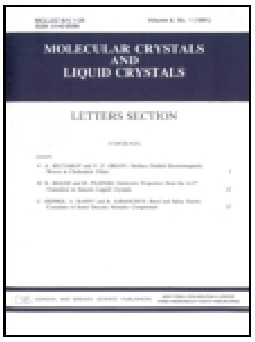

Molecular Crystals and Liquid Crystals

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Mesomorphism Dependence on Molecular Structure

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ABSTRACT
A novel homologous series of liquid crystal (LC) derivatives of general structure: $RO{\cdot}C_6H_4{\cdot}COO{\cdot}C_6H_3{\cdot}OCH_3(ortho)CH = CH{\cdot}COO{\cdot}(n)C_5H_{11}$ was synthesized and studied with a view to understanding the effect of molecular structure on liquid crystal behavior with reference to lateral $-OCH_3$ and terminal end group. Homologous series consists of 12 derivatives (C_1–C_{16}), the first five (C_1–C_5), and the last (C_{16}) members are not liquid crystals and the rest of the homologs (C_6–C_{14}) are enantiotropically smectogenic without exhibition of the nematic phase. The textures of the smectic phases are focal conic fan shaped or batonets of smectic-A or smectic-C. Average thermal stability for smectic is 81.8°C and mesophase length ranges from 9°C to 31°C. Transition curves of a phase diagram (Sm-I and Cr-Sm/I) behave in a normal manner. The Sm-I transition curve exhibits an odd-even effect. Analytical and spectral data support the molecular structures. The series is smectogenic of a middle ordered melting type. LC properties of the present series are compared with structurally similar known homologous series. Transition temperatures were determined by an optical polarizing microscope equipped with a heating stage.

KEYWORDS
Liquid crystals; mesomorphic; nematic; smectic; thermotropic

Introduction

The liquid crystalline (LC) state [1] of matter is well known and has well established its utility [1–8] in the benefit of mankind. The researchers of science and technology have shared their interest to study the LC state in different fields, such as pharmaceutical preparations, electronic devices, agriculture, biological, and/or microbiological activity, medicinal treatment, and medical instruments in addition to the study of chemistry, physics, and biology. We being chemists, synthesize novel compounds through homologous series with a view to understanding the effects of molecular structure on liquid crystal behavior. The proposed investigation of novel compounds can be useful to the scientific and technological research fields as well as to derive novel conclusions about the effects of molecular structure [9–11] on liquid crystal properties which may be useful to predict the type of moiety required to generate a required temperature range. Thus, the proposed investigation aims to provide novel materials to research groups working in other areas of LCs. Several novel homologous series have been reported [12–16] and the present proposed homologous series will consist of two phenyl rings bridged through carboxy group with lateral $-OCH_3$ group as well as –OR and

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-CH=CH-$COOC_5H_{11}$ (*n*) terminal end groups. Results will be discussed in terms of molecular rigidity and flexibility [17–20], including comparison of some LC properties of present novel series with structurally similar other known series.

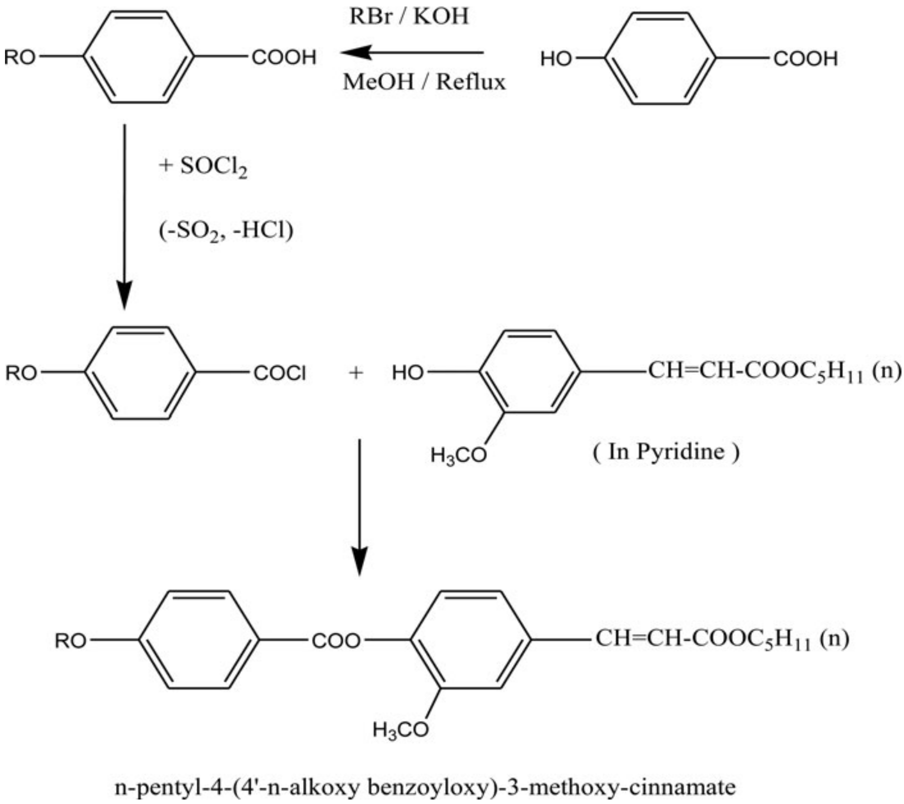
Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents (*R-X*) to provide dimeric 4-*n*-alkoxy benzoic acids through the modified method of Dave and Vora [21]. 4-Hydroxy-3-methoxy cinnamic acid (m.p. 64°C) was esterified by *n*-pentanol by using conc. H_2SO_4 by a usual established method [22]. The ester was very viscous and dense brown liquid, and was purified from distilled *n*-hexane. The yield was 61.5%. Dimeric 4-*n*-alkoxy benzoic acids were individually condensed with 4-hydroxy-3-methoxy *n*-pentyl cinnamate in dry cold pyridine through corresponding acid chlorides [23, 24]. Final products were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures 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*-pentanol, Conc. H_2SO_4, pyridine, 1:1 HCl, $NaHCO_3$, NaOH, anhydrous $CaCl_2$, silica gel, petroleum ether, methyl acetate, and *n*-hexane were used as received, except solvents which were dried and purified prior to use.



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.

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

Compound no.	Molecular formula	Mol.% of C experimental (theoretical)	Mol.% of H experimental (theoretical)
C_1	$C_{23}H_{26}O_6$	68.72 (69.33)	6.11 (6.58)
C_5	$C_{27}H_{34}O_6$	70.66 (71.34)	7.08 (7.54)
C_8	$C_{30}H_{40}O_6$	71.89 (72.55)	7.69 (8.12)
C_{12}	$C_{34}H_{48}O_6$	73.26 (73.88)	8.27 (8.75)

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. Enthalpy-Entropy concept discussed qualitative without performance on DSC scan. 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 ethyloxy homolog derivatives. The IR spectrum of the compound showed 691.18 cm^{-1} polymethylene of -C_5H_{11} group. 759.52 and 840.52 cm^{-1} as p-sub. benzene ring, 1146.45 cm^{-1} as -CO- of alkoxy group, 1243.66, 1599.67, and 1711.11 cm^{-1} confirm -COO- and -CO- of ester group, 1502.55 cm^{-1} confirms aromatic -C=C-, 1030.13 and 1114.95 cm^{-1} confirm trans -CH=CH- group, and 2961.73 cm^{-1} confirms alkyl group.

IR data supports the molecular structure.

IR spectra in cm^{-1} for hexyloxy homolog derivatives. The IR spectrum of the compound showed, 848.78–769.28 cm^{-1} confirm p-sub. benzene ring, 645.03 and 693.13 cm^{-1} confirm polymethylene of –C_6H_{13} group.

2932.76 and 2850.32 cm^{-1} confirm alkyl group, 1697.17, 1607.41, and 1250.20 cm^{-1} confirm –COO- and -CO- group, 1508.35 and 1426.32 cm^{-1} confirm aromatic -C=C-, 1067.55 and 1167.63 cm^{-1} as -CO- of alkoxy group, and 996.13 cm^{-1} confirms trans –CH=CH- group.

IR data supports the structure.

H^1 NMR spectra in ppm for butyloxy and tetradecyloxy derivatives.

Butyloxy. H^1 NMR data in δ ppm (*n*-butyloxy derivative, 400 MHz, $CDCl_3$, standard TMS): −0.9088 (-CH_3 of –C_5H_{11}), 1.4190 (-CH_2- of –C_5H_{11}) 1.5176 (m, -CH_2- of –$COOC_5H_{11}$), 1.7208 (-CH_2- of -OC_4H_9), 3.7613 (-O-CH_3), 3.9421 (-O-CH_2- of -OC_4H_9), 4.1653 (triplet, -CH_2- of –$COOC_5H_{11}$), 6.8906–7.0774 (-O-C_6H_3-CH=CH-CO-), 7.6029 (-CH = of ethylenic -CH=CH-), and 8.0440–8.0795 (p-sub. benzene ring).

The data supports the molecular structure.

Tetradecyloxy. H^1 NMR data in δ ppm (*n*-tetradecyloxy derivative, 400 MHz $CDCl_3$, standard TMS): −0.9066 (-CH_3 of –C_5H_{11}), 1.1862 (-CH_2- of –C_5H_{11}) 1.5239 (m, -CH_2- of –$COOC_5H_{11}$), 1.7392 (-CH_2- of –$OC_{14}H_{29}$), 3.7653 (-O-CH_3), 3.9419 (-O-CH_2- of -O $C_{14}H_{29}$), 4.1706 (triplet, -CH_2- of –$COOC_5H_{11}$), 6.8789–7.0840 (-O-C_6H_3-CH=CH-CO-), 7.6078 (-CH = of ethylenic -CH=CH-), and 8.0557–8.0778 (p-sub. benzene ring).

The data supports the molecular structure.

Mass spectra

Homolog:	Theoretical	Experimental
C_7	482.27	482.0
C_{10}	524.31	524.5

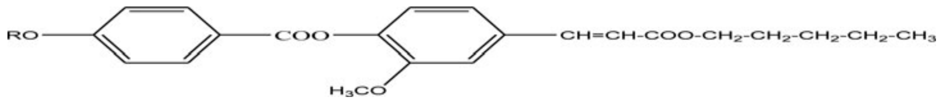
Texture Determination by Miscibility Method:

- C_6 ——→ Smectic – A
- C_8 ——→ Smectic – A
- C_{16} ——→ Smectic – C

Results and Discussion

Transition temperatures (Table 2) determined by an optical polarizing microscope are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group. The methoxy to pentyloxy (C_1–C_5) and hexadecyloxy (C_{16}) derivatives of the series are not liquid crystals. Mesomorphic properties commence from the hexyloxy (C_6) derivative and continue up to the tetradecyloxy (C_{14}) derivative of the series in an enantiotropic manner solely as a smectic phase, without exhibition the nematic phase. Transition curves (Figure 1) are obtained on linking like or related points showing phase behaviors of a series. Transition temperatures as determined by an optical polarizing microscopy were plotted against the number of carbon atoms present in left *n*-alkoxy terminal end group and the like or related points were linked to obtain Cr-I/Sm as well as Sm-I transition curves. Sm-I transition curve initially rises up to octyloxy (C_8) homolog and then descended up to C_{14} homolog after passing through maxima at C_8 homolog. Odd-even effect is observed for the curve. Transition curve (Sm-I) is extrapolated for odd member C_5 [25, 26] to intensify the effect keeping in view of the trend of respective curve. Cr-I/Sm transition curve adopts a zigzag path of rising and

Table 2. Transition temperatures in °C.



Compound no.	*n*-Alkyl chain $R = \text{-}C_nH_{2n+1}$	Sm	N	Isotropic
1	C_1	–	–	120.0
2	C_2	–	–	80.0
3	C_3	–	–	85.0
4	C_4	–	–	74.0
5	C_5	–	–	117.0
6	C_6	60.0	–	73.0
7	C_7	83.0	–	92.0
8	C_8	67.0	–	96.0
9	C_{10}	63.0	–	94.0
10	C_{12}	69.0	–	88.0
11	C_{14}	36.0	–	48.0
12	C_{16}	–	–	66.0

Sm, smectic; N, nematic.

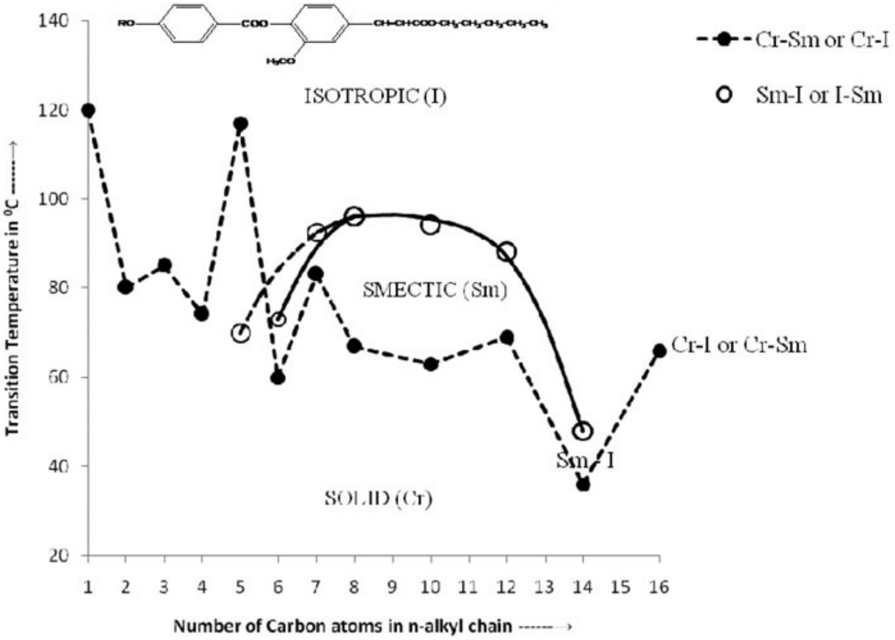


Figure 1. Phase behaviors of series.

falling as shown in phase diagram. Thus, both the curves of a phase diagram behaved in normal expected manner. Curves for odd and even members merge into each other at the octyloxy homolog, and then propagated as a single transition curve from and beyond C_8 homolog. Mesomorphic behaviors of series changes from homolog to homolog depending upon the length of *n*-alkyl chain of left *n*-alkoxy terminal end group keeping the rest of the molecular part unchanged. Disappearance of dimerization of *n*-alkoxy benzoic acids is attributed to the breaking of hydrogen bonding between two molecules of *n*-alkoxy acid by esterification process. Laterally substituted methoxy group and its polarity and polarizability increases length to breadth ratio and the suitable magnitudes of intermolecular lateral attractions as a consequence of resulted favorable molecular rigidity and flexibility; which induces mesophase formation from C_6 homolog to C_{14} homolog in enantiotropic manner. The absence of mesophase formation by C_1–C_5 and C_{16} members of the present novel series is attributed to their high crystallizing tendency arising from unsuitable magnitudes of anisotropic forces of intermolecular end to end and the lateral attractions; which neither allows statistically parallel orientational order of molecules, nor it allows sliding layered arrangement of molecules to float on the surface, but crystal lattices of respective homologs are abruptly breaking and sharply transform into isotropic liquid without passing through LC state, under exposed thermal vibrations, at which molecules under observation randomly orient in all possible directions with high order of disorder or entropy ($\Delta S = \Delta H/T$). However molecules of homologs C_6–C_{14} support lamellar packing of molecules in their crystal lattices at a suitable temperature and continues to higher temperature depending upon favorable magnitudes of molecular rigidity and flexibility until the isotropic temperature. Thus, C_6–C_{14} homologs are smectogenic. The absence of nematic property is attributed to the weaker end to end attractions which hinders the formation of statistically parallel orientational order. The extrapolated transition temperature [27] is much below the isotropic temperature for C_5, and hence it is unrealizable. The exhibition of odd-even effect by Sm-I transition curve is due to the sequential addition of a methylene unit at the left *n*-alkoxy terminal end group. The disappearance of odd-even effect from and beyond C_8 member of a present series is attributed to the flexing or bending or coiling or coupling of the *n*-alkyl chain (C_{10}–C_{14}) with the major axis of the core structure of higher homologs with longer *n*-alkyl chains. Variations in mesomorphic behaviors from homolog to homolog in the same series is due to the changing molecular length by added methylene unit and hence the changing permanent dipole moment across its long molecular axis, dipole–dipole interactions, electronic interactions, dispersion forces, etc. which are changing accordingly. Thus, changing trend varies with changing molecular rigidity and flexibility, which reflected in mesomorphic behaviors and the degree of mesomorphism from homolog to homolog in the same present series. The mesomorphic properties of presently investigated novel series are compared with structurally similar homologous series X [28] and Y [29] as shown below in Figure 2.

Homologous series of present investigation-1 and the structurally similar homologous series-X chosen for comparison are identical with respect to two phenyl rings, central bridge -COO- linking two phenyl rings, the left *n*-alkoxy terminal end group for the same homolog and the part of the right handed terminal end group -CH=CH-COO- linking to $-C_5H_{11}$ group of normal and iso-type structure for all homologs. However series 1 and X differ by laterally substituted highly polar and polarizable $-OCH_3$ group as well as $-C_5H_{11}$ (*n*) and $-C_5H_{11}$ (iso) linked terminal end groups respectively. Homologous series-1 and -Y are identical with respect to two phenyl rings and the left *n*-alkoxy terminal end group for the same homolog, but differs with respect to central bridges -COO- and -CH=CH-COO-, respectively, linking two phenyl rings, and laterally substituted $-OCH_3$ group keeping $-CH{=}CH{-}COO{-}C_5H_{11}$ (*n*) terminal (right sided) end group unchanged for all homologs of both series under discussion, respectively. Thus, LC properties and the degree of mesomorphism will vary with the differing features of each series under comparative study as a consequence of changing magnitudes of anisotropic intermolecular end to end and lateral forces due to molecular polarity, changing polarizability, rigidity, flexibility, permanent dipole moment across the long molecular axis,

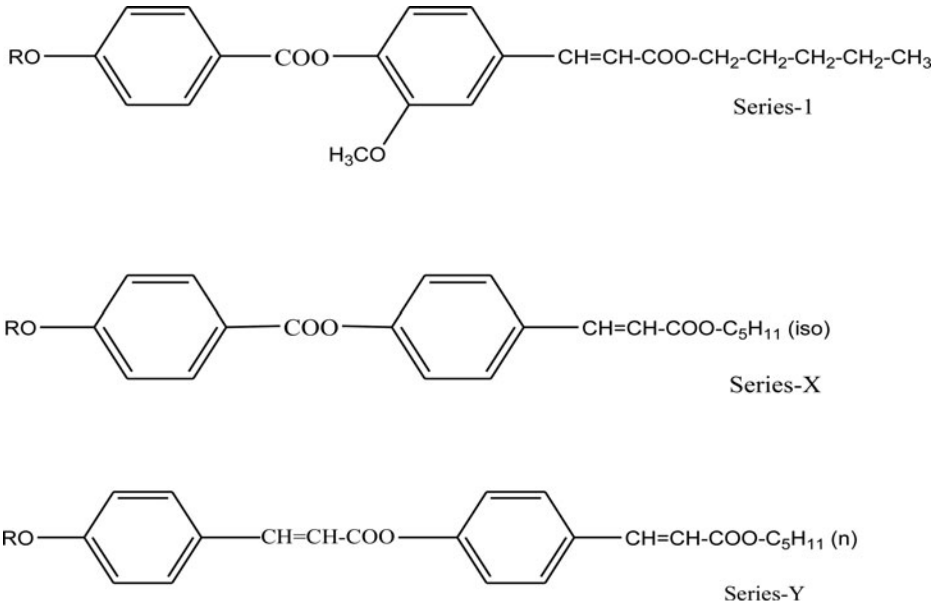


Figure 2. Structurally similar series.

dipole–dipole interactions, electronic interactions, changing dispersion forces, etc. Following Table 3 represents the variation of some LC properties for the series-1, X and Y under comparison.

Table 3 indicates that

- Presently investigated novel series-1 is only smectogenic.
- Homologous series X and Y selected for comparison are smectogenic in addition to nematogenic.
- Smectogenic mesophase commences from C_6 member of the series-1 and Y, where as it commences late from C_8 homolog of the series-X.
- Nematogenic mesophase commences from C_6 and C_5 homolog member of the series X and Y respectively, where as it does not commence till the last C_{16} member of a series-1.
- Smectic thermal stability is the lowest (81.8) for the present series-1 and the highest (122.2) for the series-X among the series under comparison.
- Nematic thermal stability of a series-Y is (169.3) higher than series-X (139.0) whereas series-1 is nonnematogenic.
- Total mesophase length range (Sm + N) of series-Y (21–53) is greater than present series-1 (09–31) and less than a series-X (11–59).
- Odd-even effects of transition curve or curves are observed for the series under comparative study.

The molecules of all the homologous series-1, X and Y under comparison are disaligned at an angle 90° or less than ninety degree on the plane of a surface under the influence of exposed thermal vibrations. The suitable magnitudes of anisotropic forces of intermolecular end to end or/and lateral attractions as a consequence of more or less molecular rigidity and/or flexibility, depending upon individual molecular structure which may arrange themselves either in statistically parallel orientational order or/and as the sliding layers, while floating on the surface. The molecules of homologous series-1, X and Y with originally present lamellar packing of molecules in rigid crystals adopts sliding-layered arrangement in floating condition for the range of temperature depending upon the magnitudes of thermal resistivity against externally exposed thermal vibrations. The molecules of series-1 with their polarizability induced by $-OCH_3$ lateral group, maintains only sliding layered molecular arrangement in floating condition (C_6–C_{14}) but the residual intermolecular forces are inadequately unable to maintain statistically parallel orientational molecular order under floating condition. Thus, series-1 is only smectogenic without exhibition of nematic property. The magnitudes of intermolecular anisotropic attractive forces of series X and Y are sufficient to maintain required molecular arrangement for smectic and nematic mesophases formation; one after another in floating condition, for definite range of temperature, called as degree of mesomorphism

Table 3. Average thermal stability in °C.

Series:	1	X	Y
Smectic-isotropic or smectic-nematic	81.8 (C_6–C_{14})	122.2 (C_8–C_{14})	118.5 (C_6–C_{12})
Commencement of smectic phase	C_6	C_8	C_6
Nematic-isotropic	–	139.0 (C_6–C_{16})	169.3 (C_5–C_{16})
Commencement of nematic phase	–	C_6	C_5
Total mesophaselength range in °C (Sm + N)	09.0 to 31.0 C_7 C_{10}	11.0 to 59.0 C_{16} C_8	21.0 to 53.0 C_5 C_{10}

or mesophaselength range. On comparing intermolecular attraction due polarizability factor, between series-1 and X the polarizability is contributed by only $-OCH_3$ lateral group in series-1, but polarizability factor is strengthened by added molecular polarizability by "iso" linked $-C_5H_{11}$ (iso) group in case of series-X. Therefore, smectic mesophase stabilizes to the highest extent among the series-1, X and Y, and more than series-1; with respect to the effect due to polarizability factor induced by broadening of molecules through lateral substitution. Therefore, residual intermolecular attractions after complete display of smectic mesophase is insufficient to maintain statistically parallel orientational order of molecules in floating condition to exhibit or stabilize nematic phase for series-1, but it is sufficient to induce nematic phase for the molecules of series-X. Thus, smectic and nematic thermal stability for the series-X are more than a series-1. Now on comparing thermal stability of series-1 and Y, the polarizability by lateral substitution, which is absent and the central bridge -COO- replaced by -CH=CH-COO- in series-Y. Therefore, inter molecular width between two molecules of series-Y is closer than the molecules of series-1. Thus, anisotropic forces of inter molecular end to end and lateral to terminal attractions for series-Y are relatively stronger than a series-1 due to longer and stronger -CH=CH-COO- central bridge. Therefore smectic and nematic mesophases are facilitated to stabilize for series-Y, more efficiently than a series-1 in which only smectic phase stabilizes with lower smectic thermal stability. Hence, the energy associated due to differing features of molecules in terms of enthalpy (ΔH) vary from homolog to homolog in same series due to changing length of *n*-alkyl chain and for the same homolog from series to series due to changing right handed terminal end group $-C_5H_{11}$ (n) and $-C_5H_{11}$ (iso), or/and central bridge, linking two phenyl rings. The commencement of smectic phase or in general mesophase occurs from C_5 or C_6 homolog except it commences late from C_8 homolog for smectic (Series-X). Early or late commencement of smectic or mesophase is related with the extent of noncoplanarity of a molecule. Early commencement of mesophase is related with less noncoplanarity of a molecule and the late commencement is related to the more extent of noncoplanarity of a molecule. The molecules of series-X are more noncoplanar than the corresponding same homolog of series-1 and Y. Therefore smectic mesophase commences a little later from C_8 homolog of series-X due to 'iso' linked $-C_5H_{11}$ end group; whereas it commences from C_6 homolog of series-1 and Y because, both series [1 and X] are equally coplanar or say equally noncoplanar. Odd-even effects observed for transition curves are attributed to the alternation of transition temperatures due to sequential addition of methylene unit or units at the left flexible *n*-alkoxy terminal end group for the same homolog from series to series and the homolog to homolog in the same series. Thus, presently investigated homologous series is smectogenic and low melting type, whose mesomorphic phaselength vary between 9°C and 31°C.

Conclusions

- Presently investigated novel homologous ester series of twelve members consisted of two phenyl rings bridged through carboxy group with laterally substituted $-OCH_3$ group and terminally substituted by -OR and $-CH{=}CH{-}COOC_5H_{11}$ (*n*) groups is smectogenic from C_6 to C_{14} and low melting type.
- Group efficiency order derived for smectic and nematic on the basis of, (i) thermal stability (ii) early commencement of LC phase and (iii) mesophaselength range are as under.
  - (i) **Smectic**:-
    $-OC_5H_{11}$ (iso) > $-OC_5H_{11}$ (*n*) > $-OC_5H_{11}$ (*n*)

Without -OCH_3 lateral group Without -OCH_3 lateral group With -OCH_3 lateral group

Nematic:-
-OC_5H_{11} (*n*) > -OC_5H_{11} (iso) > -OC_5H_{11} (*n*)
Without -OCH_3 lateral group Without -OCH_3 lateral group With -OCH_3 lateral group

(ii) **Smectic**:-
-OC_5H_{11} (*n*) = -OC_5H_{11} (*n*) > -OC_5H_{11} (iso)
With -OCH_3 lateral group Without -OCH_3 lateral group Without -OCH_3 lateral group

Nematic:-
-OC_5H_{11} (*n*) > -OC_5H_{11} (iso) > -OC_5H_{11} (*n*)
Without -OCH_3 lateral group Without -OCH_3 lateral group With -OCH_3 lateral group

(iii) **Smectic + Nematic**:-
-OC_5H_{11} (iso) > -OC_5H_{11} (*n*) > -OC_5H_{11} (*n*)
Without -OCH_3 lateral group Without -OCH_3 lateral group With -OCH_3 lateral group

- Suitable magnitudes of anisotropic forces of intermolecular attractions as a consequence of molecular rigidity and/or flexibility can induce mesomorphic behaviors in a substance.
- Molecular rigidity and flexibility are very sensitive and susceptible to molecular structure.
- Sm-I transition temperatures varies between 36°C and 96°C for mesomorphic homologs. Such mesomorphs are useful for the study of binary systems for the devices workable at room temperatures.
- Novel ester homolog derivatives may be useful for better growth of fruits and flowers in the agricultural production and to the scientific community working in application field.

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