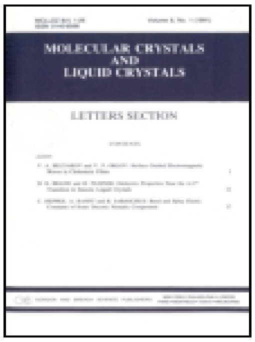

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Mesomorphism dependence on lateral substitution and central bridge

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ABSTRACT
A novel ester homologous series was synthesized and studied with a view to understanding and establishing the effects of molecular structure on liquid crystal properties with a common laterally substituted –OCH3 group and changing terminal groups. The novel series consists of twelve members. The C_1 to C_3 members are not liquid crystals and the rest of the members C_4 to C_{16} are smectogenic without exhibition of nematic character. Textures of smectic phase are focal conic fan shaped of the type A or C. The transition temperatures and textures of smectic mesophases were observed through hot stage polarizing microscopy (POM). The transition curves (Cr-I or Cr-M and Sm-I) behaved in normal manner. Analytical and spectral data support the molecular structures. Average thermal stability for smectic is 77.25°C and smectogenic mesophase ranges from 15°C to 33°C. Liquid crystal properties of the present series are compared with structurally similar homologous series. Thus, the series is smectogenic only with three homologs nonmesogenic.

KEYWORDS
Liquid crystal; mesogenic; monotropy; nematic; smectic

Introduction

Study of mesomorphism and the degree of mesomorphism are important from an application's point [1–4] of view in both thermotropic and lyotropic liquid crystals since their discovery in 1888 [5]. The present investigation is planned to synthesize novel ester [6–9] derivatives of thermotropic liquid crystals with a view to understanding the effects of molecular structure [10,11] on liquid crystal properties by selecting a −OCH3 lateral group bonded at the ortho position of the central bridge linking two phenyl rings and a para-substituted −OR and $-CH{=}CH-COO-C_6H_{13}$ (n) end groups. The steric hindrance and polarizability lowers transition temperatures, which may be useful to the researchers working specially in the applications of LC materials in LC devices workable at low temperatures or room temperature. The LC behaviors of the proposed novel substances will be explained on the basis of molecular rigidity and flexibility [12–16].

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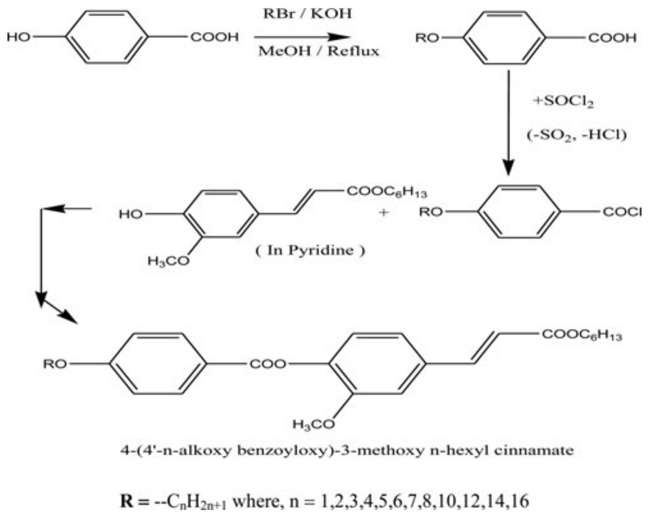
Experimental

Synthesis

4-Hydroxy 3-methoxy cinnamic acid (m.p. 64°C, yield 67%) was esterified by n-hexenol by using conc. H2SO4 by a usual established method [17]. The ester was very viscous and dense brown liquid, which was purified from distilled n-hexane. The yield was 65.3%. 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 [18]. Dimeric 4-n-alkoxy benzoic acids were individually condensed with 4-hydroxy, 3-methoxy n-hexyl cinnamate in dry cold pyridine through the corresponding acid chlorides [19]. 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.



Scheme 1. Synthetic route to the series.

The chemicals required such as 4-hydroxy benzoic acid, MeOH, KOH, alkyl halides (R-X), thionyl chloride, 4-hydroxy,3-methoxy, cinnamic acid (Ferulic acid), n-Hexenol, Conc. H2SO4, 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.

Characterization

Representative homologs of the series were selected for characterization of structure by elemental analysis, IR spectra, and 1H NMR spectroscopy.

Microanalysis was performed on a Perkin Elmer PE 2400 CHN analyzer. IR spectra were recorded on Perkin Elmer spectra GX. 1H NMR spectroscopy performed were recorded on Bruker spectrometer using $CDCl_3$ as solvent. The mesomorphic properties were investigated using a hot stage polarizing microscope.

Analytical data

Elemental analysis for ethyloxy, pentyloxy, decyloxy, and tetradecyloxy derivatives

IR spectra in cm-1 for hexyloxy and dodecyloxy homolog derivatives

Hexyloxy

The IR spectrum of the compound showed 765.47 cm-1 polymethylene of −C6H13 group. 848.26 cm-1 as p-sub. benzene ring, 1131.55 cm-1 as −CO− of alkoxy group, 1244.24, 1508.86, 1634.08, and 1706.13 cm-1 Confirms −COO− of ester group, 928.89 and 995.57 cm-1 Confirms trans −CH= CH− group, 2878.06 and 3097.77 cm-1 Confirms alkyl group.

IR supports the structure

Dodecyloxy

The IR spectrum of the compound showed 686.16 cm-1polymethylene of −C6H13 group. 748.11 and 832.78 cm-1 as p-sub. benzene ring, 1132.73 and 1217.74 cm-1 as −CO− of alkoxy group, 1298.61, 1576.69, and 1672.75 cm-1 Confirms −COO− of ester group, 941.51 and 1094.44 cm-1 Confirms trans −CH=CH− group, 3172.74 and 3229.18 cm-1 Confirms alkyl group.

IR supports the structure

^{1}H NMR spectra in ppm for hexyloxy and decyloxy derivatives

Hexyloxy

H1 NMR data in δ ppm (n-hexyloxy derivative, 400 MHz, CDCl3, standard TMS): 0.807 (−CH3 of −C6H13), 1.2516 & 1.1745 (−CH2 of − C6H13), 1.7393 (−OCH2−CH2 of − C6H13), 3.7641 (−O−CH3), 3.9579 (−O−CH2- of −C6H13), 7.0841 & 7.0684 (−O−C6H4−CH=CH−CO−), 8.0559 & 8.0781 (p-sub. Benzene ring).

The data supports the molecular structure

Decyloxy

H1 NMR data in δ ppm (n-decyloxy derivative, 400 MHz CDCl3, standard TMS): 0.8101 (−CH3 of −C10H21), 1.2356 (−CH2 of −C10H21), 1.759 (−OCH2−CH2 of −C10H21), 3.8083 (−O−CH3), 3.9598 (−O−CH2- of − C10H21), 7.0034 and 7.0074 (−O−C6H4−CH=CH−CO−), 8.058 and 8.08 (p-sub. Benzene ring).

The data supports the molecular structure

Textures of mesophase by miscibility method

- Octyloxy homolog——→ Smectic - A
- Hexyloxy homolog——→ Smectic - A
- Hexadecyloxy homolog ——→ Smectic - C

Mass spectra

Homolog:	Theoretical	Experimental
C_4	454.56	454
C_{12}	566.36	566.05

Table 1. Elemental analysis for ethyloxy, pentyloxy, decyloxy and tetradecyloxy derivatives.

Compound no.	Molecular formula	Mol.% of C Experimental (Theoretical)	Mol.% of H Experimental (Theoretical)
C_2	$C_{25}H_{30}O_6$	69.92 (70.40)	6.82 (7.09)
C_5	$C_{28}H_{36}O_6$	70.11 (71.77)	7.27 (7.74)
C_{10}	$C_{33}H_{46}O_6$	72.69 (73.57)	7.79 (8.61)
C_{14}	$C_{37}H_{54}O_6$	73.88 (74.71)	8.27 (9.15)

Results and discussion

4-Hydroxy-3-methoxy –n-hexyl cinnamate (very viscous and dense brown liquid, yield 65.3%) is a nonliquid crystal component. However, mesomorphism is induced by linking it with 4-n-alkoxy benzoic acids, from C_4 member of a series to last hexadecyloxy (C_{16}) member. Transition temperatures of esters formed have relatively lower than the corresponding dimerized n-alkoxy aromatic acids. C_1 to C_3 members are nonmesomorphic, C_4 is monotropic smectic, C_5 to C_{16} members are enantitropically smectic. Transition temperatures (Table 2) as 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. Transition curves are obtained on linking like or related points showing phase behaviors of a series. Solid-mesomorphic or isotropic transition curve partly adopt a zigzag path of rising and falling tendency as series is ascended with overall descending tendency. Smectic-Isotropic (or vice versa) transition curve gradually rises, passes through maxima at the decyloxy (C_{10}) homolog and then descended as series is ascended. Thus, Cr-M or Cr-I and Sm-I transition curve behaved in normal manner in a phase diagram (Fig. 1). Sm-I transition curve exhibited odd-even effect. Curves (Sm-I) for odd and even members are merging into each other at octyloxy (C_8) derivative of a series and then the Sm-I transition curve prolonged from and beyond C_8 homolog as a single transition curve. Analytical and spectral data supported molecular structure. Nematic mesophase formation is totally absent. The mesogenic properties vary from homolog to homolog in present series. Thus, present series is smectogenic with an average thermal stability is 77.25°C and mesogenic phase-length vary between 15°C and 33°C. The isotropic temperatures of liquid crystalline homologs are between 64°C and 107°C, hence it is a low-melting type of series.

Linking of dimerized n-alkoxy benzoic acids with 4-hydroxy-3-methoxy-n-hexyl cinnamate increases length to breadth ratio, polarity, and polarizability of molecules, end-to-end

Table 2. Transition temperatures in °C.

Compound No.	n-Alkyl group R = −CnH2n+1	Sm	N	Isotropic
1	C_1	–	–	107.0
2	C_2	–	–	106.0
3	C_3	–	–	87.0
4	C_4	(58.0)	–	66.0
5	C_5	41.0	–	64.0
6	C_6	45.0	–	60.0
7	C_7	50.0	–	74.0
8	C_8	58.0	–	91.0
9	C_{10}	88.0	–	107.0
10	C_{12}	51.0	–	84.0
11	C_{14}	38.0	–	68.0
12	C_{16}	38.0	–	70.0

() indicates monotropy.

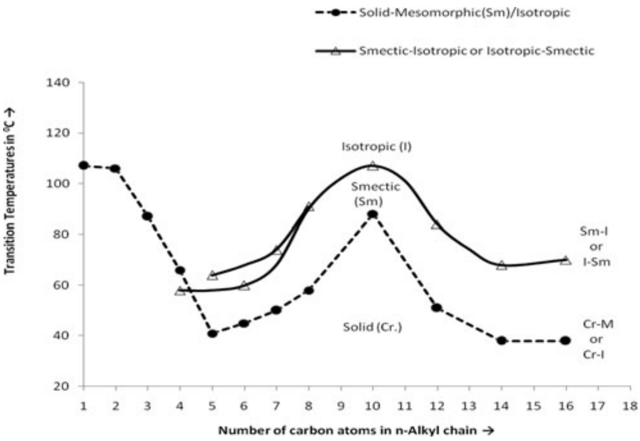


Figure 1. Phase behaviors of series.

and lateral attractions, permanent dipole moment across the long molecular axis, etc., as a result of yielded molecular rigidity and flexibility. Therefore, magnitudes of anisotropic forces of intermolecular attractions attain suitability to induced mesophase (Sm) from butyloxy homolog (C_4) to hexadecyloxy (C_{16}) homolog. The lowering of transition temperatures in comparison with corresponding n-alkoxy acids and disappearance of their dimerization is attributed to the breaking of hydrogen bonding between two molecules of aromatic acids by esterification process. Thus, smectogenic mesophase commences from butyloxy homolog derivative. Nonliquid crystalline behaviors of methoxy, ethoxy, and propyloxy (C_1–C_3) homologs is attributed to their high crystallizing tendency arising from unsuitable magnitudes of molecular rigidity and flexibility induced by low dipole-dipole interactions and low magnitudes of dispersion forces by the interactions between instantaneous dipoles produced by the spontaneous oscillations of electron clouds of the molecules. Thus, the C_1 to C_3 homologs are unable to resist exposed thermal vibrations. Hence, the crystal lattices of molecules are abruptly breaking and sharply transformed into the isotropic liquid without passing through an intermediate liquid crystalline state. Thus, exhibition of high crystallizing tendency precludes showing up of nematic property even in a monotropic condition. The exhibition of the smectic mesophase from and beyond the C_4 homolog is attributed to the layered arrangement of molecules through their lamellar packing. On cooling of the isotropic melt of the C_4 homolog a monotropically induced smectic phase arises, and the rest of the homologs (C_5 to C_{16}) exhibit an enantiotropic smectic phase. The textures of the smectic phase are focal conic fan shaped of the type smectic A or C. The terminal attractions are not sufficiently strong enough to induce a nematic phase because of the overall molecular polarizability, including polarizability due to laterally substituted $-OCH_3$ group. The odd-even effect observed for the smectic-isotropic (or vice versa) transition curve is due to alternation of transition temperatures for C_4, C_5, C_6, and C_7 homologs. The disappearance of the odd-even effect from and beyond the octyloxy (C_8) homolog is attributed to the longer n-alkyl chains, which may coil, bend or flex or couple to lie with major axis of the core structure of the molecules. The variations in mesomorphic properties for homolog to homolog in the same series is due to the sequential and progressive addition of a methylene unit in the terminal chain. The low thermal stability (77.25°C) and mesophase lengths (15°C–33°C) is attributed to the low resistivity of the molecules toward exposed thermal vibrations. The liquid crystal properties of presently investigated novel homologous series-1 are compared with the structurally similar known homologous series-X [20] and -Y [21] as mentioned below in Fig. 2.

Homologous series-1 of present investigation and the homologous series-X and -Y chosen for comparison are identical with respect to two phenyl rings, right-side terminal end group $-CH{=}CH-COOC_6H_{13}(n)$ and left terminal end group –OR for the same homolog from series to series. However, a homologous series-1 differs from series-X and -Y with respect to laterally substituted $-OCH_3$ polar group which induces polarizability factor and steric hindrance in addition to length-to-breadth ratio and the ratio of the molecular polarizability etc., which differs considerably. Homologous series-1 and -X are identical with respect to central bridge –COO–, but it differs from series-Y in which central bridge –COO– is replaced by $-CH{=}CH-COO-$. Thus, liquid crystal properties and the degree of mesomorphism depend upon the differing features of series-1, -X, and -Y as a consequence of changing magnitudes of molecular rigidity and flexibility. Table 3 represents some properties related to liquid crystal state as under.

Table 3 indicates that,

- Homologous series-1 is only smectgenic, whereas series-X and -Y are nematogenic in addition to smectogenic mesophase formation.
- Smectogenic character commences earlier from C_4 homolog in a present series-1, whereas it commences late from C_8 and C_7 homologs in series-X and -Y, respectively.
- Nematic mesophase commences from C_6 and C_3 homolog in series-X and -Y, respectively, whereas it does not commence till the last homolog (C_{16}) of a present series-1.
- Mesomorphic phaselength range of present series is the shortest (10°C–33°C), whereas it is the highest (10°C–60°C) for series-Y and 24°C–60°C for series-X.
- Smectic thermal stability gradually increases from series-1 to series-X to series-Y.
- Nematic thermal stability is zero for series-1 and it increases from series-X (136.4°C) to Y (190.9°C).
- Odd-even effects are exhibited by transition curves in a phase diagrams of series-1 and -Y, whereas it is absent for the curves of series-X.

Homologous series-1 of present investigation bears laterally substituted $-OCH_3$ group at the ortho position to central –COO– group, whereas series-X and -Y are linear lath like. Therefore, intermolecular distance between any two molecules of series-1 is wider than the series-X and -Y under identical condition. Enhancement in intermolecular distance can cause

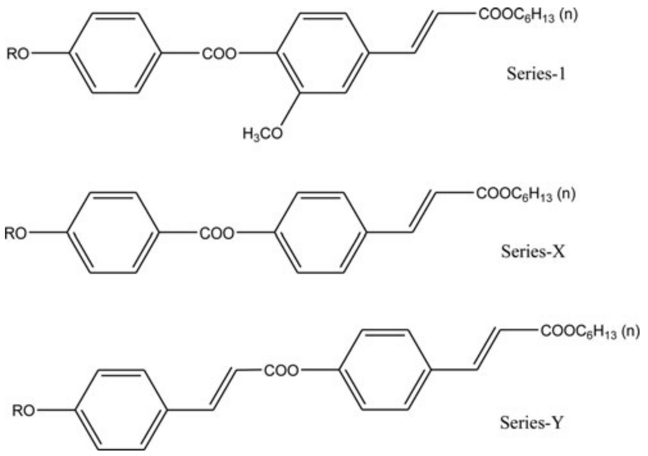


Figure 2. Structurally similar series.

Table 3. Relative thermal stability in °C.

Series:→	1	X	Y
Smectic-isotropic or Smectic-nematic	77.25 (C_5–C_{16})	93.2 (C_8–C_{14})	179.6 (C_7–C_{14})
Commencement of Smectic phase	C_4	C_8	C_7
Nematic-isotropic	–	136.4 (C_6–C_{14})	190.9 (C_3–C_{16})
Commencement of nematic phase	–	C_6	C_3
Mesophaselength (Sm +N) in °C	15–33	24–60	10–60

reduction in anisotropic forces of intermolecular end-to-end and lateral attractions on one hand and at the same time, the intermolecular attractions are raised by increasing molecular polarizability through laterally substituted $-OCH_3$ polar group in case of molecules of series-1 as compared to the corresponding molecules of series-X and -Y. Thus, two opposing forces are operated at a time for the same reason. Therefore, the resultant or effective intermolecular attractions depend upon the predominancy or effectiveness of two opposing effects operated at a time. The molecules of series-X and -Y being linear and lath like without any laterally substituted group, obviously undergo stronger intermolecular anisotropic forces of end-to-end and lateral attractions than corresponding homolog of series-1. Thus, from the values of thermal stabilities as indicated in Table 3 suggests that the increase in the intermolecular distance by the presence of lateral $-OCH_3$ group in case of series-1 predominates and surpasses the effect due to polarizability factor for the same homolog from series to series. Thus, the thermal stability and mesophase length range of series-1 are lower than the series-X and -Y. The highest value of thermal stability and mesophase length of series-Y is attributed to the presence of $-CH=CH-COO-$ as central and terminal group which increases molecular length and conjugated double bond as compared to series-1 and -X as these series contain shorter $-COO-$ central group in place of $-CH=CH-COO-$ central group. Hence, the length to breadth ratio is favorable more for the molecules of series-Y than the series-1 and -X. Thus, suitable magnitudes of anisotropic forces of intermolecular attractions resist or withstand against exposed thermal vibrations for longer degree of mesomorphism to stabilize and facilitate smectic and nematic mesophases one after another in case of series-X and -Y. The steric hindrance caused by $-OCH_3$ lateral group which hinders the stabilization of nematic mesophase formation and permits only the stabilization of focal conic fan-shaped mesophase formation of smectic A or C type due to originally present lamellar packing of molecules in crystal lattices of homologs of series-1. Unexhibition of odd-even effect by the mesomorphic homologs of series-X is attributed to the late commencement (from C_6) of mesophase (only even members) from which alternation of transition temperatures diminish, that is, early odd members C_1, C_3, and C_5 are nonmesomorphic, whereas in case of series-Y and -1 the mesophase commences from C_3 and C_4 members of respective series, which created the possibility of the effect under discussion. The suitable magnitudes of anisotropic forces of intermolecular end-to-end or/and lateral attractions which is a driving force to induce early or late mesophase, as a consequence of favorable molecular rigidity and/or flexibility which depend upon molecular structure only, and it varies from series to series. Thus, changing trend and type of mesophase for the same homolog from series to series in present comparison depend upon changing either central group or due to the presence or absence of lateral group keeping rest of the molecular part unchanged.

Conclusions

Present novel ester homologous series of twelve homologs gives rise to nine smectogenic mesomorphs by lateral substitution of $-OCH_3$ group which broadens the molecules and affects molecular polarizability and causes steric hindrance.

- Present novel series is smectogenic without exhibition of nematic property.
- Group efficiency order derived on the basis of (i) thermal stability, (ii) early commencement of mesophase, and (iii) mesophase length range for smectic and/or nematic are as under.

i. **Nematic**
$-H$ with> $-H>$ $-OCH_3$
$-CH{=}CH{-}COO-$ central group with $-COO-$ central group with $-COO-$ central group
Smectic
$-H>$ $-H>$ $-OCH_3$
with $-CH{=}CH{-}COO-$ with $-COO-$with $-COO-$

ii. **Smectic**
$-OCH_3>$ $-H>$ $-H$
with $-COO-$With $-CH{=}CH{-}COO-$ with $-COO-$
Nematic
$-H>$ $-H>$ $-OCH_3$
with $-CH{=}CH{-}COO-$ with $-COO-$with $-COO-$

iii. **Smectic**
$-H>$ $-H>$ $-OCH_3$
with $-CH{=}CH{-}COO-$ with $-COO-$ with $-COO-$

- Mesomorphic properties (LC) and the degree of mesomorphism are sensitive and susceptible to molecular structure.
- Suitable magnitudes of molecular rigidity and flexibility are the driving forces to induce mesomorphism.
- Present investigation may be useful for the following:

(i) The devices to be operated at desired temperature or room temperature by the study of mixed mesomorphism or using directly a homolog between 40°C and 60°C.
(ii) Biological activity study for the growth of flower and fruits.
(iii) The researchers working on applications of LC.

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