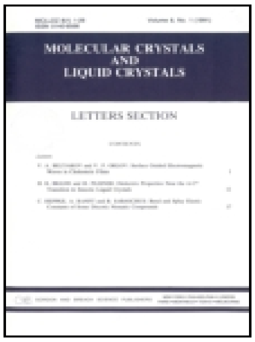

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Mesomorphism dependence on molecular rigidity

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Mesomorphism dependence on molecular rigidity

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ABSTRACT

A novel ester homologous series of thermotropic liquid crystal (LC) has been studied with a view to understanding and establishing the relation between LC property and the molecular structure. The series consists of 11 members, the C_1–C_5 and C_{16} members of the series are nonliquid crystals. LC properties commence from the C_6 homolog and continue up to the C_{14} homolog as enantiotropic nematic and smectic in addition to nematic. Transition temperatures of the homologs were determined by an optical polarizing microscope equipped with a heating stage. Textures of nematic phase are threaded or Schlieren and that of smectic is focal conic of the type-A. Analytical and spectral data confirm the structures of homologs. Thermal stability for nematic is 93 °C and 136 °C, respectively. The N–I and Sm–N transition curves of phase diagram do not exhibit odd-even effect. The N–I transition curve partly behaves in an abnormal manner. The Cr–I and Sm–N transition curves behave in normal manner. The LC behavior of the present series is compared with structurally similar known homologous series.

KEYWORDS
Enantiotropy; mesomorphism; nematic; smectic liquid crystal

Introduction

Liquid crystalline (LC) state of a substance [1] has contributed and inspired scientists and technologists to a very great extent in the benefit of mankind throughout the world [2–5]. Therefore, researchers working in LCs with different aims and objectives and disciplines require novel LC substances to extend and continue their research activities. Therefore, we being chemists, have planned to synthesize novel substances with a view to understanding the effect of molecular structure on LC properties and to establish the relation between them [6–8] through varying molecular rigidity and, or flexibility [9–12] of different moiety and changing terminal or/and lateral or central bridge or bridges or number of phenyl rings or cyclic other ring, etc. Many LC series have been reported [13–16] to date. The present novel series consists of two phenyl rings bonded through –COO– central bridge and *n*-alkoxy varying as well as *n*-alkyl (hexyl) unchanging left and right terminal end groups. LC properties are evaluated and compared with structurally similar other known series.

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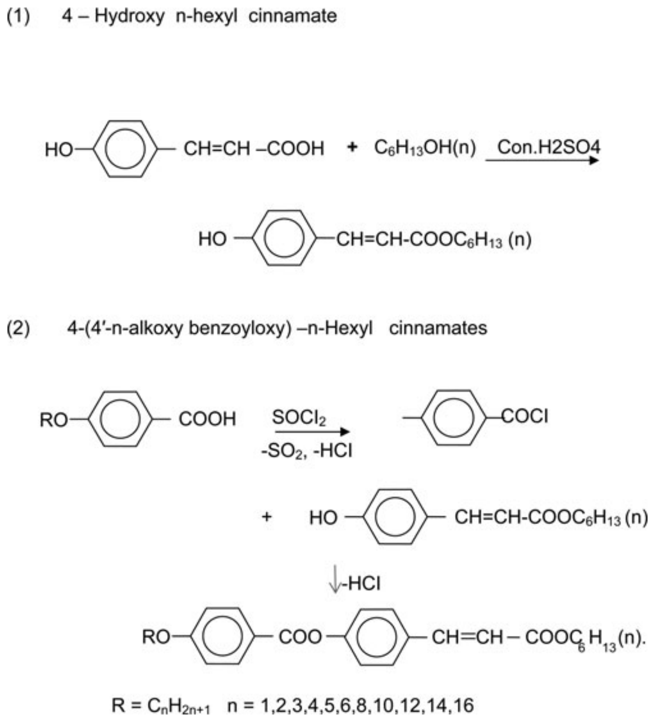


Scheme 1. Synthetic route to the series

Experimental: (Synthesis)

- *p*-*n*-Alkoxy benzoic acids were prepared by the modified method of Vora and Dave(1970) [17], using suitable alkylating agents (R-X)
- *p*-*n*-Alkoxy benzoyl chlorides were prepared by refluxing the corresponding alkoxy benzoic acids with freshly distilled [18] thionyl chloride.
- *p*-Hydroxy *n*-hexyl cinnamate was prepared by reacting *p*-hydroxy cinnamic acid with freshly distilled and dry *n*-hexyl alcohol in presence of concentrated sulfuric acid [19].
- Acid chlorides were directly condensed [Doshi and Lohar (1992,1993)] [12] with the *p*-*n*-hydroxy *n*-hexyl cinnamates dissolved in ice-cooled dry pyridine in portions with stirring reaction mixture. Products were decomposed, filtered, washed, dried, and purified, until the constant transition temperatures are 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. are 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 below in Scheme 1. The elemental analysis is shown in Table 1.

Characterization

Analytical data support the title homologous series 4-(4’-*n*-alkoxy benzoyloxy) *n*-propyl cinnamates.

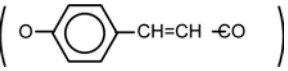
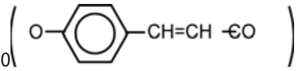
Result and discussion

Novel homologs series of vinyl ester is formed by condensing dimeric 4-*n*-alkoxy benzoic acids and common component a 4-hydroxy *n*-hexyl cinnamate. The dimerization of *n*-alkoxy

Table 1. Elemental analysis.

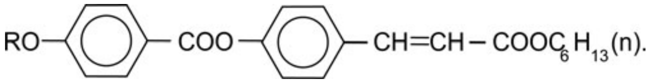
Sr. No.	$R = n$-alkyl Chain	Molecular Formula	Calculated% C	Calculated% H	Observed% C	Observed% H
1	Butyl	$C_{26}H_{32}O_5$	73.58	7.54	73.40	7.59
2	Hexyl	$C_{28}H_{36}O_5$	74.33	7.96	74.19	7.99
3	Decyl	$C_{32}H_{44}O_5$	75.59	8.66	75.49	8.77
4	Tetradecyl	$C_{36}H_{52}O_5$	76.59	9.21	76.51	9.35
Textured by miscibility method Nematic: Threaded – C6 Smectic: Smectic-A – C_8, C_{10}, C_{14}						

Homolog	IR Spectra (cm^{-1})
Decyl	2920.0, 2850.6, and1396.4 cm^{-1}→Confirms alkyl group 1685.7, 1257.5, and 1064.6 cm^{-1}→Confirms –COO- group 1168.8 cm^{-1}→Confirms ether 983.6 cm^{-1}→Confirms trans –CH=CH– group 844.8 cm^{-1}→Confirms *p*-sub. benzene ring 717.5 cm^{-1}→Confirms polymethylene of $C_{10}H_{21}$
Tetradecyl	2920.0, 2850.6, and 1396 cm^{-1}→Confirms alkyl group 1685.7, 1168.8, and 1064.6 cm^{-1}→Confirms –COO- group 1396.4 and1303.8 cm^{-1}→Confirms gem dimethyl group 1257.3 cm^{-1}→Confirms ether 972.3 cm^{-1}→Confirms trans –CH=CH- group 844.8 cm^{-1}v→Confirms *p*-sub. benzene ring 717.5 cm^{-1}→Confirms polymethylene of $C_{14}H_{29}$

Homolog	**NMR Spectra δ(ppm)**
Hexyl	0.911 ($-C\underline{H}_3$ of $-C_6H_{13}$) 1.370 ($-C\underline{H}_2$ of $-C_6H_{13}$) 1.807 ($-O-CH_2-C\underline{H}_2$ of $-C_6H_{13}$) 4.021 ($-O-C\underline{H}_2$ of $-C_6H_{13}$) 6.948 and 6.905 (Two *p*-sub. benzene ring) 8.028 and 8.071 7.258 
Octyl	0.890 ($-C\underline{H}_3$ of $-C_8H_{17}$) 1.308 ($-C\underline{H}_2-$ of $-C_8H_{17}$) 1.809 ($-O\ CH_2-C\underline{H}_2$ of $-C_8H_{17}$) 14.022 ($-O-C\underline{H}_2$ of $-C_8H_{17}$) 16.905 and 6.948 (Two *p*-sub. benzene ring) 8.025 and 8.068 7.260 

benzoic acids disappears on esterification process. C_1–C_5 and C_{16} homologs are nonliquid crystals. C_6 homologs are only enantiotropically nematogenic and C_8–C_{14} homologs are enantiotropically smectogenic in addition to nematogenic. Transition temperatures (Table 2) of the homologs were plotted versus the number of carbon atoms present in *n*-alkyl chain bonded to first phenyl ring through oxygen atom. Smooth curves are drawn through like or related points, which form Cr–I/M, Sm–N, and N–I transition curves showing phase behaviors of series in a phase diagram (Fig. 1). Cr–M/I transition curve follows a zigzag path of rising and falling manner with overall descending tendency. Sm–N transition curve commences with maxima and then descended as series is ascended with negligible deviation. N–I transition curve initially falls from C_6 to C_{14} through C_{12} homologs. Thus, Cr–I/M and Sm–N transition curves behave abnormally for its EDF path in realistic manner. However, the hypothetical

Table 2. Transition temperatures.



Series-: 4-(4′-*n*-alkoxy benzoyloxy) *n*-hexyl Cinnamates

Compound No.	*R* = *n*-alkyl group	Transition temperature in °C		
		Smectic	Nematic	Isotropic
1.	Methyl C_1	–	–	170.0
2.	Ethyl C_2	–	–	172.0
3.	Propyl C_3	–	–	119.0
4.	Butyl C_4	–	–	145.0
5.	Pentyl C_5	–	–	125.0
6.	Hexyl C_6	–	104.0	158.0
7.	Octyl C_8	96.0	107.0	156.0
8.	Decyl C_{10}	91.0	103.0	115.0
9.	Dodecyl C_{12}	72.0	78.0	128.0
10.	Tetradecyl C_{14}	75.0	85.0	125.0
11.	Hexadecyl C_{16}	–	–	88.0

unrealistic path represented by ET as a part of N-I curve is an ideal expected curve through which ideal descending behavior represented. Therefore, area within the EDT, indicates magnitudes of abnormality in mesomorphic behavior. N-I transition curve is extrapolated [20–22] to C_4 homolog to predict its probable transition temperature. Similarly, Sm-N transition curve is also extrapolated to C_6 and C_{16} homolog to predict their transition temperature. N–I and Sm–N transition curves fails to exhibit odd-even effect.

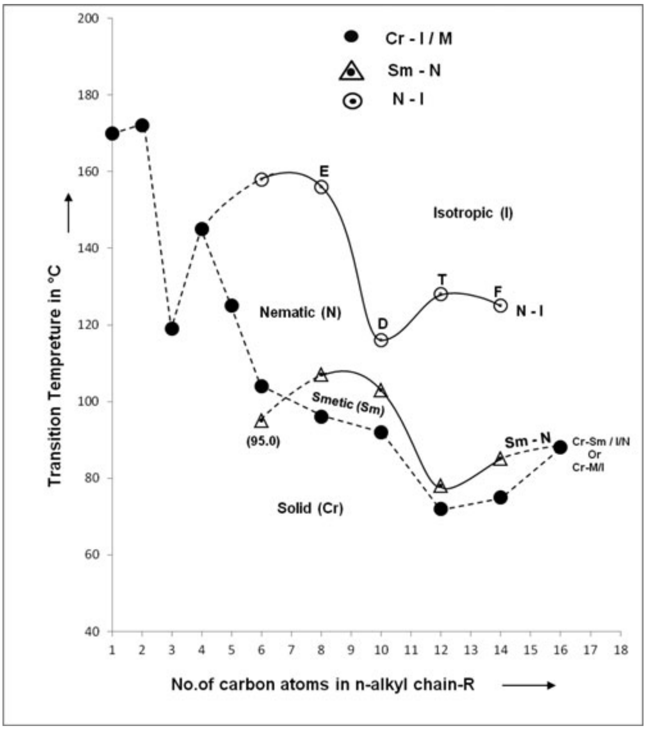


Figure 1. Phase behavior of 4-(4′-*n*-alkoxy benzoyloxy) *n*-hexyl cinnamates.

Disappearance of dimerization of *n*-alkoxy benzoic acids is due to the breaking of hydrogen bonding between two molecules of corresponding *n*-alkoxy acids by esterification process. The absence of any sort of mesophases formation by C_1–C_5 and C_{16} is attributed to their inability to withstand exposed thermal vibration arising from unsuitable magnitudes of anisotropic forces of intermolecular end-to-end attraction, which facilitate breaking of crystal lattices abruptly. Therefore, a nonmesomorphic homolog sharply transform into isotropic state without passing through LC state. At this stage, molecules under microscopic observation randomly orient in all possible direction with high order of disorder or entropy ($\Delta S = \Delta H/T$). On super cooling the isotropic melt, of nonmesogenic homologs, which transform into crystalline solid state without exhibition of monotropic LC state due to their high crystallizing tendency arising from unsuitable magnitudes of molecular rigidity and flexibility induced by low dipole-dipole interactions and low dispersion forces by interaction between instantaneous dipoles produced by the spontaneous oscillation of electron clouds of the molecules which can induce high crystallizing tendency hindering mesophase formation in monotropic condition. The molecules of the C_6–C_{14} members of the series resisted exposed thermal vibration, which disalign at an angle 90° or less than 90° with the floating surface. The suitable magnitudes of end-to-end intermolecular attractions as molecules make possible to arrange the molecule to float with statistically parallel orientational molecular order for C_6–C_{14} homologs via smectic (except C_6) phase from solid state. The molecule of C_8–C_{14} homologs exhibit smectic phase through their occupancy of sliding layered arrangement of molecules for definite range of temperatures depending upon their angle of disalignment with floating surface offering resistivity toward exposed thermal vibrations. Thus, smectic and/or nematic mesophase formation occur. The disappearance of odd-even effect in N-I and Sm-N transition curves is attributed to the late commencement of mesophase formation due to presence of longer (C_6) *n*-alkyl chain at the tail end group and C_1–C_5 or C_6–C_{16}, shorter or longer respectively *n*-alkyl chain at the left *n*-alkoxy end groups which may coil or bend or flex or couple to lie with the principal axis of the core structure inducing uncertainty in the status of molecular length, permanent dipole moment across the long molecular axis, dispersion forces, molecular rigidity and flexibility, polarity, and polarizability, etc. Interferes to fulfill the requirement to induce mesomorphism and degree of mesomorphism to the fullest extent. Thus, observe abnormality (C_{10}–C_{12}) in N-I transition temperature and transition curve behaviors can be assigned as explained in above para. The variations in mesomorphic (LC) properties from homolog to homolog in presently investigated novel series is attributed to the sequentially added methylene unit or units at the left *n*-alkoxy terminal end group keeping -C_6H_{13}(n) tail group unchanged throughout entire series. Thus, present series is partly smectogenic and partly nematogenic with middle-ordered melting type. The extrapolated N–I transition curve to C_4 homolog merges into isotropic temperature of C_4 which approves nonliquid crystal behaviors of C_4 member. Similarly, nonmesomorphicity of C_{16} homolog is approved by extrapolation of Sm–N transition curve to C_{16}. The extrapolation of Sm–N transition curve to C_6 homolog predicts monotropic transition temperature for smectic as 95 °C which is not realizable in actual practice due to its high crystallizing tendency arising for the reasons as discussed earlier in the result and discussion part this manuscript.

LC properties of present homologous series are compared with structurally similar other known homologous series-X [23] as shown in the following figure (Fig. 2).

Homologous series-X chosen for comparison and the presently reported homologous series-1 are identical with respect to two phenyl rings, tail group, $-CH=CH-COOCH_{13}$(n) and left *n*-alkoxy group for the same homolog from series to series. However, both series under

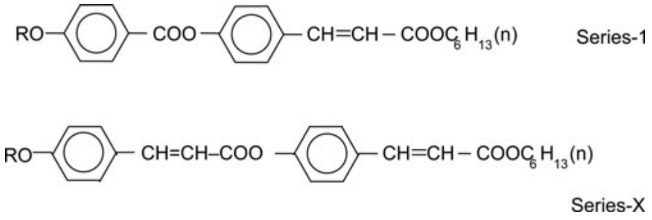


Figure 2. Structurally similar series.

comparative study differ with respect to central bridge –COO–/and –CH=CH–COO– linking first and second phenyl rings. Therefore, differing features in LC properties and the degree of mesomorphism under comparison can be attributed to the molecule rigidity contributed by carboxy (–COO–) and vinyl carboxy (–CH=CH–COO–) central bridges.

Following Table 3 represents some LC properties of the present series-1 as compared to homologous series-X which differs with respect to molecular rigidity through their central bridges, viz., –COO– and –CH=CH–CH-COO–

- Homologous series-1 and -X are smectogenic in addition to nematogenic with different mesophase length range
- Thermal stabilities for smectic and nematic for series-X is relatively higher than present series-1.
- Smectic and nematic mesophases commences earlier for series-X (C_7 and C_3) than present series-1 (C_8 and C_6).
- Maximum total phase length range is exactly same of both series-1 and -X, but minimum values differs.
- Odd-even effect is not exhibited by Sm–N and N–I transition curves of series-1 but it is exhibited by series-X under comparison.

Series-1 and -X have their differing part at central linking –COO– and–CH=CH–COO. This difference bring in with it, other differences in the display of molecular forces. The overall length of the molecules of series-1 is decreased as compared to series-X. Such difference causes differences in length-to-breadth ratio. Simultaneously, the pi electron density due to the delocalized electrons on account of added double bond which is absent for the series-1 and present for series-X which affects the overall molecular polarizability. Thus, shorter length and lesser polarizability of series-1 would cause the LC properties to undergo change for the same homolog from series-1 to series-X. In all other respects except the central bridge which is –CH=CH–COO– in case of series-X and –COO– in case of series-1 under comparative study, both series are closely similar, but central bridge vinyl carboxylate –CH=CH–COO– has greater length and causes more noncoplanarity due to the twist obtained as the oxygen

Table 3. Average thermal stabilities.

Series	1 –COO–	X –CH=CH–COO-
Smectic–isotropic	93.25	179.4
Or smectic-nematic	(C_8–C_{15})	(C_7–C_{14})
Commencement of smectic phase	C_8	C_7
Nematic-isotropic	136.4	190.9
Commencement of nematic	(C_6–C_{14})	(C_3–C_{16})
Phase	C_6	C_3
Total mesophase length in °C (Sm + N)	24—60	10–60
Cn_1 Cn_2	C_{10} C_8	C_3 C_{14}

atoms of the vinyl carboxylate group bump into the nonbonded adjacent hydrogen atoms of the aromatic phenyl ring. On account of these differences, the Sm–N and N–I thermal stability of present series 1 are lower than the series-X. Moreover, enhanced molecular length of –CH=CH–COO– unit and length which increases molecular rigidity and lateral attractions as compared to –COO– which do not link the phenyl rings through multiple bond or hydrogen-bonded ring system. Consequently the stereochemistry of the molecules, results in less thermally stable mesophase or mesophases. Thus, the difference of molecular rigidity, keeping the molecular flexibility intact, causes variations in LC properties for the same homolog from series-1 to series-X.

Conclusions

- Homologous series 4(4′-*n*-alkoxybenzoyloxy) *n*-hexyl cinnamates is partly smectogenic and partly nematogenic and middle-ordered melting type.
- The group efficiency order derived for smectic and nematic on the basis of (i) thermal stability (ii) early commencement of mesophase, and (iii) total mesophase length range with respect to central bridge are as under.

(i) **Smectic:** –CH=CH–COO– > –COO–
  i. **Nematic:** –CH=CH–COO– > –COO–
  ii. **Smectic:** –CH=CH–COO– > –COO–
  iii. **Nematic:**–CH=CH–COO– > –COO–
  iv. (iii) **Sm + Nm:** –CH=CH–COO– > –COO–

- Mesomorphic tendency of a substance is dependent upon combined effects of molecular rigidity and flexibility of a molecular structure.
- LC properties of a substance are very sensitive and susceptible to molecular structure.
- Present investigation may be useful for the study of binary systems between 72.0 °C and 115.0 °C for the devices to be operated between 52 °C and 95 °C. Also, it may be useful for agricultural products growth.

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