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Study of a new homologous series of liquid crystals: Isopropyl-p-(p′-n-alkoxy cinnamoyloxy) cinnamates

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ABSTRACT

A new homologous series: isopropyl-p-[p′-n-alkoxy cinnamoyloxy] cinnamates was synthesized and studied with a view to understanding and establishing the relation between liquid crystal property and molecular structure. Twelve homologues were synthesized. Methyl to butyl homologues are not liquid crystals, while pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl, and hexadecyl derivatives are enantiotropic liquid crystal in nature with nematogenic character. Smectogenic character is totally absent. A phase diagram is obtained by plotting a graph of transition temperatures versus number of carbon atoms is n-alkyl chain of left n-alkoxy terminal end group. Solid-isotropic or solid-nematic transition curve rises steeply from methyl to propyl derivatives and falls to pentyl homologue through butyl homologue, and follows a zigzag path of rising and falling values as the series is ascended. Nematic–isotropic transition curve shows descending tendency as series is ascended in a normal manner with exhibition of odd-even effect. Smectic mesophase does not appear even in the monotropic condition. Phase transition temperatures are determined by hot stage polarizing microscope. Analytical data support the structure of molecules. Texture of nematic mesophase is of threaded type. Mesomorphic properties are compared with structurally similar homologous series.

KEYWORDS

Liquid crystals; mesogens; mesophase; nematic; smectic

Introduction

Many homologous series [1, 2, 3, 7–13] have been reported previously to establish and understand the relation between molecular structure and liquid crystallinity. The increasing utility of liquid crystal materials in various fields of applications needs more and more such materials to satisfy the demand of research, development, and manufacture [14–20. Hence, the present work is planned to synthesize and characterize new liquid crystal materials through homologous series.

Experimental

Synthesis of p-hydroxy isopropyl cinnamates

p-Hydroxy isopropyl cinnamate is synthesized by refluxing a reaction mixture containing 0.1 mole p-hydroxycinnamic acid and 0.12 mole anhydrous isopropyl alcohol, including 1–2 mL

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concentrated sulphuric acid for 5 to 8 hr. Reaction mixture after reflux is poured into ice cold excessive quantity of water (1 L or more) to decompose and to get solid product. Final product is filtered, dried, washed, and recrystallised from alcohol; m.p.: 130.0°C, yields: 67.62%.

Synthesis of p-n-alkoxy cinnamoyl chloride

P-n-alkoxycinnamic acid is prepared from p-hydroxycinnamic acid and corresponding alkyl halide by the modified method of Dave and Vora [3]. N-alkoxycinnamic acid is refluxed with excess of freshly distilled thionyl chloride until the evolution of SO_2 gas ceased. Excess of thionyl chloride is distilled off and the corresponding acid chloride is left behind and preserved in moisture free atmosphere without purification for further reaction.

Synthesis of isopropyl-p-[p′-n-alkoxy cinnamoyloxy] cinnamates

Pre-cold solution of p-hydroxy isopropyl cinnamate in pyridine is carefully added drop-wise into a flask containing acid chloride kept in an ice bath. Reaction mixture after complete addition was warmed for half an hour and kept overnight. Next day the product decomposed in 1:1 HCl solution. Solid product was filtered, washed, dried, and purified by alcohol. Synthetic route to the homologous series is shown in Fig. 1.

Scheme of synthesis

Analytical data: Isopropyl-p-(p′-n-alkoxy cinnamoyloxy) cinnamates.

NMR (in ppm)

Hexyl

0.84 – $-CH_3$

2.38 – $O-CH_2$

3.98 – $O-CH_2$ of $O-CH_2-CH_2-CH_3$

4.34 and 4.26 – CH=CH–

6.64, 6.83, 7.75, and 7.88 – P-sub.phenyl two p-sub.benzene

7.22 and 8.02 – P-sub.phenyl two p-sub.benzene

Nuclear magnetic resonance (NMR) confirms the structure.

Hexadecyl

1.16 – $-CH_3$

1.20 – $-CH_2$

2.38 – OCH_2-CH_2-

4.00 – $O-CH_2$ of $-COOC_4H_9$

3.32 – $O-CH_2$ of $C_{14}H_{29}$

4.40 – CH=CH–

6.88 and 6.90 – two P-sub.phenyl rings

8.03 and 8.01 – two p-sub.phenyl rings

NMR confirms the structure.

Infrared (IR; in cm^{-1})

Tetradecyl

2800.0 confirms the alkyl group

1050, 1150, and 1700 confirms the –COO– group

725 confirms cis –CH=CH– group

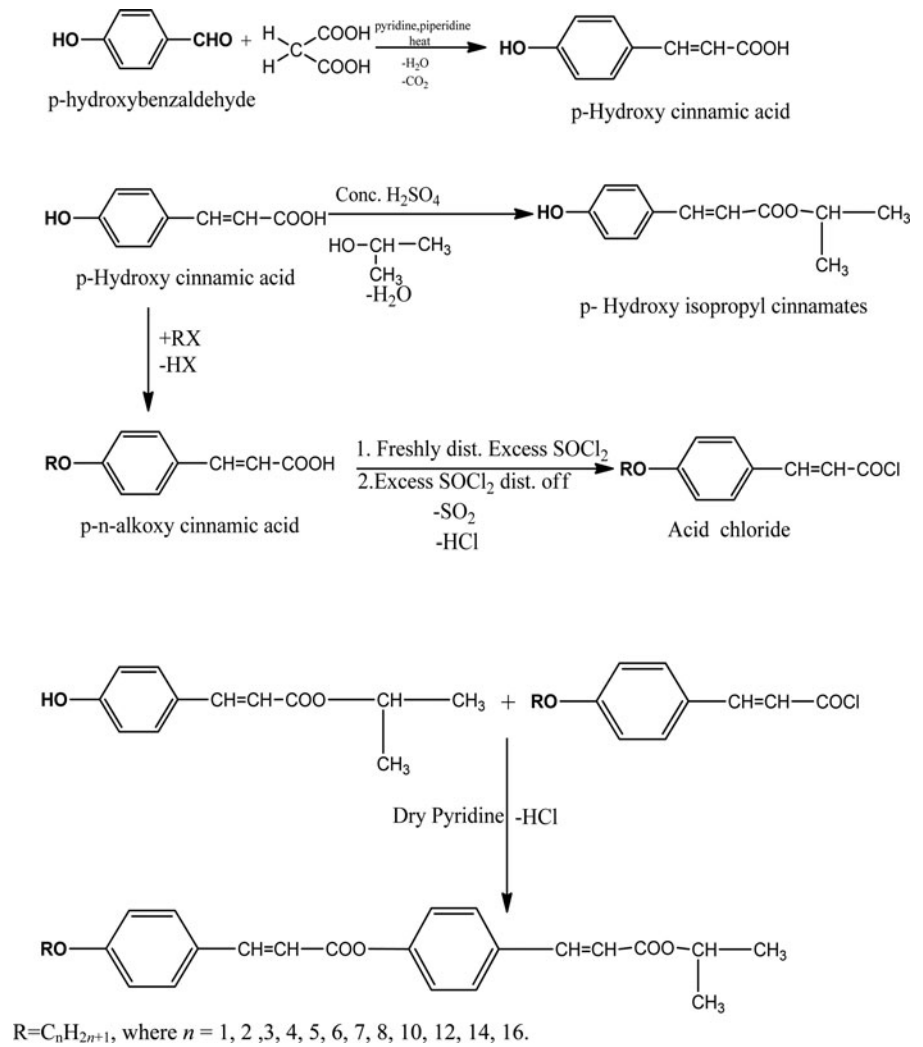


Figure 1. Synthesis route to the series.

820 confirms p-sub.phenyl ring
3100 confirms the aromatic ring
1300 and 1350 confirm polymethylene of $C_{14}H_{29}$
IR confirms the above structure.

Octyl
2800.0 confirms the alkyl group
1100 and 1750 confirm the –COO– group
660 confirms cis –CH=CH– group
830 confirms the p-sub.phenyl ring
3000 confirms the aromatic ring
740 confirms the polymethylene of C_8H_{17}
IR confirms the above structure.

Table 1. Transition temperatures.

		Transition temperatures (°C)		
		Smectic	Nematic	Isotropic
1.	Methyl	—	—	208.0
2.	Ethyl	—	—	216.0
3.	Propyl	—	—	220.0
4.	Butyl	—	—	200.0
5.	Pentyl	—	140.0	184.0
6.	Hexyl	—	140.0	244.0
7.	Heptyl	—	131.0	207.0
8.	Octyl	—	130.0	242.0
9.	Decyl	—	130.0	220.0
10.	Dodecyl	—	138.0	190.0
11.	Tetradecyl	—	130.0	170.0
12.	Hexadecyl	—	132.0	152.0

Results and discussion

The titled homologous series, isopropyl–p-[p/-n-alkoxy cinnamoyloxy] cinnamates comprises 12 homologues of cis configuration as determined from spectral data. Methyl to butyl homologues are not liquid crystals, while the rest of the homologues are liquid crystals. Liquid crystal homologues exhibit enantiotropic nematogenic type of mesophase only. Smectic mesophase exhibition is totally absent, even in the monotropic condition. Transition temperatures and melting temperatures are determined by a polarizing microscope with a heating stage. Transition temperatures of homologues (Table 1) are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end groups. A phase diagram is obtained by linking similar or related points. Careful examination of a phase diagram (Fig. 2) indicates that solid-isotropic or solid-nematic transition curve rises from methyl to propyl and

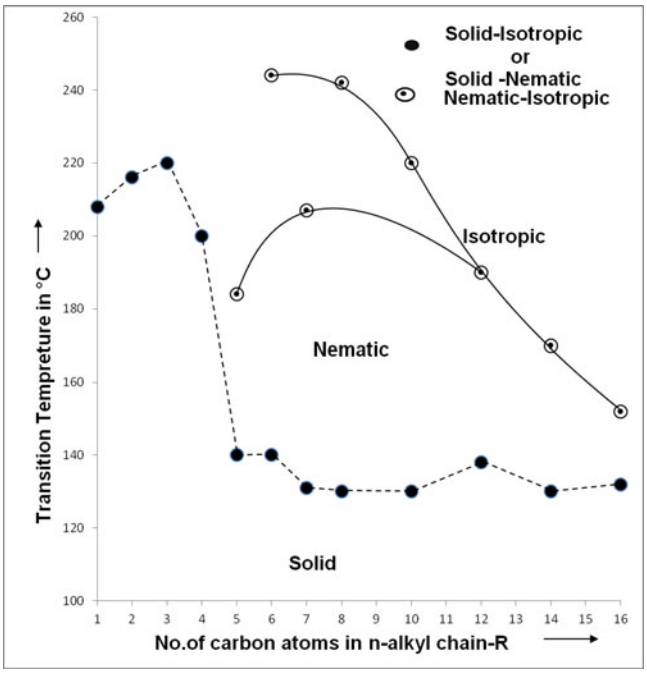


Figure 2. Isopropyl-p-(-p/-n-alkoxy cinnamoyloxy) cinnamates.

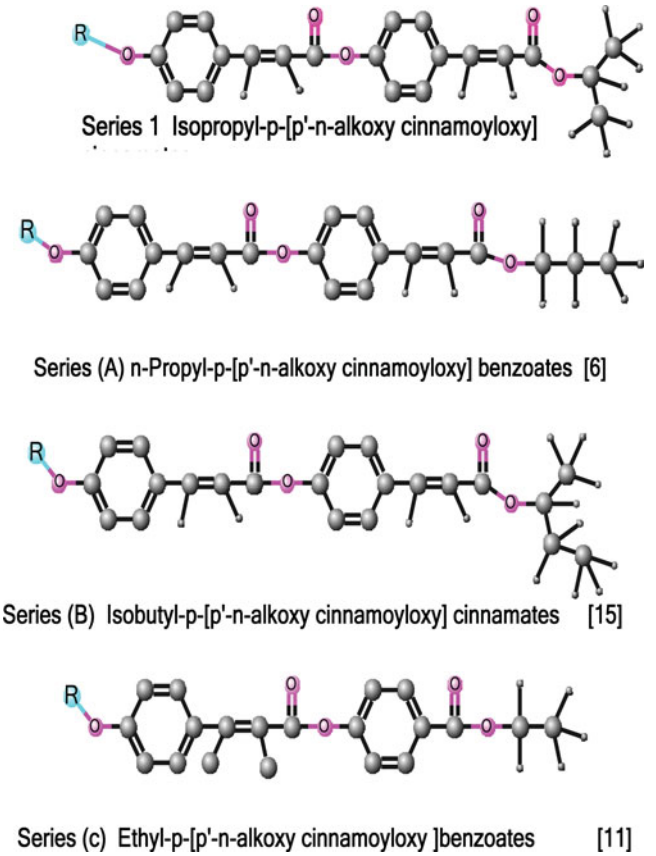


Figure 3. Similar structure series.

then steeply falls to pentyl through butyl derivative of series. Then it follows a zigzag path, as series is ascended. Thus, it behaves in a normal manner. Nematic–isotropic transition curve shows descending tendency as series is ascended, in a normal manner. Odd-even effect is observed for nematic–isotropic transition curve with alternation of transition temperatures. Mesophase length varies from 20.0°C at hexadecyl homologue to 112.0°C at octyl homologue. Thus, mesomorphic range is wide, and series is of higher middle-ordered melting type. Liquid crystal properties of titled homologous series (1) are compared with structurally similar homologous series (A), (B), and (C), as shown in Fig. 3.

N-alkoxycinnamic acids are dimeric molecules. Hydrogen bonding breaks and p-hydroxy isopropyl cinnamate molecule is bonded through esterification that yields eight homologues as liquid crystals, out of 12 homologues. Methyl to butyl homologues are missing liquid crystal properties because shorter n-alkyl chain causes stronger intermolecular end-to-end forces of attraction, which lead to high crystallizing tendency.As the left n-alkoxy terminal chain increases in length by the sequential addition of a methylene unit, the molecular crystallinity diminishes gradually and adds amorphous character. Thus, end-to-end intermolecular attractions depending upon molecular length to breath ratio and molecular polarizability and effect of molecular rigidity in combination with flexibility balances, such a magnitude of disorder resulted from anisotropic intermolecular cohesive forces among the molecules, become anisotropic and of suitable magnitude for eight homologues causing two-dimensional array of molecules favoring only statistically parallel orientation of molecules in floating condition. Thus, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl, and hexadecyl homologues

Table 2. Elemental analysis.

Sr. No.	R = n-alkyl chain	Molecular formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$C_{22}H_{22}O_5$	72.13	6.01	72.18	6.00
2.	Ethyl	$C_{23}H_{24}O_5$	73.02	6.35	73.16	6.56
3.	Proxyl	$C_{24}H_{26}O_5$	73.85	6.67	73.84	6.66
4.	Butyl	$C_{25}H_{28}O_5$	74.63	6.97	74.67	7.02
5.	Pentyl	$C_{26}H_{30}O_5$	75.16	7.25	75.42	7.34
6.	Hexyl	$C_{27}H_{32}O_5$	76.06	7.51	76.22	7.58
7.	Heptyl	$C_{28}H_{34}O_5$	76.71	7.76	76.76	7.38
8.	Octyl	$C_{29}H_{36}O_5$	77.33	8.00	77.88	7.96
9.	Decyl	$C_{31}H_{40}O_5$	78.48	8.44	78.82	8.40
10.	Dodecyl	$C_{33}H_{44}O_5$	79.52	8.84	79.80	8.80
11.	Tetradecyl	$C_{35}H_{48}O_5$	80.46	9.20	80.96	9.08
12.	Hexadecyl	$C_{37}H_{52}O_5$	81.32	9.52	80.88	9.68

maintain statistically parallel orientational order of molecules, giving rise to show-threaded type of texture in floating condition as recognized under field of view of hot stage polarizing microscope. Thus, liquid crystal homologues of the titled homologous series are nematogenic in character. None of the homologues show lamellar packing in their crystal lattices, which can give sliding layered arrangement of molecules during microscopic examination in floating condition. Thus, smectic mesophase is totally absent in the homologous series under discussion. Odd-even effect observed in nematic–isotropic transition curve is attributed to the sequentially progressive addition of methylene units at the left n-alkoxy terminal end group. Nematic–isotropic transition curves for odd-even homologues merge into each other at dodecyloxy homologue, and continuously show descending tendency as the series ascends, because in case of higher homologues, the longer left n-alkyl chain of n-alkoxy group may coil or couple to lie in the line with major axis of core. Thus, end-to-end contact would ultimately be the same for odd-even homologue.

The average thermal stabilities and commencement of mesophases in series (1), (A), (B), and (C) (Fig. 3) are recorded in Table 3.

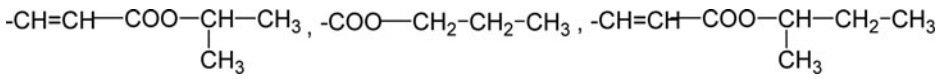
Careful examination of Table 3 indicates that benzoates homologous series (A) and (C) are partly smectogenic and partly nematogenic, while cinnamates homologous series (1) and (B) are entirely nematogenic without exhibition of any smectic character. Nematic isotropic thermal stability of the titled homologous series (1) is highest among the homologous series under comparison, i.e. the intermolecular forces of end-to-end attraction playing roll depending upon molecular shapes, size, molecular polarity of lateral and/or terminal end groups, molecular polarizability, aromaticity, etc. should operate in favor of nematogenic character in series (1) as compared with homologous series (A), (B), and (C). "Iso" linking of titled homologous

Table 3. Average thermal stability.

Series	(1)	(A)	(B)	(C)
Smectic–isotropic	—	118.0 (C_6–C_{12})	—	120.75 (C_7–C_{12})
Commencement of smectic mesophase	—	C_2	—	C_2
Nematic–isotropic	201.11 (C_5–C_{16})	115.7 (C_3–C_6)	138.1 (C_5–C_{16})	119.7 (C_5–C_6)
Commencement of nematic mesophase	C_5	C_1	C_6	C_1

series (1) and (B) widen the breadth and intermolecular separation, which may reduce end-to-end intermolecular forces of attraction. However, at the same time increased separation increases molecular polarizability, which results in increase of lateral intermolecular forces of attraction. Thus, increased molecular width creates two opposing effects operating at a time. Therefore, resultant net effect depends upon the predominant effect of intermolecular attractions. Then higher values of thermal stability for nematic in series (1) and (B) are attributed to end-to-end attractions in addition to attractions caused due to induced polarizibility by "iso" linking.

All the homologous series under comparison have two phenyl rings, left n-alkoxy end group, central bridge –CH=CH–COO–, and aromaticity as common identical features. Therefore, variation in liquid crystal properties and degree of liquid crystallinity from series to series for the same homologue depend upon polarity and polarizibility of right terminal end groups only, viz.

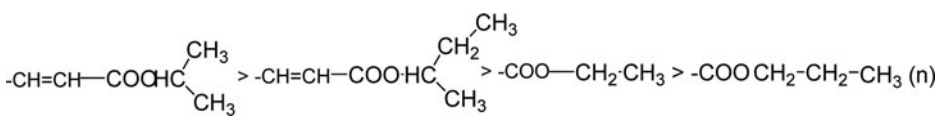


and –COO–CH_2–CH_3 of series (1), (A), (B), and (C) respectively. Thus, variation observed for liquid crystal properties for the same homologue from series to series is attributed to variation in polarity of right terminal end group. Variation in liquid crystal properties among the homologues of the same series in which right terminal end group remains unchanged and depends upon the left n-alkyl chain length only, as methylene unit, is sequentially added.

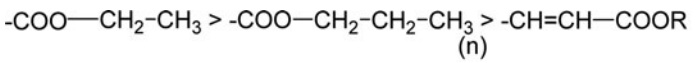
The commencement of smectic mesophase depends upon the extent of non-co-planarity caused by the molecule [5,12]. The co-planarity maintained by the molecules of homologous series under comparison depends upon –COOR and –CH=CH–COOR groups as well as the n-alkyl group of n-alkoxy terminal. Terminal/central vinyl carboxylate –CH=CH–COO– has greater length than carboxylate –COO–, which causes more non-coplanarity due to a twist obtained as the oxygen atoms of vinyl carboxy group bump into the non-bonded adjacent hydrogen atoms of aromatic ring, which causes considerable strain on the molecule and results in molecular twist around C-O bond, forcing phenyl ring out of plane of molecule. On account of this difference, the smectic–isotropic thermal stabilities of series (1) and (B) is lower or zero (absence of smectic phase) than series (A) and (C). The extent of non-co-planarity caused by the molecules of series (A) and (C) are such that smectic mesophase persisted from the second member of the series, while it does not occur until the last hexadecyl homologue of series (1) and (B).

Thus, group efficiency order derived for nematic and smectic mesophase on the basis of thermal stability is as under:

Group efficiency order for nematic



Group efficiency order for Smectic



Where R= $-C_3H_7$ (iso), $-C_4H_9$ (iso)

Conclusions

Titled homologous series is entirely nematogenic with higher middle-order melting type, long range of liquid crystallinity, and without exhibition of any smectic property.

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