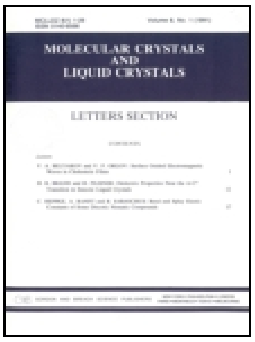

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Study of the Effect of Lateral Substitution on Mesogenic Behavior with Reference to -CH=CH- Unit

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ABSTRACT
A novel cinnamate ester homologous series has been synthesized and studied with a view to understanding and establishing the effects of molecular structure on liquid crystal (LC) properties with a focus on the highly polar methoxy group as a lateral substituent. The series consists of twelve homologs; of which C_1–C_5 are nonmesogenic, and the rest of the homologs are enantiotropically smectogenic or and nematogenic. The texture of nematic phases is threaded or Schlieren and that of the smectic is either smectic A or C, as recognized and determined through an optical polarizing microscope equipped with a heating stage. The Sm-N I and N-I transition curves exhibit odd-even effects and behave in normal manner. The Cr-I M behaves in normal manner. Analytical and spectral data confirm the molecular structures of homologs. The average thermal stabilities for smectic and nematic are 125.3 C and 129.8 C, respectively, whose total mesophase length varies from 13 C to 51 C. Some LC properties of present series are compared with the structurally similar known series.

KEYWORDS
Liquid crystal; mesogenic; smectic; nematic; Azoester

Introduction

In continuation of our study on the liquid crystalline (LC) state [1] through an ester homologous series bearing lateral substitution of -OCH_3 group, the present investigation consists of two phenyl rings bonded through -COO- central bridge and n-alkoxy (-OR) as well as -CH CH-COO-C_4H_9 (n), both left and right terminal end groups including -OCH_3 lateral group. Thus, present investigation is planed with a view to understanding and establishing the effect of molecular structure on LC properties by substituting n-C_4H_9 chain as fixed unit at the tail end for all homologs of a same series bonded to flexible -CH CH-COO- unit [2–5].

LC substances of thermotropic type are most useful for LC devices either directly or through study of binary system [6–9], the interest is developed for synthesis of LC ester substances. Several LC substances have been reported to date [10–18] through ester homologous series. Hence, the novel substances will be synthesized, characterized by thermometric, spectral, and analytical data. Experimental data will be interpreted and discussed on the basis of molecular rigidity and flexibility [19–22] and its LC behaviors will be compared and interpreted with reference to structurally similar known series, to derive group efficiency order for smectic and nematic.

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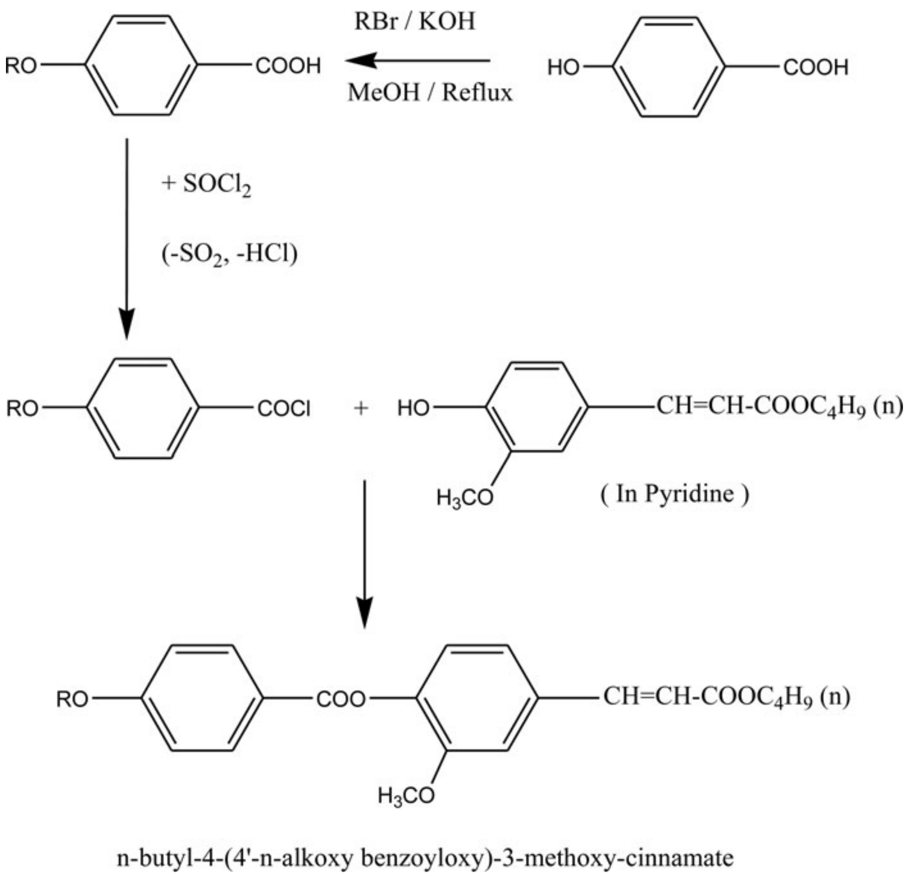


Scheme 1. Synthetic route to the series. ***R*** $-C_nH_{2n+1}$ where, *n* 1,2,3,4,5,6,7,8,10,12,14,16.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents (R-X) to convert it into dimeric 4-n-alkoxy benzoic acids by the modified method of Dave and Vora [23]. 4-Hydroxy-3-methoxy cinnamic acid (m.p. 64 C) was esterified by n-butenol by using conc. H_2SO_4 by usual established method [24]. The ester was very dense brown colored liquid (yield 64.5%), which purified from n-hexane. Dimeric 4-n-alkoxy benzoic acids were individually condensed with 4-hydroxy-3-methoxy n-butyl cinnamate in dry cold pyridine through corresponding acid chlorides [25]. Final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained.

The synthetic route to the series is shown below in Scheme 1.

The chemicals required, 4-Hydroxy benzoic acid, MeOH, KOH, Alkyl halide (R-X), Thionyl chloride, 4-hydroxy-3-methoxy cinnamic acid (Ferulic acid), n-Butenol, Conc. H_2SO_4, Pyridine, 1:1 HCl, $NaHCO_3$, NaOH, anhydrous $CaCl_2$, Silicagel, Petrolium ether, Methyl acetate, and n-Hexane were used as received, except solvents which were dried and purified prior to use.

Table 1. Elemental analysis for propyloxy, pentyloxy, octyloxy, and dodecyloxy derivatives.

Compound no.	Molecular formula	% of C Experimental (theoretical)	% of H Experimental (theoretical)
C_3	$C_{24}H_{28}O_6$	69.88 (70.57)	6.84 (7.47)
C_5	$C_{26}H_{32}O_6$	70.89 (71.45)	7.32 (7.63)
C_8	$C_{29}H_{38}O_6$	72.17 (72.57)	7.94 (8.42)
C_{12}	$C_{33}H_{46}O_6$	73.57 (73.85)	8.61 (9.05)

Characterization

Representative homologs of the series were selected for characterization of structure by elemental analysis (Table 1), IR spectra, mass spectra and H^1 NMR spectroscopy. Microanalysis was performed on Perkin Element PE 2400 CHN analyzer. IR spectra were recorded on Perkin Elmer spectra GX. H^1 NMR spectroscopy performed was recorded on Bruker using $CDCl_3$ as solvent.

Mesomorphic properties were investigated using hot stage polarizing microscope.

Analytical Data

IR spectra in cm^1 for hexyloxy homolog derivative.

The IR spectrum of the compound showed

691.60 cm^1 polymethylene of -C_6H_{13} group.

844.29 and 766.67 cm^1 as para and ortho sub. benzene ring,

1164.59 cm^1 as -CO- of alkoxy group,

1246.58, 1674.23 cm^1, and 1601.22 cm^1, conforms -COO- and -CO- of ester group,

1423.45 and 1468.30 cm^1, confirms aromatic -C C-,

933.79 and 1020.03 cm^1, confirms trans -CH CH- group,

2935.71 and 2861.18 cm^1, confirms alkyl group.

IR data support the molecular structures.

IR spectra in cm^1 for octyloxy homolog derivative.

The IR spectrum of the compound showed,

643.93 cm^1, confirms polymethylene of -C_8H_{17} group,

845.69 cm^1 and 761.67 cm^1, confirms para and ortho sub. benzene ring,

2854.36 and 2929.43 cm^1, confirms alkyl group,

1641.13 cm^1, 1606.20 cm^1, 1255.19 cm^1, confirms -COO- and -CO- group,

1512.79 and 1419.84 cm^1, confirms aromatic -C C-,

1156.31 and 1062.23 cm^1 as -CO- of alkoxy group,

967.86 cm^1, confirms trans -CH CH- group,

IR data support the molecular structures.

H^1 NMR spectra in ppm for pentyloxy and decyloxy derivatives.

Amyloxy.

H^1 NMR data in δ ppm (n-pentyloxy derivative, 400 MHz, $CDCl_3$, standard TMS):-

0.9677 (-CH_3 of -C_5H_{11}), 1.2697–1.4192 (-CH_2 of -C_5H_{11}), 1.6345–1.8558 (-OCH_2-CH_2 of -C_5H_{11}), 3.8545 (-O-CH_3), 4.0493 and 3.9740 (-O-CH_2- of -C_5H_{11}), 6.4105–7.1766 (-O-C_6H_3-CH CH-CO-), 7.5383 to 8.1700 (p-sub. benzene ring).

The data supports the molecular structure.

Homolog	Theoretical	Experimental
C_5	440.53	441.4
C_{10}	510.66	510.6

Decyloxy. H^1 NMR data in δ ppm (n-decyloxy derivative, 400 MHz, $CDCl_3$, standard TMS):- 0.8936 (-CH_3 of -$C_{10}H_{21}$), 1.1847–1.3780 (-CH_2- of -$C_{10}H_{21}$), 1.6185–1.7495 (-OCH_2-CH_2- of -$C_{10}H_{21}$), 3.7332 (-O-CH_3), 3.9117–4.1366 (-O-CH_2- of -$C_{10}H_{21}$), 6.7604–7.4537 (-O-C_6H_3-CH CH-CO-), 7.5508–8.0565 (p-sub. benzene ring).

The data supports the molecular structure.

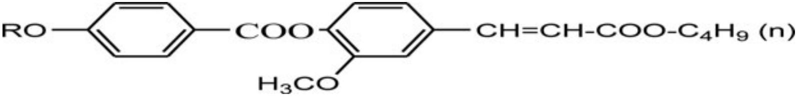
Texture determination by miscibility method.

- Hexyloxy homolog ——→ Threaded nematic
- Dodecyloxy homolog ——→ Schlieren nematic
- Octyloxy homolog ——→ Smectic – A
- Tetradecyloxy homolog ——→ Smectic – C

Results and discussion

The novel homologous series n-butyl-4(4′-n-alkoxy benzoyloxy)-3-methoxy cinnamates was synthesized by condensing dimeric n-alkoxy benzoic acids and 4-hydroxy-3-methoxy-n-butyl cinnamate (very dense brown liquid). The first five members of the series are nonmesogenic, C_6 member is only nematogenic, C_7 to C_{12} are smectogenic plus nematogenic and C_{14} to C_{16} are only smectogenic. All LC homologs are enantiotropically smectogenic or and nematogenic. Transition temperatures (Table 2) of homologs are plotted versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal end group. Transition curves (Fig. 1) are obtained on linking like or related points. Cr-I/M transition curve adopts a zigzag path of rising and falling with overall descending tendency and behaves in normal manner. Sm-N or Sm-I transition curve descended from C_8 to C_{16} for even numbered homologs and rises

Table 2. Transition temperatures in C.



Compound no.	*R* -C_nH_{2n+1}	Smectic	Nematic	Isotropic
1	C_1	–	–	125.0
2	C_2	–	–	137.0
3	C_3	–	–	115.0
4	C_4	–	–	148.0
5	C_5	–	–	140.0
6	C_6	–	99.0	121.0
7	C_7	78.0	90.0	129.0
8	C_8	98.0	124.0	140.0
9	C_{10}	88.0	117.0	136.0
10	C_{12}	88.0	107.0	123.0
11	C_{14}	76.0	–	111.0
12	C_{16}	90.0	–	103.0

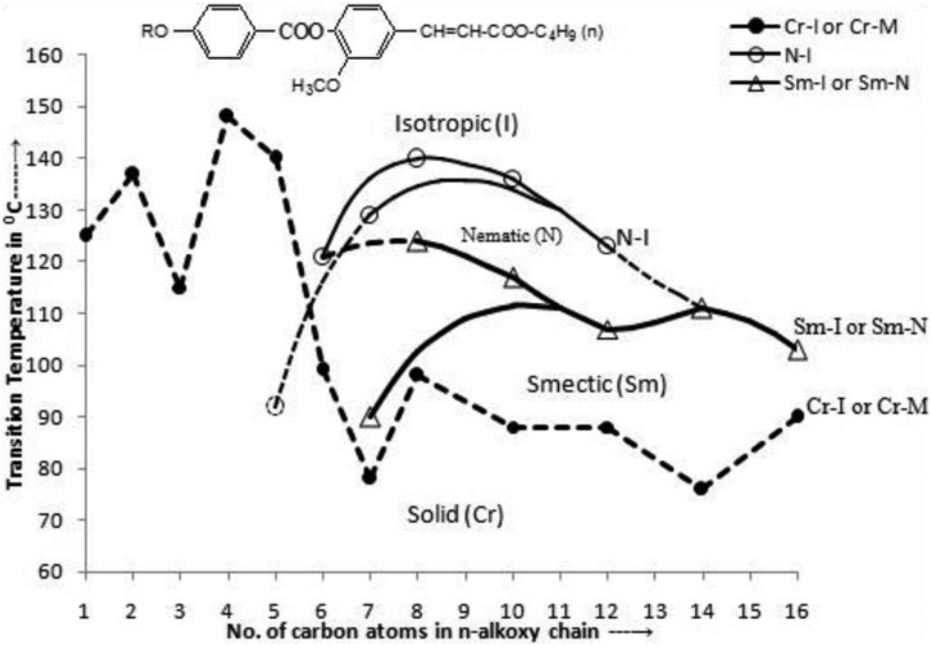


Figure 1. Phase behaviors of series.

from C_7 to C_{14} and then descended to C_{16} through C_{12} homolog with exhibition of an odd-even effect. N-I transition curves for odd and even members initially rises and then descends up to the C_{12} homolog and ceases to exhibit nematic mesophase with exhibition of odd-even effect. Transition curve of odd-members occupied lower position than a curve for even members in case of Sm-I/N and N-I transition curves exhibiting odd-even effect. Transition curves for odd and even members merge into C_{11} member of a series and then a single transition curve for N-I and Sm-N/I progressed for higher homologs C_{12}, C_{14}, and C16 from and beyond C_{11} homolog. Thus, transition curves of a phase diagram showing phase behaviors of a series behaved in normal manner. N-I transition curve is extrapolated to nonmesogenic homolog C_5 to determine its latent transition temperature (LTT). Similarly Sm-I/N transition curve is extrapolated to C_6 to predict and interpret its nonsmectogenic behavior. The mesomorphism commences from C_6 homolog and the mesogenic properties like thermal stabilities for smectic and nematic, and their mesophase length range etc. vary from homolog to homolog in the same series. Thus, present novel series is partly smectogenic and partly nematogenic whose degree of mesomorphism is low and is of middle ordered melting type.

Lowering of transition temperatures of novel homologs, corresponding to n-alkoxy benzoic acid is attributed to breaking of hydrogen bonding between two molecules by esterification process. Alternation in transition temperature is due to the odd and even number of carbon atom present in n-alkyl chain of -OR terminal. Exhibition of only smectogenic or only nematogenic or smectic and subsequent nematic phase formation is attributed to the disalignment of molecules at angle ninety or less than ninety degree with the plane of surface with presence or absence of lamellar packing of molecules in crystal lattice of rigid crystals. C_7–C_{16} homologs molecules bearing lamellar packing of molecules in their preoccupied crystal lattices, which under exposed thermal vibrations arrange themselves in two-dimensional network as sliding layers for definite range of temperature with appearance of smectogenic character. The C_7–C_{12} homologs bearing residual intermolecular end-to-end

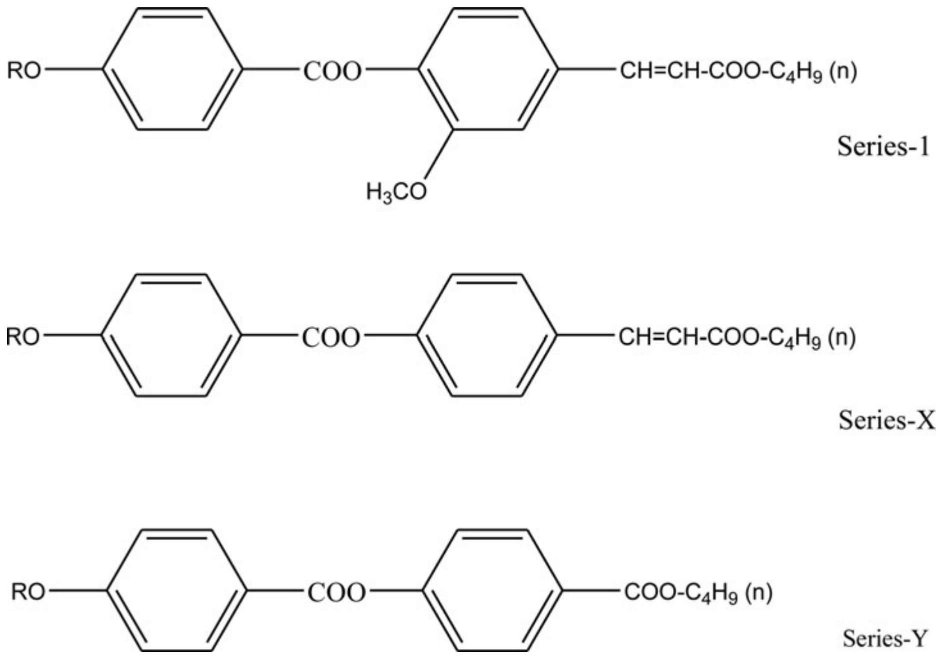


Figure 2. Structurally similar series.

anisotropic forces of suitable magnitudes arranges molecules to float with statistically parallel orientational order which induces nematogenic character beyond smectogenic character. However, C_6 homolog with absence of lamellar packing of molecules in its crystal lattices fails to exhibit smectic phase but, exhibited only nematic phase. The converse of it, C_{14} and C_{16} homologs bearing lamellar packing of molecules in their crystal lattices but, unsuitable or insufficient magnitudes of residual intermolecular end-to-end attractions and closeness fails to induce nematic phase beyond smectic phase and converted into isotropic state, at which molecules are randomly oriented in all possible directions with high order of disorder or high entropy (ΔS ΔH T). The mesogenic homologs (C_6–C_{16}) on cooling from their isotropic state carefully, it resumes or reshows their mesogenic state (smectic or nematic) in a reversible manner exactly at the same temperature at which it had appeared on heating. Odd-even effect observed for N-I and Sm-I N transition curve is attributed to the sequentially added methylene unit at the n-alkyl chain. Extrapolated [26–28] Sm-N transition curve matches with the N-I transition point of C_6 homolog, which indicates that Sm-N transition temperature and N-I transition temperature coincided to each other at isotropic temperature 121.0 C, i.e., smectogenic phaselength is 121—121 00 zero. Means, there is no practical possibility for the occurrence of the smectogenic mesophase for C_6 homolog. Similarly extrapolation of N-I transition curve at C_5 homolog to predict LTT 92 C, i.e., latent ability of C_5 homolog to exhibit LC property, which is not realizable due to its high crystallizing tendency; at far below the isotropic temperature. Nonmesogenic property of C_1 to C_5 homologs is attributed to their high crystallizing tendency arising from low dipole-dipole interactions and the law magnitudes of dispersion forces by interactions between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of the molecules as a consequence of unfavorable molecular rigidity and flexibility. Hence the molecules of C_1–C_5 are unable to resist exposed thermal vibrations and abruptly breaking their crystal lattices and smoothly and sharply transform into isotropic state without passing through LC state. Changing trend in mesogenic properties from homolog to homolog in the same series is due to the changing number of methylene unit or units at the left n-alkyl chain bonded to phenyl ring through oxygen atom, keeping rest of the molecular part unchanged. The mesogenic properties of present novel series are compared with the structurally similar known series as shown below in Figure 2.

Homologous series-1 of present investigation and the structurally similar homologous series-X [29] and -Y [30] selected for comparing some LC properties depending upon variation of molecular structure are as under. Homologous series-1 and -X are identical with respect to two phenyl rings linked through -COO- central bridge and the left and right n-alkoxy group (-OR) as well as tail group -CH CH-COO-C_4H_9, respectively, for the same homolog from series-1 to series-X, but they differ with respect to presence and absence of laterally substituted -OCH_3 group. Therefore, the molecular rigidity of series-1 and -X is identical but differs with respect to molecular flexibility for the same homolog from series to series and from homolog to homolog in the same series. Homologous series-1 and -Y are identical with respect to molecular rigidity but they differ with molecular flexibility due to presence and absence of laterally substituted -OCH_3 group, respectively, and the replacement of a part of tail end group, -CH CH-COO- by -COO-. Thus, variations in mesomorphic properties and the degree of mesomorphism of series-1, -X, and -Y will depend upon changing features of series under comparative study. Following Table 3 represent some mesogenic properties of series-1, -X, and -Y as under.

Above Table 3 indicates that

- Homologous series-1 and -X are smectogenic in addition to nematogenic, whereas series-Y is only smectogenic without exhibition of nematic property.
- Smectogenic mesophase formation commences from C_7, C_{10}, and C_5 homolog for series-1, -X, and –Y, respectively.
- Nematogenic mesophase commences from C_6 to C_5 homologs for series-1 and –X, respectively, but it does not commence till C_{16} homolog for a series-Y.
- Smectic thermal stability of series-1, -X, and -Y are in decreasing order.
- Nematic thermal stability increases from series-1 to -X, but it destabilizes nematic phase for series-Y.
- Total mesophaselength is the highest for a series-X and the lowest for a series-Y, whereas it is intermittent of present series-1.

Looking to the thermal stability for smectic, it decreases from series-1 to -X to -Y. Decreasing order is attributed to the presence of highly polar lateral -OCH_3 group which increases molecular polarizability and the suitable magnitudes of intermolecular cohesion against the decreasing intermolecular attraction by broadening of same molecule. Thus, predominancy of the polarizability factor stabilizes and facilitates smectic mesophase formation of the

Table 3. Average thermal stability in C.

Series:→	1	X	Y
Smectic-isotropic or smectic-nematic	125.3 (C_7–C_{16})	101.0 (C_{10}–C_{12})	67.8 (C_8–C_{16})
Commencement of smectic phase	C_7	C_{10}	C_5
Nematic-isotropic	129.8 (C_6–C_{12})	140.0 (C_5–C_{16})	–
Commencement of nematic phase	C_6	C_5	–
Total mesophaselength range in C (Sm + N)	13–51	15–62	09–26
C_i to C_p	C_{16} C_7	C_5 C_{12}	C_{16} C_{10}

highest magnitudes (125.3) for presently investigated series-1. Moreover, series-X and -Y are long linear lath like, whose suitable magnitudes of anisotropic forces of intermolecular cohesion and closeness reduces due to absence of lateral group like $\mathrm{-OCH_3}$. Homologous series-X contain additional -CH CH- unit as similar to series-1 in a tail group $\mathrm{-CH\ CH\text{-}COOC_4H_9(n)}$, but its thermal stability reduces by 125.3—101.0 24.3 units due to absence of lateral group. However, a homologous series-Y contain $\mathrm{-COOC_4H_9(n)}$ flexible tail group, which differs from flexible tail groups of series-1 and -X by -CH CH- unit which increases rigidity and flexibility. Thus, absence of -CH CH- unit at flexible tail group in addition to lateral group reduces more reduction in thermal stability and lowering of transition temperatures. Thermal stability is related with thermodynamic quantity ΔH and thermal resistivity towards exposed thermal vibrations, which gradually decreases from series-1 to -X to -Y for maintaining smectic mesophase. Therefore decreasing order of smectic thermal stability is observed. However the residual end-to-end attractions and closeness beyond smectic mesophase are suitable to induce nematic phase in case of series-1 and -X due to presence of -CH CH- unit in a same flexible tail group $\mathrm{-CH\ CH\text{-}COO\text{-}C_4H_9}$ (n), but it fails the exhibition of nematic phase beyond smectic phase due to absence of -CH CH- unit in $\mathrm{-COO\text{-}C_4H_9}$ (n) tail group. Thermal stability for nematic for a series-X is more than a series-1, because, the reduction in smectic thermal stability of series-X as compare to series-1 is compensated by increasing thermal stability for nematic, i.e., nematic phase has stabilize at the cost of smectic phase. Nematogenic character is totally lost at the cost of smectic phase in series-Y due to absence of -CH CH- unit at the flexible tail $\mathrm{-COO\text{-}C_4H_9(n)}$. The commencement of smectic phase, i.e., early or late commencement of smectic depends upon the extent of noncoplanarity of a molecule. The oxygen atoms of -COO- group is bumping into the nonbonded sides of the adjacent hydrogen atoms of the aromatic ring which causes considerable strain on the molecule, consequently a twist around the C-O bond occurs forcing phenyl ring and n-butyl group out of the plane of the molecule. Thus, the molecular coplanarity is reduced to some extent as compared to -CH CH- unit containing series-1 and -X. On account of this difference the Sm-I thermal stability of series-Y is the lowest and the smectic phase commences earliest from C_5 and late from C_7 and C_{10} for series-Y, -1 and –X, respectively. Total mesophase length range which is the highest for series-X is attributed to the higher phase length of its nematic mesophase length than a series-1 and -Y, respectively, whose over all thermal resistivity (Sm + N) is relatively more. Thus, the changing behaviors in LC properties and the degree of mesomorphism is attributed to changing molecular rigidity and flexibility for the same homolog from series to series and from homolog to homolog in the same series due to their changing molecular structure by left n-alkoxy group in the same series and the changing right-handed tail group from series to series for the same homolog.

Conclusions

- Presently investigated ester homologous series is partly smectogenic and partly nematogenic whose mesophase length is considerably good and is of middle-ordered melting type.
- The group efficiency order derived on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) total mesophaselength range for smectic and nematic are as under.
- The presence of -CH CH- unit in ester series is generally nematogenic and absence of -CH CH- unit is generally smectogenic or -CH CH-COO- group is nematogenic and -COO- group is smectogenic.

	Smectic:-	
-CH CH-COOC$_4$H$_9$(n) With lateral -OCH$_3$ group	-CH CH-COOC$_4$H$_9$(n) Without lateral group	-COOC$_4$H$_9$(n) Without lateral group
	Nematic:-	
-CH CH-COOC$_4$H$_9$(n) Without lateral group	-CH CH-COOC$_4$H$_9$(n) With lateral -OCH$_3$ group	-COOC$_4$H$_9$(n) Without lateral group
	(ii) **Smectic:-**	
-COOC$_4$H$_9$(n) Without lateral group	-CH CH-COOC$_4$H$_9$(n) With lateral -OCH$_3$ group	-CH CH-COOC$_4$H$_9$(n) Without lateral group
	Nematic:-	
-CH CH-COOC$_4$H$_9$(n) Without lateral group	-CH CH-COOC$_4$H$_9$(n) With lateral -OCH$_3$ group	-COOC$_4$H$_9$(n) Without lateral group
	(iii) (**Smectic + Nematic):-**	
-CH H-COOC$_4$H$_9$(n) Without lateral group	-CH CH-COOC$_4$H$_9$(n) With lateral -OCH$_3$ group Without lateral group	-COOC$_4$H$_9$(n)

- Molecular rigidity and flexibility corresponding to molecular structure are the main operators of mesophase formation.
- A mesomorphism phenomena is very sensitive and susceptible to the molecular structure.
- Presently investigated homologous series may be useful for the study of binary systems and in agriculture field to grow quality fruits and flowers.

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