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Study of Ethylene Derivatives of Liquid Crystals by New Homologous Series: α-4(-4’-n-Alkoxy Cinnamoyloxy) phenyl β-4”-Nitrobenzoyl Ethylenes.

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ABSTRACT

Titled new homologous series of liquid crystal(LC) consists of eleven homologues. Methyl to butyl and dodecyl to hexadecyl derivatives of the series are nonliquid crystals while pentyl to decyl derivatives are polymesomorphic i.e. Smectic and nematic mesophases are displayed one after another in enantiotropic manner. Phase behavior is shown in phase diagram. Texture of the smectic and nematic mesophases are focal conic of smectic-A type and schlieren or threaded type respectively. Analytical data support the molecular structures of homologues. Transition and melting temperatures were determined by hot stage polarising microscope. Average thermal stability for smectic(132.25^{0}C)and nematic (171.5^{0}C) and other liquid crystal properties of present series:1 are compared with other structurally similar homologous series.

Keywords: Liquid crystal, mesomorphic, Smectic, Nematic, Mesophase.

INTRODUCTION

Present homologous series was planed to synthesize with reference to the industrial utility of liquid crystal material and effect of molecular rigidity and flexibility on liquid crystal properties of the molecules. Number of homologous series with carboxy and vinyl carboxy central bridges are reported till the date but, very rare series of LC are reported with –CH=CH-CO- central group in combination with –COO- or –CH=CH-COO-. Present series was planned to consist of three phenyl rings bridged through CH=CH-COO- and –CH=CH-CO- groups as rigid core of a moiety as well as 4’-n-alkoxy and 4”-Nitro groups as flexible part of moiety, situated at left and right terminal end. Presently, molecular structure and its relation to liquid crystallinity of the substance will be studied.

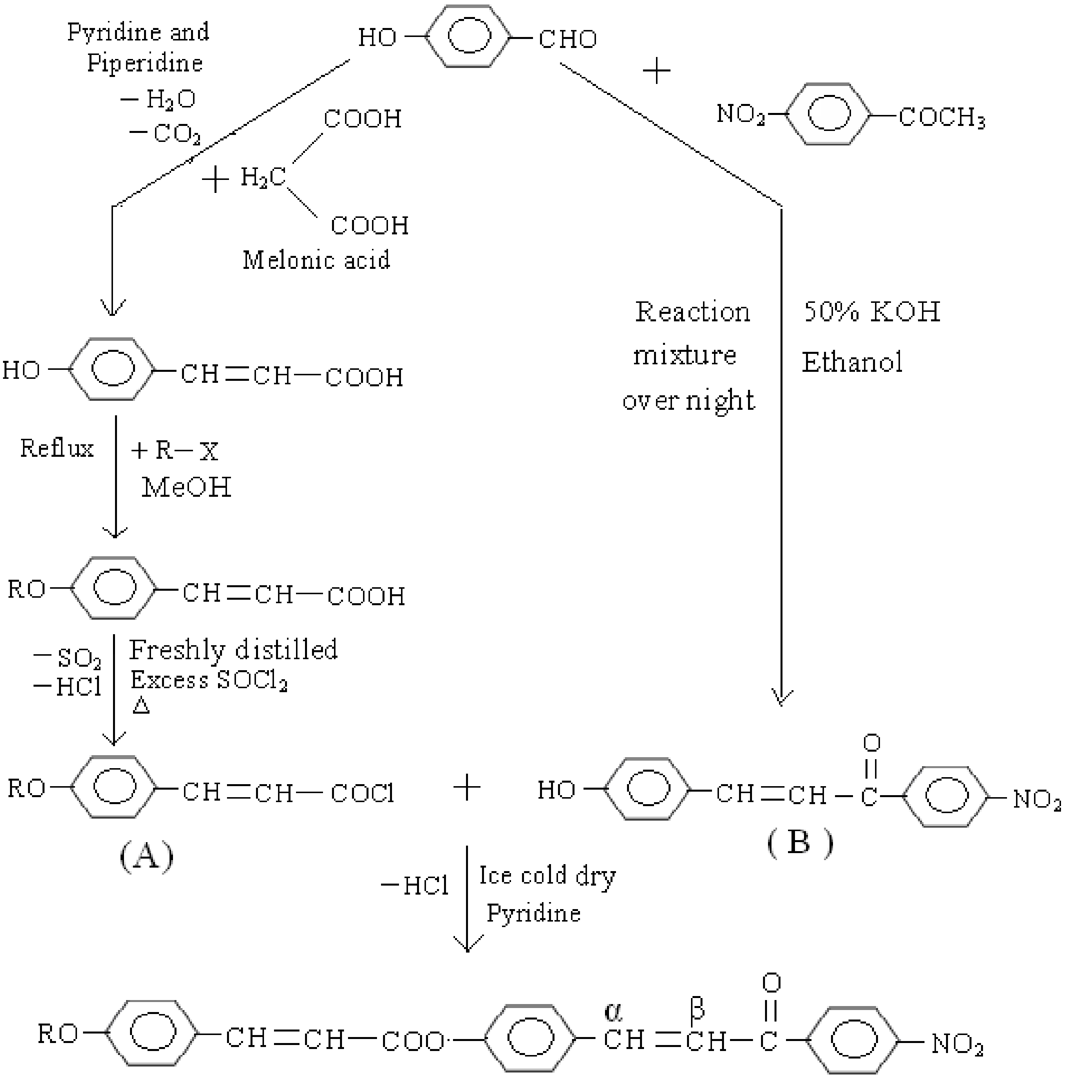
MATERIALS AND METHODS

Synthesis:

4-Hydroxy cinnamic acid was synthesized by the reaction between p-hydroxy benzaldehyde and malonic acid in pyridine in presence of few drops of piperidine [7].

Hydroxy group was alkylated by suitable alkylating agent (RX) by the modified method of Dave and Vora [4]. Cis-n-Alkoxy cinnamic acids were converted to corresponding n-alkoxy cinnamoyl chloride (A) using thionyl chloride.

α-4-hydroxy phenyl β-4'-nitro benzoyl ethylene (B) was prepared by the usual established method [4,7]. Constituent components (A) and (B) were condensed in ice cooled dry pyridine[8]. Final products were purified and recrystallised in alcohol till constant transition temperatures (Table-2) were obtained. Synthetic route to the series is mentioned below in scheme-1.



α-4(-4'-n-Alkoxy Cinnamoyloxy) phenyl β-4"-Nitrobenzoyl Ethylenes.

Where R= C_nH_{2n+1}, n=1,2,3,4,5,6,8,10,12,14,16.

Scheme-1 Synthetic route to the series

Constituent components were used as received.

Characterization:

Some selected members of the series were characterized by IR,^{1}HNMR spectra and elemental analysis. NMR spectra were recorded using $CDCl_3$ as solvent. Microanalysis was performed on CHN analyzer as shown in table-1. Transition and melting temperatures and liquid crystal properties were observed on hot stage polarizing microscope. Texture of the mesophases were determined by miscibility method.

Table: 1 Elemental analysis for propyloxy, butyloxy, dodecyloxy and tetradecyloxy derivatives.

Sr.No	Molecular formula	Elements % found (% Calculated)		
		C	H	N
1	$C_{27}H_{23}NO_6$	70.93 (70.90)	5.07 (5.03)	3.10 (3.06)
2	$C_{28}H_{25}NO_6$	71.30 (71.34)	5.29 (5.31)	2.94 (2.99)
3	$C_{36}H_{41}NO_6$	74.12 (74.10)	7.10 (7.03)	2.43 (2.40)
4	$C_{38}H_{45}NO_6$	74.68 (74.63)	7.32 (7.36)	2.27 (2.29)

Spectral data:

NMR in ppm for octyloxy derivative:

0.950 (−CH_3 of OC_8H_{17}group), 1.122 (-CH_2-)$_n$ Polymethylene group of –OC_8H_{17}), 3.690(Triplet) (-OCH_2-CH_2- of –OC_8H_{17}), 5.077 &5 5.121 broad (-CH=CH- group), 6.557 & 6.579 (-CH=CH-CO-group), 7.483,70586 & 7.607 (p-substituted phenyl ring)

NMR confirms the structure.

NMR in ppm for decyloxy derivative:

0.959 (−CH_3 of -$OC_{10}H_{21}$group), 1.179 (-CH_2-)$_n$ Polymethylene group of –$OC_{10}H_{21}$), 3.698 (Triplet) (-OCH_2-CH_2- of –$OC_{10}H_{21}$), 6.579& 6.601 (-CH=CH-CO-group), 6.579,7.608& 7.630 (p-substituted phenyl ring). NMR confirms the structure.

IR in cm^{-1} for pentyloxy derivative:

700cm^{-}1(polymethylene -(CH_2)n- group of OC_5H_{11}), 845 cm^{-}1(p-substituted phenyl ring), 1165cm^{-}1(>C=O group),1260,1610 & 1680 cm^{-1}(–COO ester group), 1430 & 1510 cm^{-1} (–NO_2 group), 920 cm^{-1} (– CH=CH- group),2875 cm^{-1}satu C-H str. Of alkyl. IR confirms the structure.

IR in cm^{-1} for Hexyloxy derivative:

700cm^{-}1(polymethylene -(CH_2)n- group of OC_6H_{13}), 840 cm^{-}1(p-substituted phenyl ring), 1140cm^{-}1(>C=O of OC_6H_{13} group),1250,1610 & 1700 cm^{-1}(–COO ester group), 1435 & 1520 cm^{-1}(–NO_2 group), 950 cm^{-1} (- CH=CH-) group. IR confirms the structure.

Texture: by miscibility Method:

1.Hexyloxy homologue:	Threaded Nematic,
2.Octyloxy homologue:	Schlieren
3. Pentyloxy homologue :	Smectic-A Type.

RESULTS AND DISCUSSION

Cis-n-Alkoxy cinnamic acid and α-4-hydroxy phenyl β-4'-nitro benzoyl ethylene(B) are nonliquid crystal. However, on linking cis n-alkoxy cinnamic acid with α-4-hydroxy phenyl β-4'-nitro benzoyl ethylene(B) through corresponding acid chloride(A) gives rise to a ketoester final product with liquid crystal property. Thus, titled homologous series showed liquid crystal property from pentyl to decyl derivatives of the series. Remaining homologues of the series are nonliquid crystal in nature.Transition temperatures in C^0 (table-2) are plotted versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal and on joining the points related to each other, a phase diagram (figure-1) is obtained for the series. On careful observation of figure-1, it indicates that, solid-isotropic or smectic transition curve follows zigzag path of rising and falling with overall rising tendency as series is ascended. Smectic-nematic transition curve initially rises and continue to rise up to decyloxy homologue with exhibition of odd-even effect. Liquid crystal property is absent from and beyond decyloxy homologue. Nematic-isotropic transition curve adopt a descending tendency as series is ascended without showing of odd-even effect. Nematic-isotropic transition curve is extrapolated for dodecyloxy, tetradecyloxy and hexadecyloxy homologues fitting the trend of the curve. The predicted probable latent transition temperatures (LTT) for dodecyl, tetradecyl and hexadecyl derivatives are 154^{0}C,145^{0}C and 138^{0}C respectively in monotropic manner. The liquid crystal property ranges minimum from 36^{0}C to a maximum 76^{0}C in pentyloxy and hexyloxy homologues respectively. Smectic and nematic mesophases commences from pentyl derivative of the series. The extent of liquid crystal property vary from homologue to homologue in the same series. Nonliquid crystal property of methyl to butyl and dodecyl to hexadecyl derivatives is due to their high crystallizing tendency which arises from unsuitable magnitudes of anisotropic intermolecular forces of attractions as a consequence of molecular rigidity and flexibility[123]. Which restricts the molecules to float in two dimensional ordered array. The exhibition of liquid crystal property by pentyl, hexyl, octyl and decyl derivatives of the series is attributed to the molecular disalignment at an angle less than 90^0, withstanding external thermal vibrations exposed upon them as a result of suitable magnitudes of intermolecular anisotropic forces of attractions. Such situation is favourable to induce lamellar packing of molecules which causes smectogenic character by occurring sliding layered arrangement of molecules and then at higher temperature maintain statically parallel orientational order of molecules in floating condition. Thus, smectic and nematic mesophases are observed under hot stage polarizing microscopy; for four homologues. The liquid crystal properties and thermal stability of titled homologous series1 are compared with structurally similar homologous series Z as shown in figure-2 and table-3 respectively.

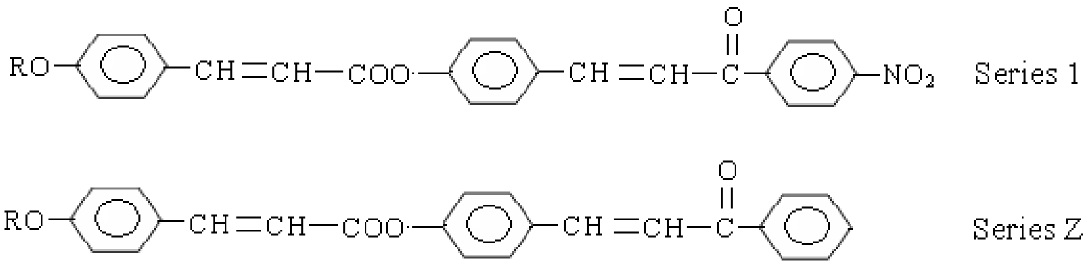


Figure:2 Structurally similar homologous series

Series 1 and Z are identical with respect to their rigidity caused by three phenyl rings and molecular aromaticity but they differ with reference to their magnitudes of flexibility due to the difference of right handed terminal end group $–NO_2$ and –H. This difference causes difference in their molecular length, length to breath ratio, molecular polarity and polarizability, steric hindrance, molecular size and hidden magnitudes of anisotropic intermolecular forces of attractions, which are responsible to induce smectic and/or nematic mesophase formation in floating condition, commencement of mesophase, degree of mesomorphism, transition temperature, average thermal stability of smectic and nematic phase etc. Table-3 depicts the average thermal stability of smectic and nematic mesophases as mentioned below.

Table-3: Average Thermal stability in ^{0}C

Series→	Series-1	Series-Z
Smectic-Nematic Commencement of Smectic phase	132.25 (C_5—C_{10}) C_5	--
Nematic-Isotropic Commencement of Smectic phase	171.5 (C_5—C_{10}) C_5	144.5 (C_6—C_{16}) C_6

Table-3 indicate that smectic and nematic thermal stability of series1 are higher than seriesZ under comparison. Moreover mesophase formation takes place from pentyl to decyl derivatives in series1 while, it takes place from hexyl to hexadecyl derivatives for seriesZ with relatively shorter phase length as compared to series1. Such behavior is attributed to the higher polarity of $–NO_2$ terminal end group as compared to –H of seriesZ; which causes relatively higher magnitudes of intermolecular end to end terminal attraction and sliding layered formation from lamellar packing in case of series1 while sliding layered arrangement in series Z fails to form due to absence of lamellar packing of molecules. Moreover extent of molecular noncoplanarity difference in series 1 causes early commencement of smactic phase which does not appear till the last hexadecyl homologue of seriesZ. Thus, present series1 is equiprapotionally smectogenic and nematogenic with high melting type. The variations in mesogenic property observed from homologue to homologue in the same series is attributed to the sequentially added methylene unit at the left n-alkoxy terminal end group and variation in mesogenic property observed for the same homologue from series to series is attributed to the right terminal end group of fixed polarity for all the homologues of the series.

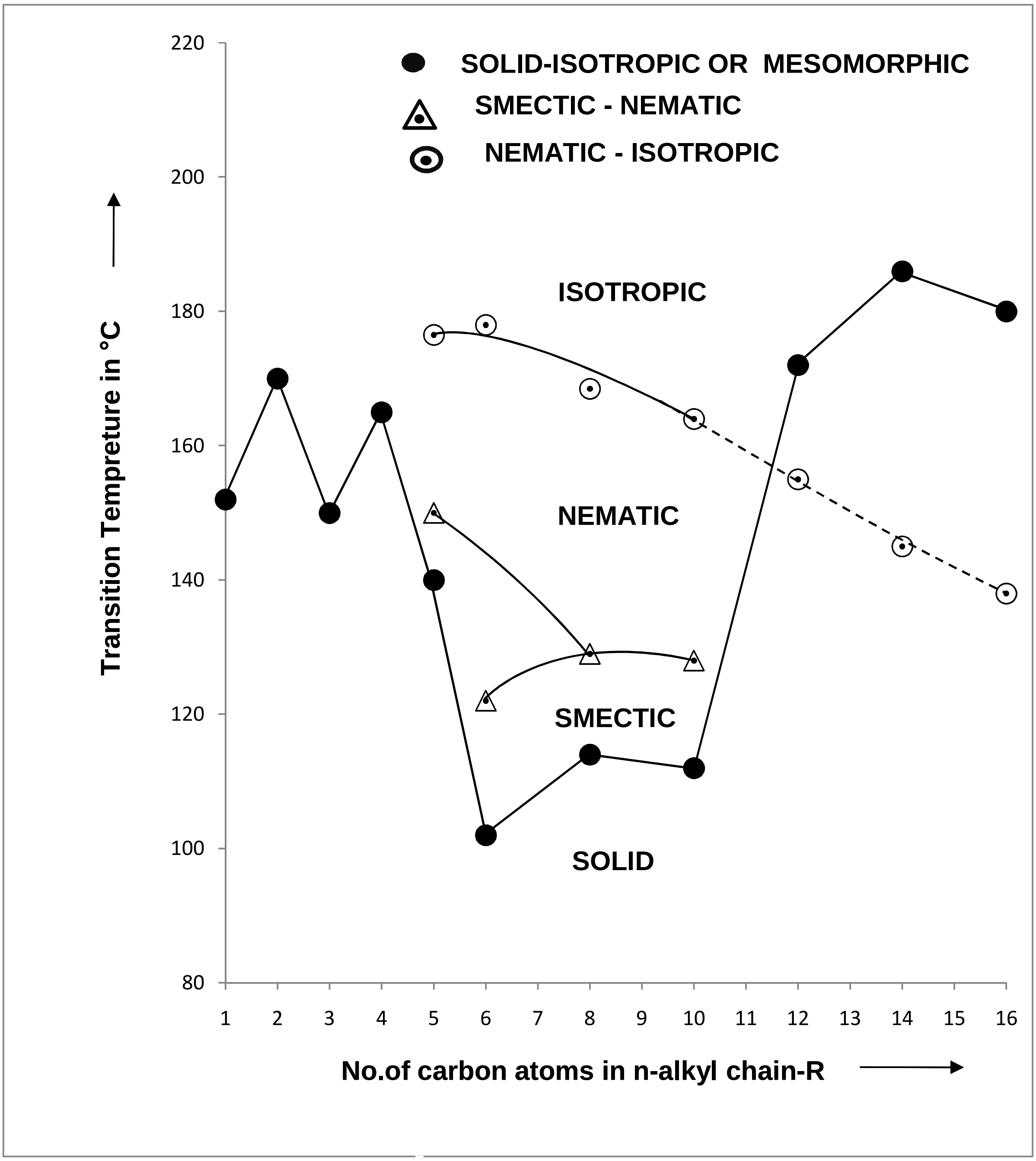


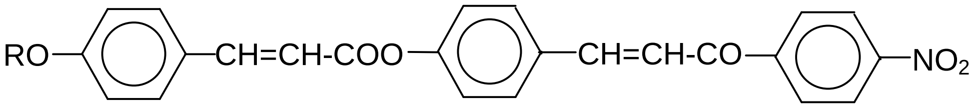
Figure :1 Phase Behavior of Series

Table-2: Transition Temperatures in ^{0}C of series-1.

Compound No.	R=C_nH_{2n+1} (n)	Sm	Nm	Isotropic
1	1	-	-	152.0
2	2	-	-	170.0
3	3	-	-	150.0
4	4	-	-	165.0
5	5	140.0	150.0	176.0
6	6	102.0	122.0	178.0
7	8	114.0	129.0	168.0
8	10	112.0	128.0	164.0
9	12	-	-	172.0
10	14	-	-	186.0
11	16	-	-	180.0

Sm= Smectic; Nm= Nematic.

Homologous Series: α-4-[4'-n-Alkoxy Cinnamoylokxy] phenyl β-4''- Nitrobezoyl ethylenes



CONCLUSION

(1) Group efficiency order derived for smectic and nematic mesophases on the basis of thermal stability is, NO_2 > H

(2) Variation in molecular moiety causes variation in molecular polarity, polarizability as a consequence of molecular rigidity and flexibility which are responsible to occur mesophase formation.

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