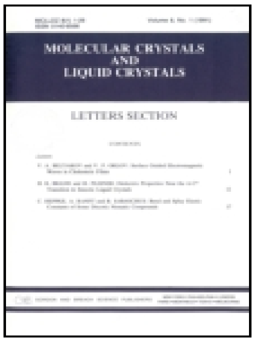

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Mesomorphism and Molecular Structure of Ester Homologous Series Containing Carboxy and Vinyl Carboxy Linking Groups

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A novel homologous series 4-(4′-n-alkoxy benzoyloxy)-isopentyl cinnamates consisting of eleven homologs is reported. Mesomorphism commences from the hexyloxy homolog up to the hexadecyloxy homolog. The hexyloxy and hexadecyloxy derivatives are only enantiotropically nematogenic while, but the octyl, decyl, dodecyl, and tetradecyl homologs exhibit enantiotropic nematogenic and smectogenic mesophases. The rest of the homologs are nonmesogenic. The textures of nematic phase are threaded or Schlieren and that of the smectic mesophase is focal conic smectic A or C type. The transition curves of the phase diagram behave in a normal manner without the exhibition of an odd-even effect. Analytical and spectral data confirm the molecular structure of the homologs. Overall mesogenic phase temperature range varies from 11.0°C to 59.0°C. The average thermal stabilities of smectic and nematic are 122.25°C and 139.0°C, respectively. The series is predominantly nematogenic and partly smectogenic with a middle-ordered melting type and a considerable range of liquid crystallinity. Melting points and transition temperatures were determined using an optical polarizing microscope equipped with a heating stage. The mesomorphic properties are compared with structurally similar series.

Keywords Liquid crystals; mesogen; mesomorphs; nematic; smectic

Introduction

Liquid crystal materials find importance in various fields of life in the present era [1,2,3]. Therefore, liquid crystal materials of suitable range of temperature or composition are required to manufacture various articles [4] at economical cost. Hence, the present investigation is planned to synthesize novel LC materials through homologous series of “iso” linking terminal end group, which may yield LC materials of lower transition temperatures with a considerable range of liquid crystallinity. Thus, the present investigation is restricted to a novel ester homologous series of cinnamic acids [5,6] with —OR and – C_5H_{11}(iso) terminal end group as flexible part of a novel series and two end phenyl rings bridged through – COO- central bridge as rigid core of a molecule. Hence, proposed present work is aimed to understand and establish the effects of molecular structure on LC behavior

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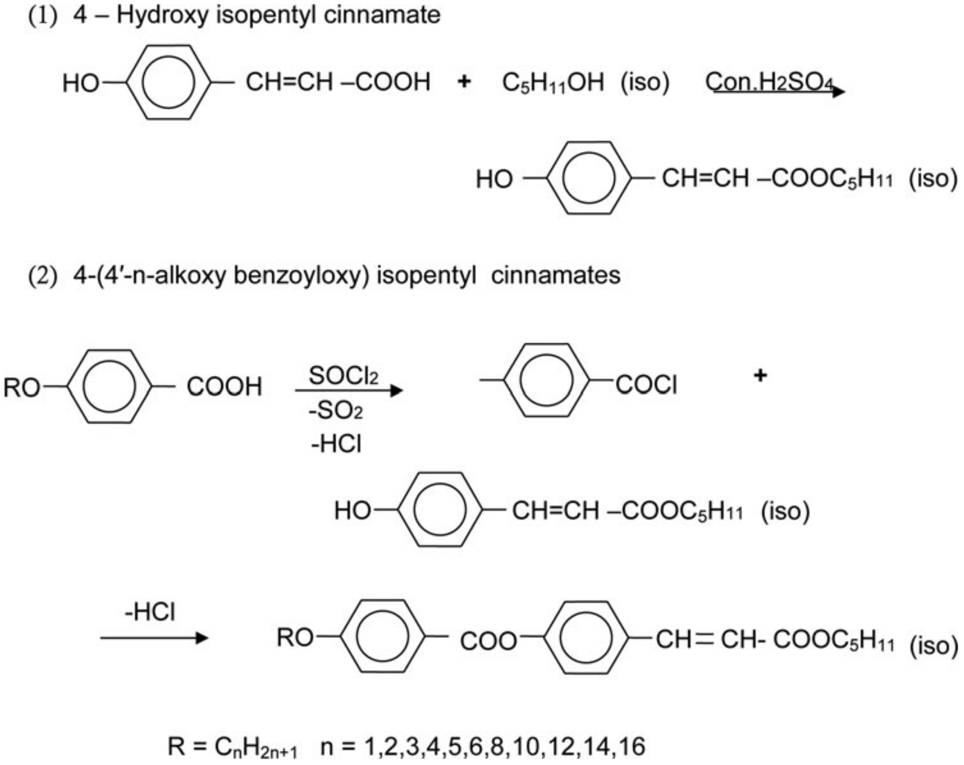
of novel substances which may be suitable for applications at an economical cost. The variation of the combined effects of molecular rigidity and flexibility [7,8,9] can yield LC materials of different mesogenic behavior.

Experimental

Synthesis

4—Hydroxy benzoic acid was alkylated with suitable alkylating agents (R-X) by a modified method of Dave and Vora [10]. 4–Hydroxy isopentyl cinnamate was synthesized by the usual method of esterification using conc. sulfuric acid [11]. Alkoxy benzoic acids were converted to the corresponding acid chlorides using thionyl chloride and then directly condensed with 4–hydroxy isopentyl cinnamate in dry cold pyridine [12,13]. The final ester homolog derivatives were individually decomposed, filtered, washed, dried, and purified until constant transition temperatures were obtained. A synthetic route to the novel series is mentioned below in Scheme 1.



Scheme 1. Synthetic route to the series.

4–Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH) 4–hydroxy cinnamic acid, sulfuric acid, isopentyl alcohol, thionyl chloride, pyridine ethanol, etc. required for synthesis were used as received except solvents which were dried and purified prior to use.

Table 1. Elemental analysis

Sr.	$R = n$-alkyl	Molecular	Calculated %	Observed %		
No.	Chain	Formula	C	H	C	H
1	Methyl	$C_{22}H_{24}O_5$	71.73	6.52	71.79	6.59
2	Ethyl	$C_{23}H_{26}O_5$	72.25	6.80	72.15	6.88
3	Propyl	$C_{24}H_{28}O_5$	72.72	7.07	72.61	6.99
4	Butyl	$C_{25}H_{30}O_5$	73.17	7.31	73.09	7.41

IR Data in cm^{-1} for pentyl and octyl homologs.

Homolog	IR spectra (cm^{-1})
Pentyl	3398.3 cm^{-1}→H- bonded O-H group 2931.6, 2854.5, and 1396.4 cm^{-1}→Confirms alkyl group 1685.7, 1257.5, and 1056.9 cm^{-1}→Confirms –COO-group 1168.8 cm^{-1}→Confirms ether 983.6 cm^{-1}→ Confirms trans –CH=CH- group 829.3 cm^{-1}→ Confirms p-sub. benzene ring IR confirms the structure
	3421.5 cm^{-1}→H- bonded O-H group 2927.7 and 2854.5 cm^{-1}→ Confirms alkyl group 1685.7, 1257.0, and 1126.4 cm^{-1}→Confirms –COO-group

(Continued on next page)

Table 1. Elemental analysis *(Continued)*

Homolog	IR spectra (cm^{-1})
Octyl	1396.4 and1303.8 cm^{-1}→ Confirms gem dimethyl group 1168.8 cm^{-1}→ Confirms ether 960.5 cm^{-1}→ Confirms trans –CH=CH- group 844.8 cm^{-1}→ Confirms p-sub. benzene ring 717.5 cm^{-1}→Confirms polymethylene of C_8H_{17} IR confirms the structure

^{1}HNMR spectra in ppm for: Tetradecyloxy and hexadecyloxy homologs.

Homolog	NMR spectra δ(ppm)
Tetradecyl	0.879 (-C$\underline{H}_3$ of –$C_{14}H_{29}$) 1.261 (-C$\underline{H}_2$ of –$C_{14}H_{29}$) 3.528 (-O-C$\underline{H}_2$ of –$C_{14}H_{29}$) 4.275 (-O-C$\underline{H}_2$ of –C_5H_{11}) 6.903 and 6.946→(p-sub. benzene 8.021 and 8.064 ring) 7.260
Hexadecyl	0.876 (-C$\underline{H}_3$ of –$C_{16}H_{33}$) 1.256 (-C$\underline{H}_2$- of –$C_{16}H_{33}$) 1.764 (-O CH_2-C$\underline{H}_2$ of –$C_{16}H_{33}$) 3.453 (-O-C$\underline{H}_2$ of –$C_{16}H_{33}$) 4.013 (-O-C$\underline{H}_2$ of –C_5H_{11}) 6.898 and 6.941→(p-sub. benzene 8.017 and 8.061 ring) 7.258

Texture by miscibility method.
Hexyl: Threaded nematic.
Hexadecyl: Schlieren.
Octyloxy: Smectic—A.
Tetradecyloxy: Smectic—C.

Table 2. Transition temperature in °C

		Transition temperature in °C		
Sr. No.	$R = n$-alkyl group	Smectic	Nematic	Isotropic
1.	Methyl	—	—	130.0
2.	Ethyl	—	—	180.0
3.	Propyl	—	—	123.0
4.	Butyl	—	—	141.0
5.	Pentyl	—	—	116.0
6.	Hexyl	—	107.0	152.0
7.	Octyl	96.0	114.0	155.0
8.	Decyl	97.0	124.0	144.0
9.	Dodecyl	75.0	129.0	132.0
10.	Tetradecyl	85.0	122.0	126.0
11.	Hexadecyl	—	114.0	125.0

Characterization

Representative members of the series were characterized by elemental analysis through Perkin Elmer PE 2400 CHN analyzer, infrared spectra were recorded on a Perkin Elmer Spectrum GX, ^{1}HNMR spectra on a Bruker spectrometer using $CDCl_3$ as solvent and by mass spectra (Table 1). The transition temperature and the liquid crystal properties were determined by a miscibility method through an optical polarizing microscope equipped with a heating stage.

Results and Discussion

4–Hydroxy isopentyl cinnamate is a nonmesomorphic vinyl ester. However on linking it with 4–*n*–alkoxy benzoic acids through their acid chlorides induces mesomorphism as nematic (Hexyloxy and hexadecyloxy) or as smectic in addition to nematic for mesogenic homologs. The rest of the homolog derivatives, viz., methoxy to pentoxy are nonmesogenic. Transition temperatures of the novel homologs are relatively lower than the corresponding *n*-alkyl benzoic acids. Transition temperatures (Table 2) of the homologs are plotted as the numbers of carbon atoms in *n*-alkyl chain of the left *n*-alkoxy terminal end group. A phase diagram (Fig. 1) showing phase behavior of a novel series is obtained by linking like or related points. The solid mesomorphic transition curve adopts a zigzag path of rising and falling as the series is ascended in normal manner. The smectic-nematic transition curve initially rises, passes through maxima and then descends as the series is ascended without the exhibition of an odd-even effect and behaves in normal established manner. The smectic-nematic transition curve is extrapolated [14,15] for butyloxy, hexyloxy, and hexadecyloxy homologs on the basis of the trend of the curve to predict the latent transition temperature (LTT) for smectic of the homologs concerned which are 92.0°C, 102°C, and 103.0°C, respectively. The mesomorphic behavior of series varies homolog to homolog. Nematic and smectic mesophase length varies from 45°C to 03°C and 54°C to 18°C, respectively. Isotropic transition temperature of LC homologs varied between 155°C and 125°C. Thus, present novel series is predominantly nematogenic and partly smectogenic and of middle ordered melting type.

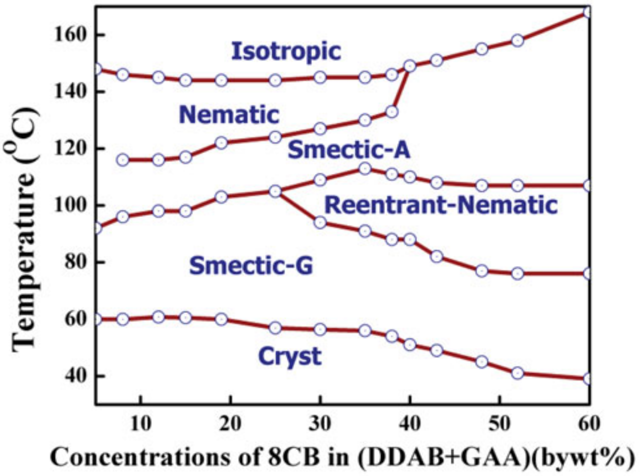


Figure 1. 4-(4′-*n*-alkoxy benzoyloxy) isopentyl Cinnamates.

The nonmesomorphic behavior of methoxy to pentyloxy homologs is observed for their inability to resist exposed thermal vibrations as a consequence of unfavorable molecular rigidity and flexibility, induced by low dipole–dipole interaction and low magnitudes of dispersion forces by the interaction between instantaneous dipoles produced by spontaneous oscillations of the electron clouds of the molecules which induced high crystallizing tendency of a molecules with absence of mesomorphism. Mesomorphic homologs from and beyond hexyloxy homolog which resist exposed thermal vibrations and disabling at an angle less then 90° on the floating surface. The molecules of all the mesomorphic homologs arrange themselves with statistically parallel orientational order on the floating surface and showing threaded or schlieren texture of nematic type mesophase, whereas octyloxy, decyloxy, dodecyloxy, and tetradecyloxy homolog molecules exhibited sliding layered arrangement on floating surface due to having lamellar packing of molecules in their crystal lattices which facilitated smectogenic mesophase formation prior to nematic mesophase formation within definite range of temperatures. Thus, heating process of a homolog against cohesive forces gradually reduces the intermolecular end to end and lateral attractions and a sample under examination as soon as acquires suitable magnitudes of anisotropic forces of intermolecular attractions to facilitate only nematic or smectic prior to the nematic phase. The absence of an odd-even effect in N-I and Sm-N transition curve is attributed to the absence of mesomorphism in the sorter homologs. Variations observed from homolog to homolog in the same series are due to the sequentially changing methylene unit in the left *n*-alkoxy (-OR) terminal end group. The variations observed from series to series for the same homolog is attributed to the common fixed group of each series, which are present at the other end of the molecule {viz., $-CH{=}CH\text{-}COOC_5H_{11}$ (iso), $-COOC_5H_{11}(n)$, and $-OC_5H_{11}(n)$}.

Extrapolation of nematic-isotropic transition curve to the left side at the butyloxy homolog suggests that solid-isotropic and nematic-isotropic transition temperatures merges into each other giving single temperature 140.0°C, i.e., there is no possibility of nematogenic phase formation for butyloxy homolog and its LTT for smectic should be 82.0°C, but is not actually realizable due to its high crystallization tendency. Similarly predicted LTT for

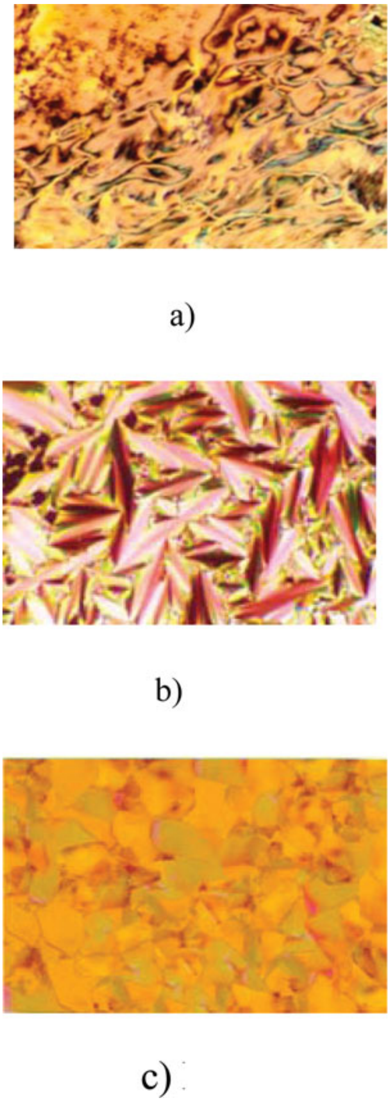


Figure 2. Structurally similar homolog series.

hexyloxy and hexadecyloxy homolog (102°C and 103°C) below solid-nematic transition temperatures are also not realizable due to their high crystallizing tendency.

Mesomorphism or LC property of present series-1 are compared with the structurally similar homolog series-1, series-X [16], and series-Y [17] as shown below in Fig. 2.

Homolog series-1, X, and Y are identically similar with respect to rigid core, and consist of two phenyl rings bonded through a –COO- central bridge and a flexible unit of the left *n*-alkoxy terminal end group. However, they differ by the flexible terminal group bonded from series to series at other end of the molecules, which are $–CH{=}CH\text{-}COOC_5H_{11}$ (iso), $\text{-}COOC_5H_{11}$(*n*), and $–OC_5H_{11}$(*n*), respectively, for series-1, *X*, *Y*. Therefore, combined effects of varying molecular rigidity and flexibility operates the variations in mesomorphic properties and the degree of mesomorphism [18].

Table 3. Average thermal stabilities in °C

Series	Series-1	Series-X	Series-Y
Smectic nematic	122.25	51.5	71.0
Smectic isotropic	(C_8–C_{14})	(C_6–C_{12})	(C_{10}–C_{14})
Commencement of smectic phase	C_8	C_5	C_{10}
Nematic isotropic	139.3	—	109.0
Commencement of nematic phases	(C_6–C_{16})		(C_5–C_8)
	C_6		C_5

Following Table 3 represents average thermal stabilities for smectic and nematic, commencement of smectic and nematic mesophase or phases, exhibition of mesomorphism from homolog to homolog, etc. for a presently investigated series-1 and series-X and series-Y chosen for comparison.

Table 3 indicates that

- Smectic thermal stability of ester homologs series-1 is higher than ester homolog series-X of the lowest thermal stability and are etheroester homologous series-Y
- Smectic mesophase formation commences earliest from pentoxy homolog of series-X, while, it commences from octyloxy and decyloxy homologs for series-1 and Y, respectively.
- Nematic thermal stability of series-1 is greater than series-X and Y in which nematic mesophase formation is totally absent for a series-X.
- Nematic mesophase commences from pentyloxy homolog for a series Y and it commences from hexyloxy homolog of a series-1 with absence of nematic mesophase in series-X.
- Homologous series-1 and Y are partly smectogenic and partly nematogenic, whereas homologous series-X is smectogenic only.

The highest thermal stability for smectic and nematic of series-1 is attributed to the iso linkage present in Pentyl hydrocarbon chain, and the presence of conjugated double bond in vinyl carboxy group which increases molecular rigidity as compared to –COO- group of series-X and Y. Moreover presence of iso linking (series-1) enhances molecular polarizability which contributed more than the intermolecular attraction which occurred by intermolecular cohesion. Moreover the part of a terminal end group –CH=CH-COO- has relatively greater length than –COO- group present as a part of a terminal group of series-X, and ether group –O- of series-Y. Therefore, vinyl group of series-1 causes more noncoplanarity due to the twist obtained as the oxygen atoms of the vinyl carboxy group bump into the non bonded adjacent hydrogen atoms of the aromatic rings. On account of above effects, the suitable magnitudes for anisotropic forces of intermolecular attractions as a consequence of differing molecular rigidity and flexibility, the thermal stability, and commencement of smectic and nematic mesophases are higher than series chosen for comparison X and Y. Thus, variations in suitable magnitudes of anisotropic forces of intermolecular attractions causes variation in disalignment of molecules at an angle less than 90° on floating surface, presence or absence of lamellar packing of molecules in their respective crystal lattices, extent of molecular noncoplanarity, type of maintenance of two dimensional order of molecules in floating a condition, etc. which result into variations in mesogenic behavior for the same homolog from series to series.

Conclusion

(1) Presently investigated novel homologous series is predominantly nematogenic and partly smectogenic with middle-ordered melting type and considerable degree of mesomorphism.
(2) Group efficiency order derived on the bases of (a) thermal stability and (b) early commencement of mesophase for smectic and nematic are as under

   (a) Smectic: –CH=CH-$COOC_5H_{11}$ (iso) > –OC_5H_{11}(*n*) > -$COOC_5H_{11}$(*n*) Nematic: –CH=CH-$COOC_5H_{11}$ (iso) > –OC_5H_{11}(*n*) > -$COOC_5H_{11}$(*n*)
   (b) Smectic: -$COOC_5H_{11}$ (*n*) > –CH=CH-$COOC_5H_{11}$ (iso) > –OC_5H_{11}(*n*) Nematic: –OC_5H_{11}(*n*) > –CH=CH-$COOC_5H_{11}$ (iso) > -$COOC_5H_{11}$(*n*)

(3) Molecular rigidity and flexibility are the important factor to induce mesomorphism.
(4) Suitable magnitudes of anisotropic forced of intermolecular attractions emerging as a consequence of favorable molecular rigidity and flexibility are very sensitive and susceptible to molecular structure.

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