Study of novel liquid crystals of ethylene derivatives: α-4-[4'-n-alkoxy cinnamoyloxy] phenyl β-4"-methoxy benzoyl ethylenes

Chauhan H. N.[a&b] and Doshi A.V.[c*]

[a] *Shri JJT University, Rajsthan*
[b] *K. K. Shah Jarodwala Maninagar Science College, Ahmedabad, Gujarat, India*
[c] *Shri JagdishPrasad Jhabarmal Tibrewala University, Jhunjhunu, Rajasthan, India*

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ABSTRACT

Titled homologous series consists of eleven homologues. Methyl to n-butyl and hexadecyl derivatives are nonliquid crystal while rest of the homologes Viz. n-pentyl to n-tetradecyl derivatives are only enantiotropic nematogenic without exhibition of any smectic character. Odd even effect is observed in nematic-isotropic transition curve. A phase diagram shows that Solid-isotropic or nematic transition curve follows.zigzag path of rising and falling. Nematic-isotropic transition curve behaves in normal manner. Analytical data support the structures of molecules. Texture of nematic mesophase is schlierens or threaded type. Transition and melting temperatures of homologues are determined from hot stage polarising microscope. Liquid Crystal (LC) properties of the series are compared with other structurally similar homologous series. Series is entirely nematogenic with relatively high melting type.

Keywords: Liquid crystal, Nematic, Mesophase, Enatiotropy, Monotropy.
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INTRODUCTION

Liquid crystal materials with –CH=CH-CO- central group in combination with carboxy or vinyl carboxy central groups were rarely reported, which may be useful as biologically active molecules. Therefore present work was planed to synthesize novel type of benzoyl ester Liquid Crystal molecules of varying terminal end groups. Presently Benzo-ester molecules with methoxy right terminal end group at para position are synthesized and studied with a view to understand and establish liquid crystal behavior of titled homologous series.

MATERIALS AND METHODS

Experimental : Some representative members of the series were selected for characterization to determine their structure by IR and ^{1}HNMR techniques. NMR spectra were recorded using $CDCl_3$ as solvent. Micro analysis was performed on CHN analyzer as shown in Table-1. Transition and melting temperatures as well as liquid crystal properties were observed on polarizing microscope with heating stage. Thermodynamic quantities enthalpy (ΔH) and entropy(ΔS) are qualitatively discussed instead of DSC scan. The texture of the nematic mesophase determined by miscibility method.

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Synthesis:

4-Hydroxy cinnamic acid was synthesized by the reaction between p-hydroxy benzaldehyde and malonic acid in usual manner [10]. Hydroxy group was alkylated by suitable alkylating agent. Constituent reacting components were used as received. The synthetic rute to the series is shown as under in Scheme-1. α-p-Hydroxy phenyl β-p'-methoxy Benzoyl ethylene [B] was synthesized by established method [10] and p-n-Alkoxy cinnamoyl chlorides [A] were synthesized by a modified method of Dave and Vora [5]. Homologues of the series were synthesized by condensing equimolar proportion of [A] and [B] in dry cold pyridine. The final products were purified and recrystalised from Alcohol till constant melting points were obtained.
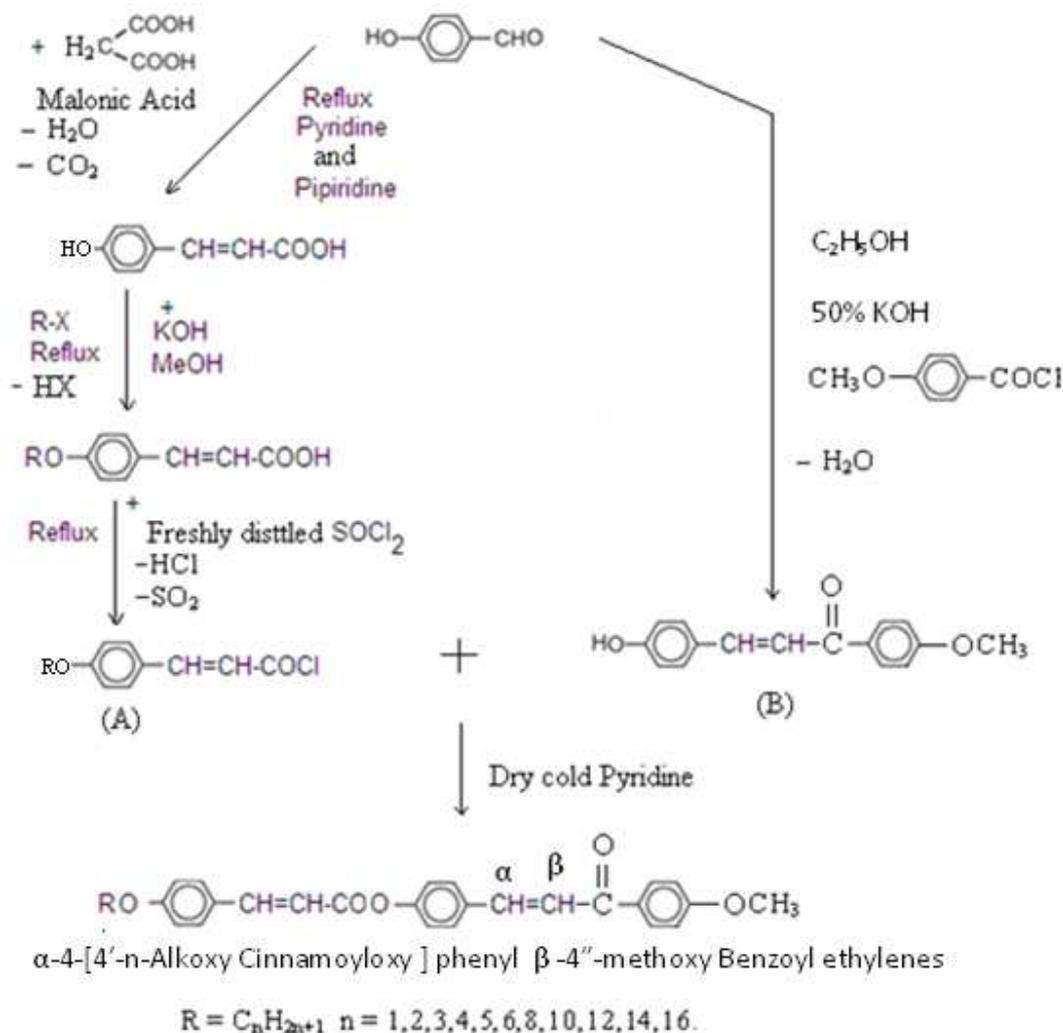
Scheme -1 : Synthetic Route to the Series

Spectral data for series-1 :
NMR in ppm
Octyl derivative :
0.887 - CH_3 of $-OC_8H_{17}$,1.288 – $(CH2)n$ of $-OC_8H_{17,}$ 4.019 (Triplet) $-OCH_2-CH_2$ of $C_8H_{17,;}$ 3.889 (Singlet) - O-CH_3,4.86 (Broad) – CH=CH-,6.943 & 8.036 P-Sub.phenyl ring.

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IR: in cm^{-1}
Hexyl derivative : 1700 & 1260 Confirms COO- group,820 Confirms p-sub. phenyl ring,1120 Confirms-CO- of alkoxy.

Dodecyl derivative :
1200,1250 & 1670 Confirms –COO- group,1150 Confirms –CO – group,820 Confirms p-sub. Phenyl ring , 720 confirms –$(CH_2)_n$ of $C_{12}H_{25}$.

Table 1 : Elemental analysis for Butyl, Decyl, Tetradecyl derivative

Sr. No.	Molecular Formula	Elements % Found (% Calculated)	
		C	H
1	$C_{29}H_{28}O_5$	76.34(76.30)	6.16(6.14)
2	$C_{35}H_{40}O_5$	77.75(77.77)	7.37(7.40)
3	$C_{39}H_{48}O_5$	78.59(78.52)	8.11(8.05)

Texture : By miscibility method : Pentyl, Decyl, Tetradecyl derivatives Threaded/Schlieren type.

RESULTS AND DISCUSSION

Cis p-n-Alkoxy cinnamic acid and α-p-hydroxy phenyl β-p'-methoxy benzoyl ethylene are nonliquid crystals, however Liquid Crystal property is induced in six members of the series enantiotropically. Methyl to butyl and hexadecyl derivatives of the series are nonliquidcrystal and smoothly passes directly from solid to isotropic state without showing up of either nematic or smectic character even in the monotropic condition. Thus, liquid crystal (nematogenic) character commences from pentyloxy homologue with absence of smectic property. Transition temperatures and melting temperatures are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal as recorded in table-2; as observed from hot stage polarizing microscope. The resultant phasediagram obtained on joining related points is shown in figure-1.The phase, behavior is discussed on the basis of phasediagram obtained(Figure-1).

Solid-nematic or isotropic transition curve adopt a zigzag path of rising and falling with alternation of transition temperature as series is ascended and behaves in normal expected manner. The nematic-isotropic transition curve initially rises and then falls gradually as series is ascended from pentyl to tetradecyl derivative without any abnormality and behaves in usual manner. Odd-even effect is observed in nematic-isotropic transition curve upto octyloxy homologue. Odd-even effect diminishes as series is ascended because, longer n-alkyl chain may coil, bend or flex for chain length from and beyond octyloxy member of the series. Hexadecyl derivative of the series is nonmesomorphic. i.e. nematic mesophase disappears completely. Therefore on extrapolation, nematic-isotropic transition curve merges into solid-isotropic transition curve as indicated by doted line.

Table-2: Transition Temperatures of series in ^{0}C

Compound no.	n-alkyl group -C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	195.0
2	Ethyl	-	-	200.0
3	Propyl	-	-	189.0
4	Butyl	-	-	205.0
5	Pentyl	-	143.0	166.0
6	Hexyl	-	124.0	160.0
7	Octyl	-	110.0	168.0
8	Decyl	-	145.0	170.0
9	Dodecyl	-	129.0	164.0
10	Tetradecyl	-	150.0	160.0
11	Hexadecyl	-	-	170.0

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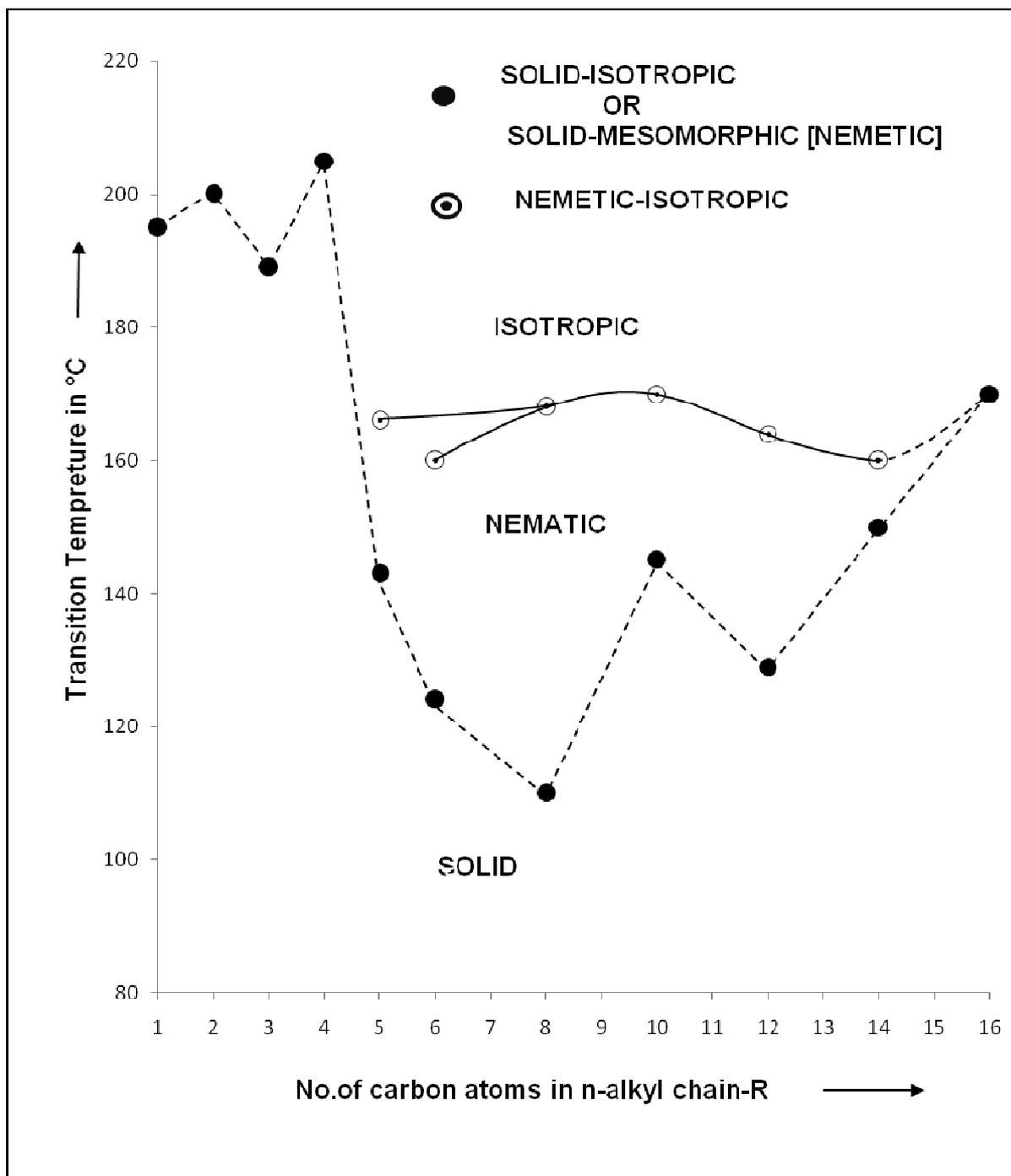
igure :1 Phase Behavior of Series
α-4-[4'-n- Alkoxy Cinnamoyloxy]phenyl β-4"-methoxy Benzoyl ethylenes

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The nonliquid crystal property of Methoxy to Butyloxy and Hexadecyloxy homologues of the series is attributed to the high crystallising tendency of homologues concern, which arises from relatively stronger intermolecular attractions generated as a consequence of unsuitable magnitude of molecular rigidity and flexibility which neither allow statistically parallel orientational order of molecules nor it allows layered arrangement (two dimensional) of molecules in floating condition to cause mesophase formation. Occurrence of a nematic mesophase from Pentyloxy to tetradecyloxy homologues observed is due to the strong polar nature of methoxy terminal at right end and left n-alkoxy terminal which causes end to end intermolecular attractions of suitable magnitude as a consequence of molecular rigidity and flexibility depending upon linear geometrical shape of the molecules concern. Thus, nematogenic molecules float with maintenance of statistically parallel orientational order in two dimensional array. Absence of smectic property is attributed to the absence of lamellar packing and layered lattices in the crystal structure of molecules concern.

Odd-even effect in nematic-isotropic transition curve observed due to the progressively and sequentially added methylene unit in left n-alkoxy terminal. Variation in liquid crystal property from homologue to homologue in a same series is attributed to the varying n-alkoxy left terminal. Similarly, variation in liquid crystal properties from series to series for same homologue in structurally similar homologous series is attributed to the varying right terminal end group of fixed polarity selected for comparison of liquid crystal properties.Figure-2 represents structurally similar homologous series X for comparing Liquid Crystal properties of presently investigated homologous series 1.
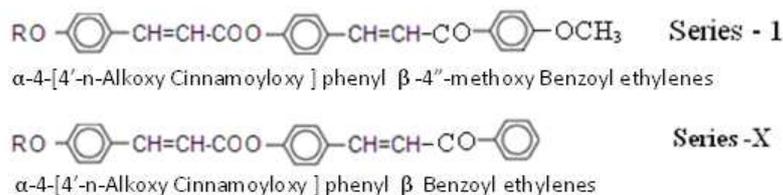
Figure 2 :Structurally Similar Homologous Series

Homologous series 1 and X consist of left n-alkoxy terminal, three phenyl rings, vinyl carboxylate and vinyl keto central groups as identical features. But they differ in right terminal end group Viz., $-OCH_3$ and $-H$ respectively. Therefore molecular length and hence length to breadth ratio, molecular polarity and polarizability, molecular rigidity and flexibilities vary only with terminally situated end groups $-OCH_3$ and $-H$ without varying molecular aromaticity and effects due to central groups. Therefore intermolecular adhesion anisotropic forces of attraction and suitable magnitude of end to end molecular adhesion as a consequence of molecular rigidity and flexibility are responsible to cause or induce liquid crystal properties like thermal stability occurrence or commencement of mesophase and type of mesophase etc. which vary only with presence of varying $-OCH_3$ and $-H$.The observed variation in liquid crystal properties from homologue to homologue in same series and in the same homologue from series to series are thus, attributed to the sequentially added methylene unit in left n-alkoxy terminal and varying right terminal end groups respectively. Table-3 indicates average thermal stability of series 1 and series X as under.

Table -3 : Average thermal stabilities in ^0C

Series	Average transition temperatures in ^0C	
	Series (1)	Series(X)
Nematic-isotropic	166.6 (C_5-C_{14})	144.5 (C_6-C_{16})
Commencement of Mesophase [Nematic]	C_5	C_6

It is seen from table-3 that, thermal stability of nematic mesophase of presently investigated homologous series is more than the series-X. The terminally situated $-OCH_3$ group being highly polar and polarizable as compared to $-H$ which causes higher value of thermal stability and early commencement of nematogenic mesophase. Moreover presence of $-OCH_3$ end group preferably induces nematic mesophase by generation of statistically parallel orientational order of molecules in floating condition. Such conclusions are drawn by earlier researchers.[7] Thus, present investigation very well support the earlier views. The value of thermal stability of a any sample substance is

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directly related with the thermodynamic quantity enthalpy change ΔH at a given temperature and 1 atmospheric pressure. A thermodynamic system [homologue substance] on investigation by polarising microscopic observation shows that, supplied heat from surroundings, a sample is gaining heat and exposed heat operates against intermolecular attractions within the molecular arrangement. The value of ΔH vary with temperature and sample molecular arrangement aquire gradual molecular disorder. The molecular disorder or entropy [$\Delta S=\Delta H/T$] reaches to the value, such that anisotropic forces of attractions of suitable magnitude amongst the molecules occure at a given temperature T, at which molecules of sample substance disalign at an angle less than 90º with the plane of the surface and float with statistically parallel orientational order systematically. Such molecular floating start at T_1 temperature and end at higher temperature T_2 and nematic mesophase apperars under microscopic observations for presently investigated six mesomorphic homologues (series -1).The difference of Temperature T_2-T_1 is called range of liquid crystallinity or mesognic range or mesophaselength. On continuing heating the sample from and above T_2, the mesophase disappears and molecules start dancing and moving randomly in all possible directions in an irregular manner i.e.,high order of molecular disorder or high value of molecular randomness or entropy of transition [$\Delta S= \Delta H/T$] occure. At this stage [Above T_2] isotropic phase appears under microscopic observation. Thus, group efficiency order for nematic derived on the basis of thermal stability is as under. $-OCH_3 >$ $-H$.

CONCLUSION

(1) $-OCH_3$ terminal end group is preferably nematogenic.
(2) Conclusions support the earlier views of researchers, and raises the credibility to the conclusions drawn earlier.
(3) Present series is entirely nematogenic with middle ordered range of liquid crystallinity and high melting type.

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