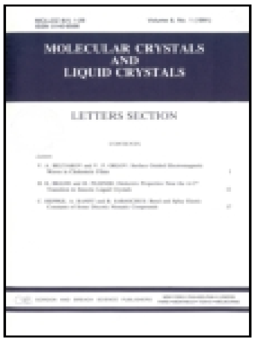

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Synthesis and Study of Novel Mesogenic Homologous Series: 4-(4′-*n*-alkoxy benzoyloxy)-*n*-propyl Cinnamates

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A novel homologous series of liquid crystals viz. 4-(4′-n-alkoxy benzoyloxy) n-propyl cinnamates comprising of 11 homologues has been synthesized. It is a middle ordered melting type of series with exhibition of smectic and nematic mesophases. The first to fifth members of the series are non-mesomorphic. Mesomorphic behavior commences from the sixth homologue. The octyloxy (C_8) and decyloxy (C_{10}) homologues are polymesomorphic. The smectic–nematic and nematic–isotropic transition curves behave in a normal manner except for the hexadecyl derivative, which slightly deviates from normal behavior (N–I). An odd–even effect was not observed for the N–I or Sm–N transition curves. The texture of nematic phase is threaded or Schlieren and that of the smectic phase is focal conic fan shaped of the smectic-A type. Transition temperatures and textures of mesophases were observed through an optical polarizing microscope equipped with a heating stage. Thermal stability and mesomorphic characteristics are compared with a structurally related series. Analytical and spectral data support the structure of the molecules.

Keywords Liquid crystals; mesogen; mesomorphic; nematic; smectic

1. Introduction

Liquid crystalline state of matter is exploited in electronic display devices, medical instruments pharmaceuticals, and medicinal preparations and many other fields of applications. [1] Our continuous efforts of studying the effects of molecular structure on liquid crystal behavior continue with the present study, which is aimed at *n*-propyl cinnamates [2, 3] with an *n*-alkoxy (-OR) group at the other end of a molecule. A central bridge of –COO- and two phenyl rings included, and the left *n*-alkoxy group is varied in size in order to investigate the effect of adding sequential –CH_2- units on mesomorphic behavior.[4, 5] Our present study is restricted to synthesize novel substances, their characterization, thermal transition temperatures, and the discussion on the effect of molecular structure on liquid crystal behavior of a substance [6–8] in terms of molecular rigidity and flexibility.

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2. Experimental

2.1. Synthesis

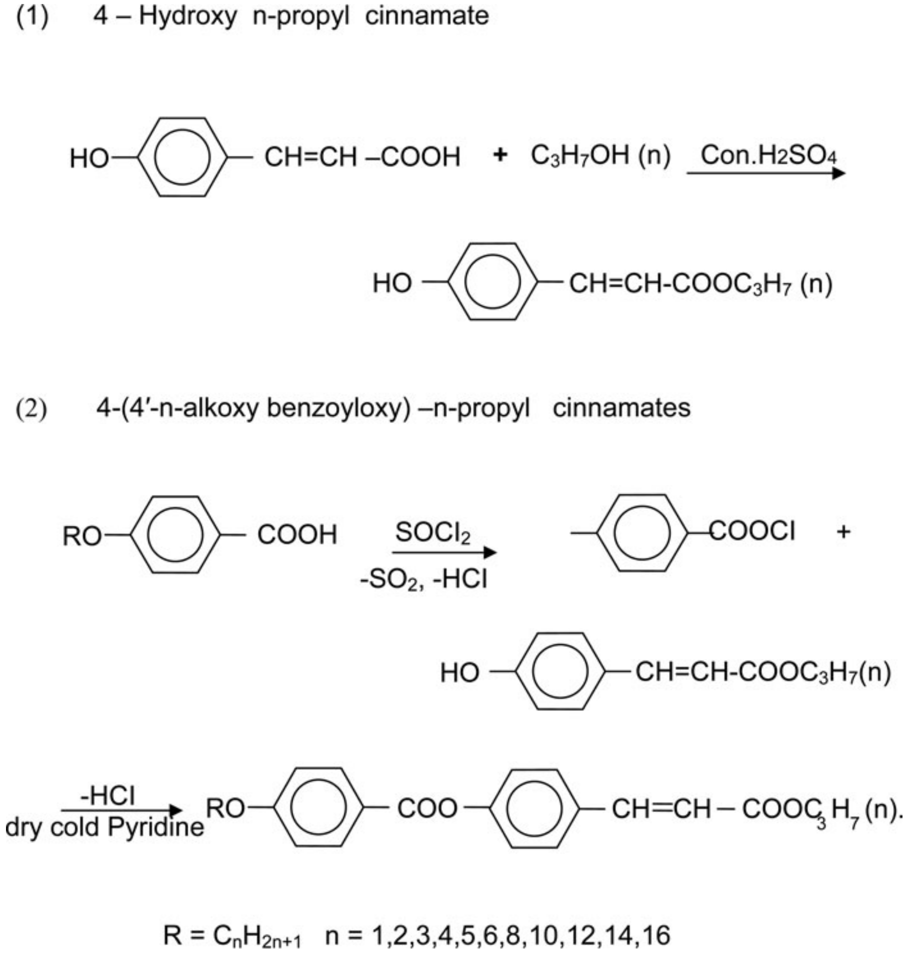
- *p*-*n*-Alkoxy benzoic acids were prepared by the modified method of Vora and Dave (1970) [9], using suitable alkylating agent (R-X)
- *p*-*n*-alkoxy benzoyl chlorides were prepared by refluxing corresponding alkoxy benzoic acids with freshly distilled [10] thionyl chloride.
- *p*-Hydroxy *n*-propyl cinnamates was prepared by reacting *p*-Hydroxy cinnamic acid with corresponding freshly distilled and dried *n*-propyl alcohol in presence of concentrated sulfuric acid.[11]
- Acid chlorides were directly condensed (Doshi and Lohar 1992, 1993) [12] with the *p*-*n*-hydroxy *n*-propyl cinnamates dissolved in ice cooled dry pyridine in portions with stirring reaction mixture. Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. 4-Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH, thionyl chloride, 4-Hydroxy cinnamic acid, *n*-propyl alcohol, con. H_2SO_4, pyridine 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 shown in Scheme 1.

2.2. Characterization

Representative members of the series were characterized by elemental analysis through Perkin Elmer PE 2400 CHN analyser, infrared spectra as recorded on a Perkin Elmer Spectrum GX, ^{1}HNMR spectra on Bruker spectrometer using $CDCI_3$ as solvent and mass spectra (Table 1). Transition temperature and the liquid crystal properties of textures of mesophases were determined by a miscibility method through an optical polarizing microscope equipped with a heating stage (Table 2).

3. Results and Discussion

The titled novel homologous series 4-(4′-*n*-alkoxy benzoyloxy)-*n*-propyl cinnamates is mesomorphic in nature. Mesomorphism is displayed by the members of the series in an enantiotropic manner. The first five members of the homologous series are non-mesomorphic in nature. The rest of homologues are mesomorphic. The octyloxy and decyloxy homologues are polymesomorphic, while the remaining mesomorphs are only nematogenic with reversible transition temperatures. Mesomorphic transition temperatures are relatively lower than the corresponding *n*-alkoxy acids. Transition temperatures are plotted against the number of carbon atoms in the terminal alkoxy chain. The transition curves (N–I and Sm–N) are obtained in phase diagram by linking like or related points are shown in Fig. 1. The transition curves of N–I and Sm–N of the series do not exhibit an odd–even effect. The solid–mesomorphic transition curve partly follows zigzag path of rising and falling values and finally descends as series is ascended. The smectic–nematic (Sm–N) transition curve rises and then on extrapolation [13, 14] merges into nematic–isotropic (N–I) transition temperature curve at dodecyloxy homologue and then matches with solid–nematic point of tetradecyloxy homologue. Thus, both transition curves behave in a normal manner. The N–I transition curve is descended from the hexyloxy to tetradecyloxy homologues as series is ascended and behave in a normal manner, but the hexadecyloxy homologue behaves in an abnormal manner, i.e. the N–I transition curve shows an ascending tendency instead



Scheme 1. Synthetic route to the series.

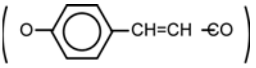
of a descending tendency. The Sm–N transition curve is extrapolated to the dodecyloxy and tetradecyloxy derivatives by keeping in view of a trend of curvature and normal expected trend to determine their Sm–N transition temperatures as found absent in reality. Mesomorphic phase length vary between 12°C and 44°C at tetradecyloxy and octyloxy homologue, respectively. Smectic and nematic mesophase length vary from 12°C to 18°C and 11°C to 34°C, respectively. Smectic and nematic thermal stabilities are 107.5 and 121.0, respectively. Smectic and nematic mesophases commences from octyloxy and hexyloxy homologues respectively. Smectogenic mesophase formation discontinued from and beyond dodecyloxy homologue derivative due to unfavorable magnitudes intermolecular attractions consequence of unsuitable molecular rigidity and flexibility to induce lamellar packing of molecules in their crystal lattices. Thus, variations in mesomorphic properties from homologue to homologue in presently investigated series is attributed to the changing $–CH_2$—unit or units added progressively in *n*-alkyl chain of the left *n*-alkoxy terminal end group which causes variations in molecular length, polarity and polarizability, end to end and lateral intermolecular attractions. 4-Hydroxy *n*-propyl cinnamate is nonmesomorphic

Table 1. Elemental analysis

Sr. No.	R = *n*-alkyl Chain	Molecular formula	Calculated %		Observed %	
			C	H	C	H
1	Ethyl	$C_{21}H_{22}O_5$	71.18	6.21	71.03	6.29
2	Octyl	$C_{27}H_{34}O_5$	73.97	7.76	73.83	7.89
3	Tetradecyl	$C_{33}H_{46}O_5$	75.86	8.81	75.61	8.92
4	Hexadecyl	$C_{35}H_{50}O_5$	76.36	9.09	76.19	9.01

IR Data in cm^{-1} for pentyl homologue.

^{1}HNMR Spectra in ppm for tetradecyloxy homologue.

Homologue	IR Spectra (cm^{-1})
Pentyl	3402.2 cm^{-1} → H- bonded O-H group 2927.7, 2869.9 & 1183.7 cm^{-1} → alkyl group 1685.7, 1269.1 & 1056.9 cm^{-1} → Conforms –COO- group 1199.6→ ether group 983.6 cm^{-1} → –CH=CH- group 825.5 cm^{-1}→ p-sub. benzene ring
Homologue	NMR Spectra (δ ppm)
Tetradecyl	0.88 ($-C\underline{H}_3$ of $-C_{14}H_{29}$) $\left.\begin{matrix}6.908 & 6.949\\ 8.045 & 8.063\end{matrix}\right\}$ (Two p-sub. benzene ring) 1.261 ($-C\underline{H}_2-$ of $-C_{14}H_{29}$) 4.021 ($-O-C\underline{H}_2$ of $-C_{14}H_{29}$) 7.263 

Note. Textures by miscibility method for Hexyl, Hexadecyl, Dodecyl, Octyl and Decyl derivatives.
Hexyl: Threaded nematic Dodecyl: Threaded nematic.
Hexadecyl: Schlieren nematic Octyl: Smectic – A
Decyl: Smectic –A.

(M.P. 240°C), however on linking it with n- alkoxy benzoic acid through corresponding acid chlorides yielded esters with lower transitions, because of the breaking of hydrogen bonding between two molecules of *n*-alkoxy benzoic acids through esterification process. Nonmesomorphicity of methoxy to pentyloxy homologues is attributed to their high crystallizing tendency arising from unfavorable magnitudes of molecular rigidity and flexibility [6, 7, 8] which results into their inability to resists the exposed thermal vibrations to float on the surface with two-dimensional array, but their molecules are sharply transformed into isotopic liquid from crystalline solid state without passing through mesomorphic state. Thus, molecules of non mesomorphs are randomly oriented in all possible directions with high order of molecular disorder or high entropy ($\Delta S = \Delta H/T$). The exhibition of smectogenic property by octyloxy and decyloxy homologues is attributed to the presence of lamellar packing of molecules in their crystal lattice which resisted exposed thermal vibrations and maintained molecular dis alignment at an angle 90° or less than 90° with the plane of a floating surface and molecules occupy themselves as sliding layered arrangement in

Table 2. Transition temperatures

Sr. No.	*n*-alkyl Group		Transition temperatures in °C Smectic	Nematic	Isotropic
1	Methyl	C_1	—	—	260.0
2	Ethyl	C_2	—	—	265.0
3	Propyl	C_3	—	—	230.0
4	Butyl	C_4	—	—	148.0
5	Pentyl	C_5	—	—	113.0
6	Hexyl	C_6	—	102.0	136.0
7	Octyl	C_8	90.0	102.0	134.0
8	Decyl	C_{10}	95.0	113.0	124.0
9	Dodecyl	C_{12}	—	78.0	109.0
10	Tetradecyl	C_{14}	—	92.0	104.0
11	Hexadecyl	C_{16}	—	99.0	119.0

floating condition for definite range of temperature and then on continued exposure of thermal vibrations at higher temperature same molecules occupy themselves to float with the ordered arrangement as statistically parallel orientational order of molecules with threaded or schlieren texture of nematic mesophase. However on further heating the same from and beyond isotropic temperature, molecules acquire isotropic state. On cooling the same, the reversal of mesophase, viz. nematic and then smectic reappears at the same temperature at which relevant mesophase was appeared on heating. Rest of the nematogenic mesomorphs, except octyl and decyl homologue derivatives, exhibited only nematic mesophase formation from and below isotropic temperature, in which dis-aligned molecules arrange themselves to float on the surface with maintenance of statistically parallel orientational, two-dimensional order of molecules reversibility by favorable end to end attractions showing only nematogenic mesophase formation. The absence of odd–even effect for Sm–N and N–I transition curve is due to late (i.e. from hexyloxy homologue) commencement of mesophase and Nonmesomorphicity exhibited by prior homologues no. 1, 2, 3, 4, 5. Extrapolation of Sm–N transition curve indicate that, Sm–N transition temperature ranges into N–I transition temperature 109°C which conforms and prove the absence of smectic mesophase in dodecyloxy homologue derivative. On extending the extrapolation of Sm–N transition curve up to tetradecyloxy homologue, the Sm–N transition temperature matches exactly at 104°C which is a solid–nematic transition temperature of a tetradecyloxy homologue derivative. It means that there is no possibility to occur smectic mesophase formation by tetradecyloxy homologue. Sm–Nm transition curve is not extended to extrapolate up to hexadecyloxy homologue because N–I transition curve deviates from normal behavior to some extent for hexadecyloxy homologue. The discussion and extrapolation ruled out for the same (C_{16}). The changing mesomorphic behaviors of presently investigated novel homologues of present series-1 are compared with the structurally similar known other homologous series-*X* [15] and series-*Y* [16] chosen for comparison as shown in Fig. 2.

Homologous series (1), (*X*) and (*Y*) under comparison contain two phenyl rings and central bridge –COO– as common identical part as rigid core of the molecules. Left *n*-alkoxy group varies from homologue to homologue in the same series but characteristics

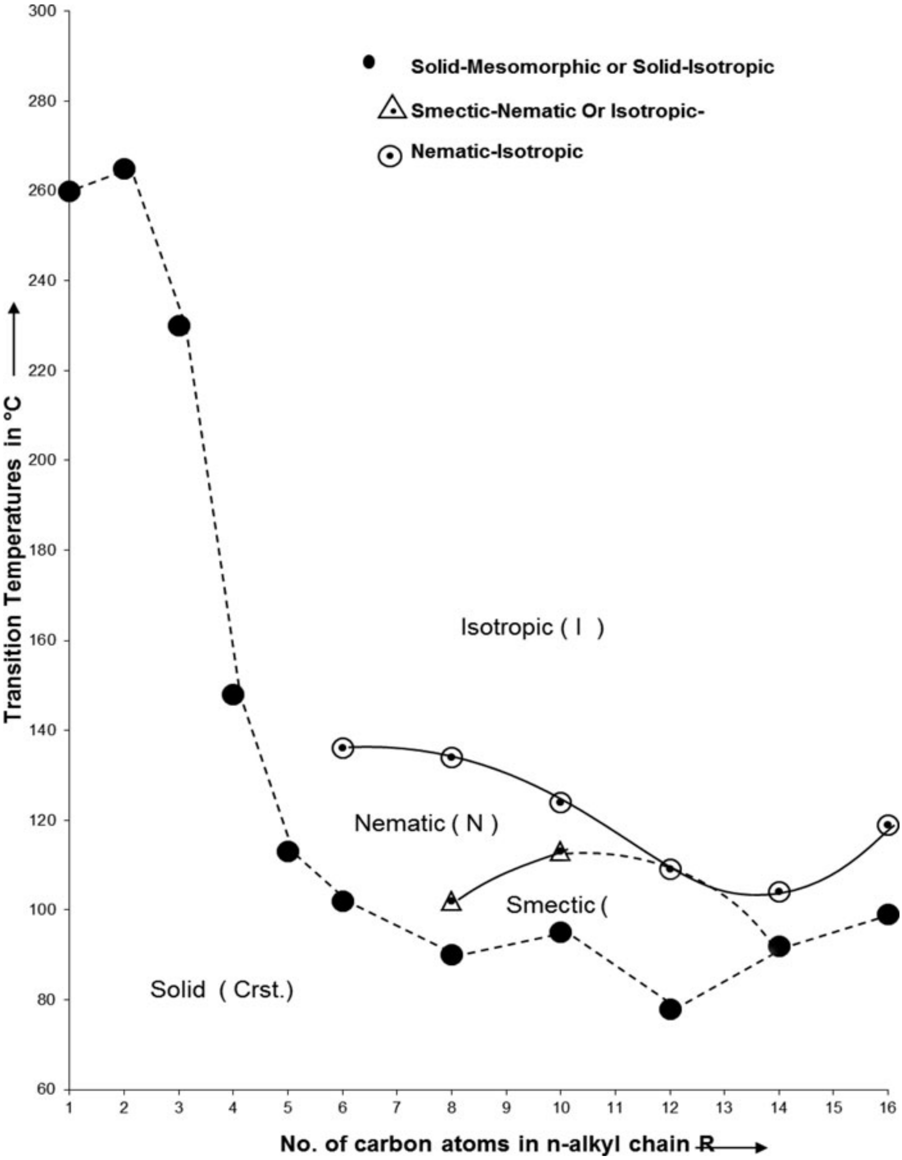


Figure 1. Transition curves (N–I and Sm–N) are obtained in phase diagram by linking like or related points.

are comparable for the same homologue from series to series. Right terminal end groups are varied from series to series. Left and right terminal end groups of the molecules are acting as flexible parts of the molecules. Therefore, variations in mesomorphic characteristics and degree of mesomorphism are attributed to the variations of the terminal end-to-end attraction due to combine effects of molecular rigidity and flexibility responsible to words variations of mesomorphic behavior from series to series. Homologous series-1 and series-*X* differs by $-CH_2-$ unit at the end group for the same homologue of series. Therefore molecular length of series-*X* is relatively shorter for same homologue from series-1 to

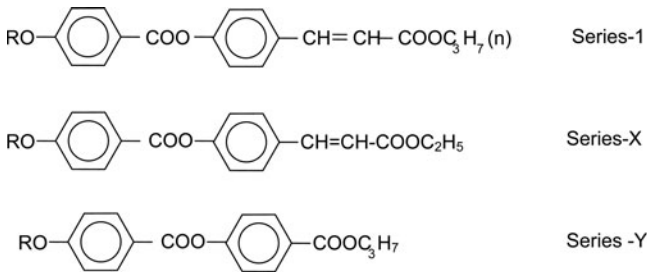


Figure 2. Structurally similar homologous series.

series-*X*. Homologous series-1 and series-*Y* differs with respect to terminal end groups –CH=CH-COO-, and –COO- respectively for the same homologue. Therefore observe difference in molecular length, length to breadth ratio, molecular polarizability, dispersion forces, intermolecular end-to-end attraction permanent dipole moment across the long molecular axis, dipole–dipole interactions etc. contributes to the variation in mesomorphic behaviors for same homologue from series to series. Table 3 represent thermal stabilities for commencement of smectic and/or nematic mesophase and exhibition of mesomorphism of homologues etc. as under.

Table 3 indicates that,

- Smectic thermal stability of present series -1 is greater than the series –X and series – Y chosen for comparison.
- Nematic mesophase formation is exhibited by the homologous series-1 and series-*X* containing –CH=CH-COO- terminal end group to which -C_3H_7 (n) and –C_2H_5 group bonded.
- Nematic mesophase formation is absent for series-*Y* containing –$COOC_3H_7$ (n) end group.
- Nematic thermal stability of presently investigated series-1 is greater than the series-*X* and series-*Y*.
- Smectic mesophase commences later (from C_8) than the series-*X* and series-*Y* (from –C_6)
- Nematic mesophase commences earlier (from –C_4) by series-*X* than present series-1 and it does not commences till the last hexadecyloxy homologue for series-*Y*.
- Homologous series-1 and series-*X* containing conjugated double bond as –CH=CH- are predominantly nematogenic and partly smectogenic whereas homologous series-*Y* containing –$COOC_3H_7$ (n) end group with absence of –CH=CH- unit for end group is smectogenic without exhibition of nematic character.

Table 3. Average thermal stabilities in °C

Series	(1)	(*X*)	(*Y*)
Smectic–nematic or smectic–isotropic	107.5 (C_8–C_{10})	—	82.75 (C_6–C_{12})
Commencement of nematic phase	C_8	—	C_6
Nematic–isotropic or isotropic–nematic	121.0 (C_6–C_{16})	89.0 (C_6-C_{12})	—
Commencement of smectic phase	C_6	C_6	—

Looking to the above comparative points, the differences are mainly associated with the presence and the absence of –CH=CH- unit at the end group, including effect due to linking of –C_3H_7 (n) and –C_2H5 bonded to –COO- group. Decreasing order of thermal stability for present series-1 and series-X is attributed to the decreasing transitions as the chain length decreased from –C_3H_7 (n) to –C_2H_5 at the right handed terminal end group. Thus, decreasing tendency of suitable magnitudes of anisotropic forces of intermolecular attractions is very well supported by present study. Now on comparing thermal stabilities which is higher of present series-1 and lower for the series-*Y* which containing common –C_3H_7 (n) group bonded to –CH=CH-COO- and –COO- respectively at the end of the molecules. In all other respects except the terminally situated end group –CH=CH-COO- in case of a homologous series-1 and –COO- in case of series-*Y* are closely similar to each other. Both these end groups are comparable though the vinyl carboxylate –CH=CH-COO- has greater length and causes more noncoplanarity due to a twist obtained as the oxygen atoms of the vinyl carboxy group bump into the non-bonded adjacent hydrogen atom of the phenyl ring. On account of these difference, the smectic thermal stabilities of homologous series-1 is in general way higher than series-*Y* (or smectic thermal stability of *Y* is lower than series-1). Exhibition of nematic property by series-1 in addition to smectic property is also attributes to added –CH=CH- unit which increases intermolecular end-to-end attractions as a consequence of higher molecular rigidity of series -1 as compared to series-*Y*. The extent of noncoplanarity caused by the molecules differs from series to series due to differing –CH=CH-COO- and –COO- as well as –C_2H_5 and –C_3H_7 (n) group which facilitate early or late commencement of mesophase or mesophases. Thus, all the homologous series-1, series-*X*, and series-*Y* under comparison though possess linear lath like geometrical shape, but their mesomorphic behavior vary with the differing end groups –CH=CH-$COOC_3H_7$ (n), –CH=CH-$COOC_2H_5$ and –$COOC_3H_7$ (n) from series to series for the same homologue.

4. Conclusions

- Variations in mesomorphic properties from homologue to homologue in the same series is attributed to the sequentially and progressively added methylene unit at the *n*-alkyl chain of the left *n*-alkoxy terminal end group.
- Variations in mesomorphic property from series to series for the same homologue is attributed to the changing right handed end group. viz. –CH=CH-$COOC_3H_7$ (n), -CH=CH-$COOC_2H_5$, and –$COOC_3H_7$ (n).
- Presently investigated novel series is a predominantly nematogenic and partly smectogenic with middle ordered melting type and mesomorphic range.
- Group efficiency order derived on the basis of (i) thermal stability and (ii) the early commencement of smectic and nematic phase is as under.

(i) Smectic:
-CH=CH-$COOC_3H_7$(n) > –$COOC_3H_7$ (n) > -CH=CH- $COOC_2H_5$
Nematic:
-CH=CH-$COOC_3H_7$(n) > -CH=CH- $COOC_2H_5$ > –$COOC_3H_7$ (n)
(ii) Smectic:
–$COOC_3H_7$ (n) = -CH=CH- $COOC_2H_5$ > -CH=CH-$COOC_3H_7$(n)
Nematic:
-CH=CH- $COOC_2H_5$ > -CH=CH-$COOC_3H_{7(n)}$ > –$COOC_3H_7$ (n)

- –CH=CH-COO- group is preferably nematogenic while -COO- group is preferably smectogenic.
- Phenomenon of mesomorphism depends upon favorable molecular rigidity and flexibility and very sensitive and susceptible to the suitable magnitudes of anisotropic forces of intermolecular adhesion as a consequence of molecular rigidity and flexibility.

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