synthesis of novel substances through homologous series, [16–19], the present proposed study is planned to synthesize an ester homologous series of three phenyl rings and two central bridges viz. –COO- and –COO-  $CH_2$ - with –Br and –OR terminal end groups and their LC characteristics to be discussed and interpreted in terms of molecular rigidity and flexibility [20–23], depending upon changing novel molecular structures.

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# Experimental

#### Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agent R-X to form *n*-alkoxy benzoic acid by modified method of Dave and Vora [24] as main component of a series. 4-Hydroxy-4'-bromobenzyl benzoate (m.p: 115–122°C) was prepared from 4-bromo benzyl bromide or alcohol and 4-hydroxy benzoic acid by applying the method of European patent and the modified method of Doshi, Patel, and Marathe [25]. *n*-Alkoxybenzoic acids through their corresponding acid chlorides and 4-hydroxy-4'-bromobenzyl benzoate were condensed in dry pyridine to form final products by a usual established method [26]. Final esterified products were individually decomposed, filtered, washed, dried, and purified until their constant transition temperatures obtained.

4-Hydroxy benzoic acid, alkyl halides, methanol, KOH, 4-bromo benzyl bromide or alcohol, N,N-dimethyl formamide, NaHCO<sub>3</sub>, HCl, dry pyridine, thionyl chloride, EtOH etc. required for the synthesis were used as received, except solvents which were dried and purified prior to synthesis. The synthetic route to the series is shown in Scheme 1.

# Characterization

The selected members of novel homologues series were characterized and analyzed for elemental analysis. The structure elucidated by Infra-red spectra, <sup>1</sup>HNMR spectra, and mass spectra. Textures and transition temperatures of homologues as well as of related materials were determined by an optical polarizing microscope, equipped with a heating stage. Elemental analysis was performed on Perkin–Elmer PE 2400 CHN analyzer. IR spectra were recorded on Perkin–Elmer spectrum GX. <sup>1</sup>HNMR spectra were determined on Bruker spectrometer using CDCl<sub>3</sub> solvent. Textures of smectic mesophase of some homologues were recognized either directly from the microscopic observations or by miscibility method.

## **Analytical data**

# Spectra data

#### <sup>1</sup>HNMR in ppm for Dodecyloxy and Hexyloxy Derivatives

<sup>1</sup>*HNMR in ppm for the Dodecyloxy Derivative:* 1.0 (-CH<sub>3</sub> of  $C_{12}H_{25}$ ), 1.50 (-CH<sub>2</sub>- of  $C_{12}H_{25}$ ), 2.70(-O-CH<sub>2</sub>-CH<sub>2</sub>- of  $-C_{12}H_{25}$ ), 4.04 (-O-CH<sub>2</sub>- of  $C_{12}H_{25}$ ), 4.14 (-COO-CH<sub>2</sub>-Aromatic) 6.25–6.29 (p-substituted phenyl ring), 7.82–7.84 (p-substituted benzene)

<sup>1</sup>HNMR in ppm for the Hexyloxy Derivative: 0.93 (-CH<sub>3</sub> of C<sub>6</sub>H<sub>13</sub>), 1.35 (-CH<sub>2</sub>- of -C<sub>6</sub>H<sub>13</sub>), 1.78 (-O-CH<sub>2</sub>-CH<sub>2</sub>- of -C<sub>6</sub>H<sub>13</sub>), 4.02 (-O-CH<sub>2</sub>- of C<sub>6</sub>H<sub>13</sub>), 6.92-6.97 (p-substituted phenyl ring), 7.51-7.57 (p-substituted benzene), 7.91-8.13 (p-substituted benzene).

NMR data confirm the structure.

## IR in cm<sup>-1</sup> for Pentyloxy and Decyloxy Derivatives

*IR in cm*<sup>-1</sup> *for Pentyloxy Derivative:* 844para-substituted phenyl ring, 1096, 1251, 1729 ester linkage of (COO-C<sub>5</sub>H<sub>11</sub>),759 Aromatic –Br linkage, 1070 ether linkage of (C<sub>5</sub>H<sub>11</sub>-O-C<sub>6</sub>H<sub>4</sub>).

*IR in cm*<sup>-1</sup> *for Decyloxy Derivative:* 844para substituted benzene, 1173, 1258, 1714 ester linkage of (COO-C<sub>10</sub>H<sub>21</sub>), 756 Aromatic –Br linkage, 1122ether linkage of (C<sub>10</sub>H<sub>21</sub>-O-C<sub>6</sub>H<sub>4</sub>).

IR data confirm the structure



R = CnH2n+1 where- n = 1,2,3,4,5,6,8,10,12,14,16.

Scheme 1. Synthetic route to the series.

# Mass spectra

# Mass spectra for Methoxy Derivative:

Molecular weight: Calculated: 442 Experimental: 445.

# Texture of smectic phase by miscibility method

Butyloxy(C<sub>4</sub>) derivative  $\rightarrow$  Smectic—A Octyloxy (C<sub>8</sub>) derivative  $\rightarrow$  Smectic—A Tetradecyloxy (C<sub>14</sub>) derivative  $\rightarrow$  Smectic—C

# **Results and discussion**

4-Hydroxy-4'-bromobenzyl benzoate is not a liquid crystal (M.P.115°–122°C, Yield- 70%). Liquid crystallinity is induced on linking it with dimeric 4-*n*-alkoxy benzoic acids through their corresponding acid chlorides. Transition temperatures of final novel ester derivatives

		% Elements calculated (Experimental%)		
Sr.No.	Molecular formula	С	Н	Br
1	$C_{22}H_{10}BrO_5$	60.63 (62.19)	4.17 (4.50)	17.57(18.0)
2	$C_{24}H_{21}BrO_5$	61.38 (60.88)	4.47 (4.23)	17.05 (16.9)
3	$C_{25}^{2}H_{23}^{2}BrO_{5}^{2}$	61.98 (61.22)	4.75 (4.86)	16.52 (17.8)
4	$C_{37}^{23}H_{47}^{23}BrO_{5}^{3}$	68.13 (68.66)	7.21 (7.00)	12.28 (12.5)

Table 1. Elemental analysis for ethoxy, propyloxy, butyloxy, and hexadecyloxy derivatives.

are relatively lower than the corresponding *n*-alkoxy benzoic acids. Only smectogenic mesomorphism induced throughout a series i.e. enantiotropic mesomorphism is commences from very first member of series to last C<sub>16</sub> member of a series. Nematogenic mesophase formation is totally absent for all the homologues. Transition temperatures (Table 2) of novel homologues are plotted versus the number of carbon atoms present in *n*-alkyl chain of *n*-alkoxy terminal end groups. Cr-Sm and Sm-I transition curves are obtained, which shows phase behavior of the series as shown in phase diagram (Fig. 1). An odd-even effect is observed for Sm-I transition curve. Cr-Sm transition curve follows a zigzag path of rising and falling with overall descending tendency and behaved in normal manner. Sm-I transition curves for even members initially falls upto hexyloxy ( $C_6$ ) homologue and it rises (from  $C_1$ ) and falls to  $C_5$  homologue, then both curves are merging into each other at the hexyloxy ( $C_6$ ) derivative and then gradually rises through C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub> homologues and finally maximum at C<sub>14</sub> homologue. Then a single Sm-I transition curve is descended to C<sub>16</sub> homologue after passing through maxima at C<sub>14</sub> homologue derivative. Thus Sm-I transition curve behaved in normal expected manner. The odd-even effect diminishes as series is ascended and transition curves for odd and even members transformed into a single Sm-I transition curve after merging into each other from and beyond hexyloxy homologue (C<sub>6</sub>) derivative. The mesomorphic properties and the degree of mesomorphism vary from homologue to homologue in present novel series. Thus, present series is entirely smectogenic whose mesophaselength (smectic) ranges minimum from 3.6°C at ( $C_{16}$ ) to maximum of 39.3°C at ( $C_2$ ). Smectic thermal stability is 91.2 and it is middle ordered melting type series with the absence of nematic mesophase formation.

Linking of dimeric 4-*n*-alkoxy benzoic acids through their corresponding acid chlorides with 4-hydroxy-4'-bromobenzylbenzoate which increases the molecular length, length to breadth ratio, ratio of the polarity to polarizability, permanent dipole moment across the

		Т	Transition temperature in °C		
Compound no.	$R = C_n H_{2n+1}(n)$	Sm	Nm	Isotropic	
1	C <sub>1</sub>	88.7	_	93.0	
2	C2	92.3	_	131.6	
3	C <sub>3</sub>	75.1	_	98.2	
4	C <sub>4</sub>	80.0	_	100.2	
5	Ċ,	77.0	_	83.1	
6	C	61.8	_	74.0	
7	C	67.7	_	72.9	
8	C <sub>10</sub>	70.7	_	80.8	
9	C <sub>12</sub>	70.3	_	81.4	
10	C14	71.9	_	102.3	
11	C <sub>16</sub>	82.2	_	85.8	
Sm: Smectic	Nm:Nematic				

Table 2. Transition temperatures of series in °C.



Figure 1. Phase behaviour of series.

long molecular axis, dipole-dipole interactions, electronic interactions and dispersion forces of suitable magnitudes to build up lamellar packing of molecules in crystal lattices to form layered arrangement in crystalline solid state and then, on exposure of thermal vibrations on crystalline state, the C<sub>1</sub> to C<sub>16</sub> homologues under individual microscopic observations resisted thermal vibrations for same range of temperatures, during which sample homologue acquire sliding layered arrangement of molecular network in floating condition on the surface, to show smectic mesophase formation due to end to end and lateral attractions as a consequence of favorable molecular rigidity and flexibility. The smectogenic mesophase formation disappears from and beyond isotropic temperatures on further heating. The molecules of present homologue derivatives randomly orient in all possible directions with high order of disorder or high entropy ( $\Delta S = \Delta H/T$ ). The same sample of homologues (C<sub>1</sub> to C<sub>16</sub>) on cooling with appropriate rate from and below isotropic temperature exhibit same textures of smectic mesophase, i.e. smectic mesophase reappears in reversible manner for same temperatures range which appeared on heating. The lowering of transition temperatures as compared to 4-n-alkoxy acids are due to the breaking of hydrogen bonding between two molecules of aromatic *n*-alkoxy acids by the process of esterification through their corresponding acid chlorides. Alternation of transition temperatures and odd-even effect observed upto C<sub>6</sub> homologue are due to the sequentially and progressively added methylene unit or units at the nalkyl chain bonded to phenyl ring through oxygen atom. Disappearance of odd-even effect from and beyond  $C_6$  homologue derivatives of longer *n*-alkyl chain is attributed to the unusual coiling or bending or flexing or coupling of *n*-alkyl chain with major axis of core structure. Thus, uncertainity in the status of *n*-alkyl chain hinders the odd–even effect. The absence of nematogenic mesophase formation throughout a present series is attributed to the absence of residual suitable magnitudes of anisotropic forces of end to end intermolecular attractions after the completion of smectic mesophase. The residual intermolecular end to end attractions are inadequate or insufficient to maintain statistically the parallel orientational order of molecules to float on the surface which disallows or restricts nematic mesophase formation. Variations in mesomorphic behaviours or properties from homologue to homologue in present series is attributed to the changing number of methylene unit or units at the n-alkyl chain, keeping rest of the molecular part including right handed terminal or lateral group intact or unchanged; throughout the same series. Low thermal stability (91.2) is associated with enthalpy change ( $\Delta H$ ) occurred by the difference of enthalpies between products and reactants, for particular homologue derivatives which differ from homologue to homologue with respect to mesophase stabilization energy and related to respective transition temperature. Thus, suitable magnitudes of anisotropic forces of intermolecular end to end and/or lateral attractions are sufficient to facilitate, induce, and stabilize smectic phase but hinders to facilitate and stabilize nematic phase formation against exposed thermal vibrations. The smectogenic mesophase length 3.6°C to 39.3°C depends upon the magnitudes of thermal resistivity against exposed thermal vibrations as a consequence of molecular rigidity, flexibility, intermolecular closeness, the extent of disalignment of molecules with the plane of a floating surface or the extent of noncoplanarity of the molecules. The liquid crystal properties of present homologous series-1 are compared with the structurally similar known series-X [27] and series-Y [28] as shown below in Fig. 2.

Homologous series-1 of present investigation and a structurally similar homologous series-X, chosen for comparison are identical with respect to three phenyl rings, central bridges – COO- and –COO-CH<sub>2</sub> and left *n*-alkoxy –OR, terminal end groups for the same homologue from series-1 to series-X. But, they differ with respect to other terminal end group –Br and –H. Homologous series-1 and series-Y are identical with respect to three phenyl rings, two terminal end groups –OR and –Br, but they (1 and Y) differ with respect to one of the central bridges i.e. –COO-CH<sub>2</sub>- (series-1) and –N=N– (series-Y), excluding a common –COO-central bridge linking first and middle phenyl rings. Therefore, variations in mesomorphic



Figure 2. Structurally similar series.

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Series $\rightarrow$	1	Х	Y
Smectic–Nematic Or	91.2		149.7
Smectic– Isotropic Commencement of smectic phase	(C <sub>1</sub> – C <sub>16</sub> ) C1	—	(C <sub>1</sub> -C <sub>16</sub> ) C <sub>6</sub>
Nematic–Isotropic Commencement of Nematic phase	_	78.8 (C <sub>6</sub> - C <sub>14</sub> ) C <sub>6</sub>	231.2 (C <sub>1</sub> - C <sub>10</sub> ) C <sub>1</sub>
Range in °C	Sm- 3.6 to 39.3	02 to 13	20 to 130

#### Table 3. Average thermal stability in °C.

properties and the degree of mesomorphism arising among the structurally similar series-1, X and Y will depend upon varying molecular part either right ended end group or a central bridge linking middle and third phenyl ring. Following Table 3 represents some LC properties of series-1, X, and Y which shows differences in thermal stability, commencement of mesophase or mesophases, mesophase length ranges and odd–even effects etc. depending upon molecular structures as a result of changing molecular rigidity and/or flexibility which related to internal energy or enthalpy change values of different homologues of same series or for the same homologue from series to series.

Homologous series-1 of present investigation and a structurally similar homologous series-X chosen for comparative study are identical with respect to three phenyl rings and two central bridges -COO- and -COO-CH<sub>2</sub>- i.e. aromaticity of series-1 and series-X contributing to the molecular rigidity are almost equal. The left n-alkoxy terminal end groups though, vary from homologue to homologue for the same series, but remain unaltered for the same homologue from series to series. Therefore, the molecular flexibility due to n-alkoxy terminal end group for the same homologue from series to series remains unaltered but alters from homologue to homologue in the same series. However, series-1 and series-X differ with respect to terminal end group -Br and -H at the other end of the molecules contributing to total molecular flexibility. Thus, magnitudes of combined effects of molecular rigidity and flexibility governing the tendency of a substance to induce or facilitate and stabilize liquid crystal property which vary from homologue to homologue in the same series. It also vary for the same homologue from series to series. Therefore, the mesomorphic (LC) property and the degree of mesomorphism are depended upon the suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of individual molecular rigidity and flexibility as emerged due to dipole-dipole interactions, permanent dipole moment of molecule, dispersion forces, intermolecular closeness etc which vary with molecular structure and induce variations in mesomorphic behaviour of every substance. Following Table 3; represents some liquid crystal properties, like thermal stability, commencement of liquid crystal phase, type of mesophase and the mesophase length range etc. for present novel series-1 and series-X chosen for comparison purpose.

From the Table 3, it is clear that,

- Homologous series-1 of present investigation is smectogenic only, without exhibition of nematic property whereas series-X is nematogenic only without exhibition of smectic property. Series-Y is smectogenic in addition to nematogenic character.
- Smectogenic mesophase of series-1 commences from very first member of a series and that of series-Y, it commences from hexyloxy ( $C_6$ ) homologue, but it does not commence till the last member of a series-X.

- Nematic mesophase commences from very first member of a series-Y and from hexyloxy (C<sub>6</sub>) member of a series-X, but it does not commence till the last member of a present series-1.
- Thermal stability for smectic of present series-1 is lower than a series-Y.
- Nematic thermal stability of series-Y is more than a series-X.
- Total mesophase length of present series is higher than a series-X, but it is lower than a series-Y.
- Odd-even effect is exhibited by the series-1, X, and Y, under comparative study.

On comparing thermal stability for smectic in case of series-1 and Y, which is lower for a series-1(91.2) than series-Y(149.7). Both these series are though structurally similar in all other respects except the central bridges which are -COO-CH<sub>2</sub>- in case of present series-1 and azo -N=N- in case of series-Y under study are closely similar to each other. Both these central bridges are comparable. The oxygen atom of the central  $-COO-CH_2$ - group containing carboxy group in the molecule of series-1 will be bumping into the nonbounded sides of the adjacent hydrogen atoms of the aromatic ring which causes considerable strain on the molecule. Consequently, a twist around C-O bond occurs, forcing the phenyl ring out of the plane of a molecule. Thus, the molecular co-planarity is reduced to some extent making them thick. The central bridge -N=N- certainly endows the molecular coplanarity in Trans position. Thus, on account of these differences, the smectic-isotropic thermal stabilities of series-1 is in general way lower than corresponding smectic thermal stability of a homologous series-Y. As regards to the commencement of smectic phase, it depends upon the extent of noncoplanarity of molecules. The molecules of series-Y are relatively shorter in length due to shorter -N=N- central group than -COO-CH<sub>2</sub>- longer central group of series-1. Thus, molecular coplanarity for the same homologue from series-1; to series-Y, varies. Hence, smectic mesophase commences from very first member of present series-1 while it commences late from  $C_6$  homologue of series-Y. The absence of nematic property in present series-1 and presence of nematic mesophase in series-X and Y is attributed to the difference of suitable magnitudes of anisotropic forces of intermolecular end to end attractions needed for occurrence of statistically parallel orientational order of molecular arrangement, while floating on the surface, under the influence of identically rated exposed thermal vibrations; for the same homologue from series to series, which commences earliest from very first  $(C_1)$  member of a series-Y, from  $C_6$  member of a series-X and it does not commence till the last member ( $C_{16}$ ) of present series-1. Alteration of transition temperature in all the series-1, X, and Y under comparative study which alternates for exhibition of odd-even effect. The mesophase length ranges depends upon suitable magnitudes of the degree of molecular rigidity and flexibility which causes mesophase stabilization energy related to differing values of enthalpies ( $\Delta H$ ) for the same homologue from series to series, which may resist more or less exposed thermal vibrations depending upon characteristics of molecular structure to facilitate appropriate molecular arrangement to cause smectic and/or nematic mesophase formation with different degree of mesomorphism.

# Conclusions

- Presently investigated homologous series is entirely smectogenic without exhibition of nematic property and of middle-ordered melting type.
- Mesophase range varies between 3.6°C and 39.3°C and of low thermal stability.

- Group efficiency order derived on the basis of (i) Thermal stability (ii) Commencement of mesophase (iii) Mesophase length range for smectic and/or nematic are as under
- (i) Smectic:



- Suitable magnitudes of molecular rigidity and flexibility are operating parameter for exhibition of LC properties.
- Phenomena of mesomorphism and the degree of mesomorphism are very sensitive and susceptible to molecular structure.
- Present study is useful for study of mixed mesomorphism and biological activity for agricultural productions and physiological therapy.

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