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Synthesis and study of a new homologous series of Cis Cinnamate Esters of Mesogens: *n*-Hexyl-*p*-(*p*/-*n*-alkoxy cinnamoyloxy) Cinnamates

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ABSTRACT

Ester homologous series of mesogens of cis configuration viz. n-Hexyl-p-(-p/-n-alkoxy cinnamoyloxy) cinnamates is synthesized and studied to understand and establish the relation between the molecular structure and mesogenic properties. Twelve homologues are synthesized. Methyl and ethyl derivatives of homologues are nonmesogenic while, n-propyl to n-octyl, n-decyl, n-dodecyl, n-tetradecyl and n-hexadecyl derivatives of the homologues are enantiotropically nematogenic in nature. Enantiotropic smectogenic character commences from heptyloxy derivative and end to tetradecyl homologue. Smectic mesophase is absent in hexadecyloxy homologue. Transition temperatures and melting temperatures of homologues are observed through hot stage polarizing microscope. A phase diagram obtained from transition temperatures of homologues. The solid-isotropic/ mesomorphic transition curve adopt a zigzag path of rising and falling tendency in normal manner. Smectic-nematic transition curve rises from n-heptyloxy homologue and exhibit falling tendency up to tetradecyloxy homologue and behaves in normal manner without odd-even effect. Nematic-isotropic transition curve initially rises from propyloxy homologue and passes through a maxima at the octyloxy homologue and then smoothly falls to the hexadecyl homologue with exhibition of odd-even effect. Thus nematic-isotropic transition curve behaves in usual manner. The texture of the nematic mesophase is of focal conic fan or batonnate shaped. Analytical data support the molecular structure of homologues. Thus, series is predominantly nematogenic and partly smectogenic in enantiotropic manner.

Keywords: Liquid crystals, Smectic, Nematic, Mesogens, Mesomorphs.

INTRODUCTION

The physical and chemical properties of a substance depend upon its molecular structure. Number of liquid crystal substances are synthesized through homologous series and reported till the date. In present investigation new homologous series of mesogens is synthesized with a view to understand and establish the relation between liquid crystal properties and molecular structure by linking the terminal end group viz, -CH=CH-$COOC_6H_{13}$ (n). Thus, variation made in the molecular structure by changing central, terminal or lateral group or moity or geometrycal shape of molecule may result into production of newer substances which may replace a substance which is already in use. Moreover, a new liquid crystal substance may avail at a reduced cost, serving with the same purpose or giving better work at economical cost than earlier substance used. The application of liquid crystals in various fields like electronic display [LCD], devices, thermographic materials in medical field, testing and analysis of drugs and chemical etc. has attracted to synthesis new liquid crystals substances.

MATERIALS AND METHODS

Experimental

(a) Synthesis of p-n-alkoxy cinnamic acids from p-hydoxy cinnamic acid:
p-Hydroxy cinnamic acid prepared from p-hydroxy benzaldehyde and malonic acid in presence of pyridine and few drops of piperidine is alkylated by corresponding alkyl halide by the modified method of Dave and Vora (3)

(b) Synthesis of p-n- alkoxy cinnamoyl chloride :
p-n-Alkoxy cinnamic acids are refluxed with excess of freshly (5) distilled thionyl chloride. Excess of thionyl chloride is removed by distillation and acidchloride formed is preserved as it is, without further purification in the same flask by air tight cork in moisture free atmosphere under ice cooled temperature.

(c) Synthesis of p-hydroxy n-hexyl cinnamate. (6)
p-Hydroxy n-hexyl cinnamate prepared by refluxing a mixture containing equimolar proportion of p-hydroxy cinnamic acid and anhydrous n-hexanol in presence of two milliliter sulphuric acid on sand bath for seven hours. The reaction mixture poured in excess of ice cooled water after reflux. Product filtered, washed and purified from alcohol M.P.160^{OC} yield 61.68%.

(d) Synthesis of n-Hexyl-p-(-p$^{/}$-n-alkoxy cinnamoyloxy) cinnamates:
Ice cooled solution of p-hydroxy n-hexyl cinnamate in pyridine (c) is cautionly added to ice cooled flask containing acid chloride (b) drop wise with constant shaking and resulting mixture warmed for half an hour and kept over night. Next day product decomposed by 1:1 HCl solution. Solid product filtered, washed, dried and purified.

Schematic rout of synthesis is represented in figure-III seperatly.

(e) Transition temperatures of homologues are observed through hot stage polarizing microscope. Structure of some selected homologues are confirmed by elemental analysis, IR and ^{1}HNMR spectra. Attempt is made to determine enthalpy change (ΔH) from peak value of temperature by D.S.C. scan, but, it has been not possible due to inconveniency of laboratory concern. Therefore qualitative approach to enthalpy (ΔH) and entropy (ΔS) is discussed. The type of textures for nematic and smectic mesophases are determined by miscibility method and by observing a sample directly in the field of view of polarizing microscope.

Table-1: Homologous Series: n-Hexyl-p-[p/-n-alkoxy Cinnamoyloxy] Cinnamates.

Sr.no	R= n-alkyl group	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	192.0
2	Ethyl	-	-	186.0
3	Propyl	-	160.0	170.0
4	Butyl	-	167.0	187.0
5	Pentyl	-	170.0	192.0
6	Hexyl	-	178.0	206.0
7	Heptyl	171.0	195.0	213.0
8	Octyl	168.0	198.0	219.0
9	Decyl	172.0	190.0	208.0
10	Dodecyl	145.0	179.0	196.0
11	Tetradecyl	110.0	136.0	170.0
12	Hexadecyl	-	136.0	148.0

Where n=1,2,3,4,5,6,7,8,10,12,14 and 16.

Analyticaldata:
NMR: in ppm :
Octyl
0.840 – -CH_3 ; 2.490 – O-CH_2 ; 4.20 – O-CH_2 of –$COOC_6H_{13}$; 3.98-O-CH_2 of –C_8H_{17}; 4.4 and 4.0 – CH=CH-; 6.80, 6.83, 7.74 and 7.78 – P-sub.phenyl two p-sub.benzene; 7.24and 8.02 - P-sub.phenyl two p-sub.benzene

Dodecyl
0.88 – -CH_3; 1.55 – -CH_2 ; 2.40- -OCH_2-CH_2-; 4.00– O-CH_2 of–$COOC_6H_{13}$; 3.31-O-CH_2 of $C_{12}H_{25}$; 4.48 – CH=CH-; 6.896 and 6.925, – Two p-sub.phenyl ring; 8.039 and 8.011, - Two p-sub.phenyl ring

IR in cm^{-1}
Tetradecyl
2900.0 Confirms alkyl group; 1080, 1260, & 1700 Confirms –COO- group; 660 Confirms cis –CH=CH- group; 860 Confirms p-sub. phenyl ring; 3000 Confirms aromatic ring; 750 Confirms polymethylene of $C_{14}H_{29}$
IR confirms above structure

Hexyl
2850.0 Confirms alkyl group; 1050,1150, & 1710 Confirms –COO- group; 660 Confirms cis –CH=CH- group; 850 Confirms p-sub. phenyl ring; 2900 Confirms aromatic ring; 750 Confirms polymethylene of C_6H_{13}

Table-2: Elemental Analysis

Sr. No.	R=n-alkyl chain	Moleculaformula	Calculation %		Observation %	
			C	H	C	H
1.	Ethyl	$C_{26}H_{30}O_5$	73.93	7.11	73.63	7.11
2.	Butyl	$C_{28}H_{34}O_5$	74.57	7.56	74.57	7.56
3.	Pentyl	$C_{29}H_{36}O_5$	75.00	7.76	75.13	7.36
4.	Heptyl	$C_{31}H_{40}O_5$	75.61	8.13	75.56	7.13

Texture of the mesophase by miscibility methods: *Nm. n=1,3,10,16 and Sm. n= 10, 12 14.*

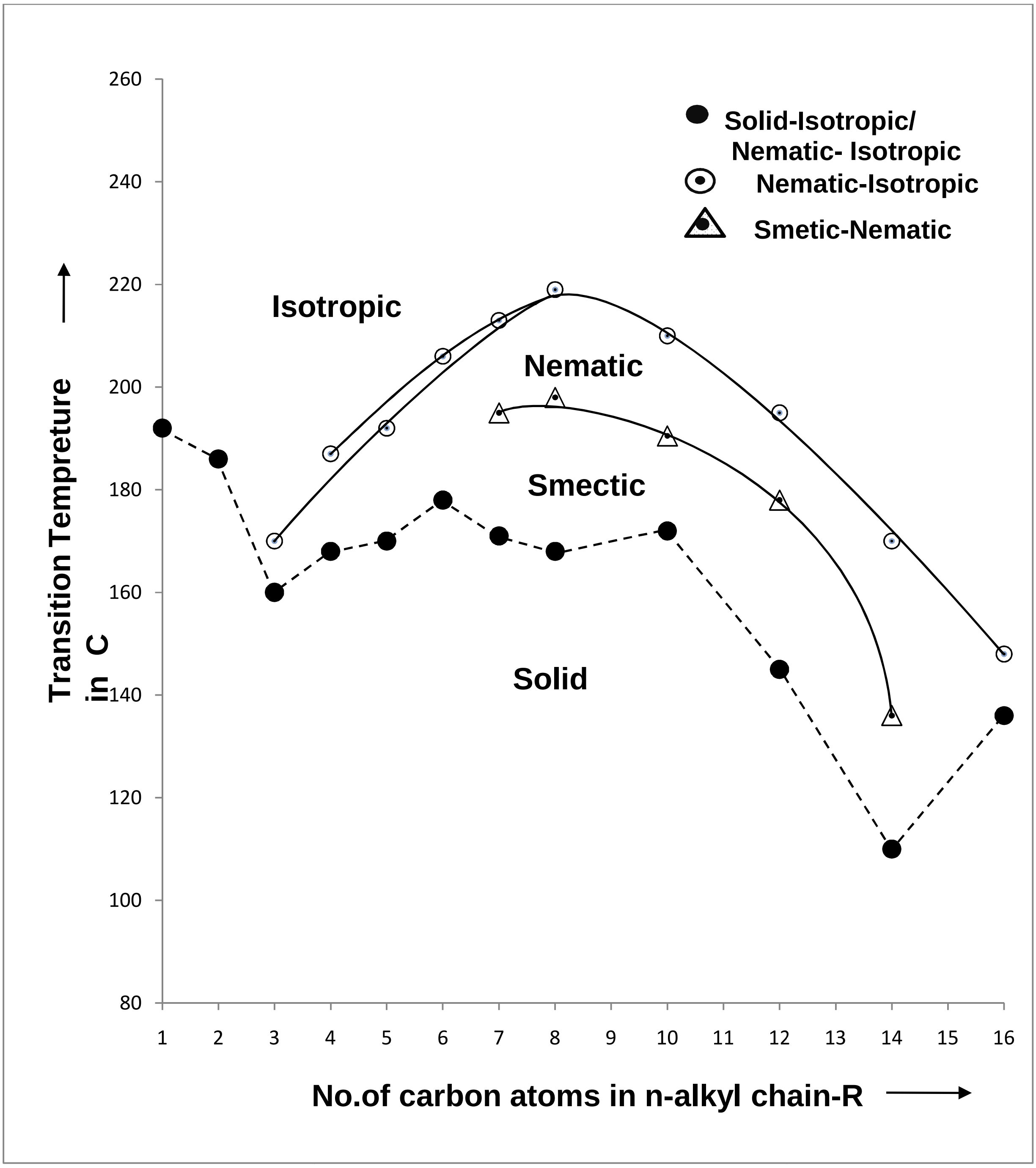


Figure: I Homologous Series: n-Hexyl-p-[p/-n-alkoxy Cinnamoyloxy] Cinnamates.

RESULTS AND DISCUSSION

Homologues of the homologous series entitled n-hexyl-p-[p/-n-alkoxy Cinnamoyloxy] Cinnamates are geometrically cis isomers as determined from spectroscopic data. Methoxy and ethoxy homologues are nonmesogenic while, propyloxy to octyloxy, decyloxy,dodecyloxy, tetradecyloxy and hexadecyloxy derivatives are enantiotropically nematogenic. Heptyloxy, octyloxy, decyloxy, dodecyloxy and tetradecyloxy homologues exhibits enantiotropically smectogenic mesophase in addition to nematogenic mesophase. Smectogenic character is missing in hexadecyloxy homologue. Transition and melting temperatures are carefully observed through hot stage polarizing microscope and recorded in table-1. Transition temperatures of homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n- alkoxy termally situated end group. Like points are linked and a phase diagram is obtained as shown in figure-I.

Carful examinations of a phase diagram (Figure-I) reveals that, solid-isotropic / mesomorphic transition curve adopt a descending tendency as services is ascended following a zigzag path of overall rising and falling tendency. It falls from methoxy to propyloxy homologue and rises to hexyloxy homologue, then it falls to tetradecyloxy homologue with intermitant rise of only four degree centigrad at decyloxy homologue and considerable rise at hexadecyloxy homologue take place without disturbing overall falling tendency. Thus, solid-isotropic / mesomorphic transition curve behaves in normal manner.

Smectic-nematic transition curve slightly rises from heptyloxy to octyloxy homologue and then it falls to the tetradecyloxy homologue in usual manner without exhibition of odd-even effect. Texture of nematic and smectic mesophases determined by miscibility method. Smectic-A type of mesophase is exhibited by heptyloxy, octyloxy, decyloxy and dodecyloxy derivatives. Tetradecyloxy derivative shows smectic-C texture as judged directly from fields of view of microscope. Texture of nematic mesophase is of threaded type.

Nematic- isotropic transition curve initially rises, passes through maxima at the octyloxy derivative and than it smoothly falls to the hexadecyloxy derivative in normal manner. Odd-even effect is observed for nematic-isotropic transition curve. Thus, nematic isotropic transition curve fits two curves which rises to late maxima at the octyloxy homologue and merge into each other at the maxima (15 to 20) before smooth falling to hexadecyloxy homologue.(14).

Methoxy and ethoxy derivatives of titled homologous series are nonmesogenic, though the geometrical shape of molecules is long linear lath like or rod like with sufficient rigidity and flexibility. However, because of their shorter left n-alkoxy terminals viz. Methoxy and ethoxy causes strong intermolecular forces of attractions amongst the molecule inducing high crystalising tendency. High crystalising tendency gives rise to formation of thermodynamically more stable system of crystal lattices by releasing energy (ΔH) from system to surroundings. Conversely on heating the thermodynamically stable system, it destabilizes by absorbing heat energy (ΔH) from surrounding to system which correspond to magnitude of intermolecular adhesion forces. Thus, intermolecular end to end and lateral attractive forces being too strong, the thermal vibrations exposed upon the molecules having highly polarizable methoxy and ethoxy left terminal end groups become unable to resist such high energetic thermal vibrations.

So that, thermodynamically stable system (crystals) tend to destabilize to a state of higher entropy or randomness at particular temperature t_1^{0C} and continue for higher temperature t_2^{0C} where $(t_2 - t_1)$ = range of temperature and entropy, $\Delta S = \Delta H / T$ and $T = t^{0C} + 273$. Where T = absolute temperature in degree Kelvin and t = transition temperature in degree centigrade. For, nonmesomorphic homologues like methyl and ethyl derivatives of series $(t_2 - t_1) = 0$ i.e. $t_2 = t_1 = t$ but for enantiotropic transition $t_2 > t_1$ and for monotropic $t_2 < t_1$. Thus, sample molecules of methyl and ethyl homologues under examination are unable to maintain adequate ordered arrangement of molecules in floating condition because, inter molecular forces are neither anisotropic nor of suitable magnitude as a consequence of molecular bending, molecular rigidity and flexibility. Hence, molecules of methyl and ethyl homologues having individually lath like shape disalign at an angle less than 90^{0C} on the plane of surface and molecules are randomly oriented without any ordered arrangement in floating condition corresponding to inadequate magnitude of entropy. Under this situation, disaligned molecules restricts the formation of statistically parallel orientational order of molecules as intermolecular cohesion forces are neither anisotropic, nor of suitable magnitude, which inhibits the formation of nematogenic mesophase. Thus, high order of disorder exists amongst the molecules under very low intermolecular mutual adhesion forces resulting into direct normal melting (8) of solid crystals into isotropic liquid without passing through an anisotropic liquid state called liquid crystal state or mesogenic state. Hence, molecular arrangement on thermal disturbance causes molecules to move out of alignment adopting Brownian movement. Thus, entropy (ΔS) or randomness or disorderness cause thermodynamically stable system to destabilize preventing exhibition of mesogenic state of existence.

As left n-alkoxy chain is lengthened by sequential addition of methylene unit progressively, the crystalline character decreases and amorphous character gradually rises. On increasing temperature, intermolecular forces of attractions are weakened with increase of temperature and hence,entropy or randomness increases in usual manner. But, magnitude of randomness or disorder does not allow to disalign the molecules of sample substance under investigation. Thus, molecules under vibrational motion are able to resist thermal vibrations imposed upon them which do not restrict the occurrence of statistically parallel orientational order of molecules in floating condition within definite range of temperature for propyloxy to octyloxy, decyloxy, dodecyloxy, tetradecyloxy and hexadecyloxy homologues of the series. Thus, propyloxy to hexadecyloxy homologues exhibit nematogenic mesophase.

Exhibition of smectic mesophase by heptyloxy, octyloxy, decyloxy, dodecyloxy and tetradecyloxy homologues are attributed to the originally present lamellar packing of molecules in layered crystal lattices of molecular structure and thereby sliding layered arrangement of molecules in floating condition is maintained without any disturbance for particular range of temperature. Thus, magnitude of randomness or entropy of heptyloxy to tetradecyloxy homologue molecules resist thermal vibrations from imposed thermal energy which maintain two dimensional array of molecules to move with sliding layered arrangement relatively at lower temperature than nematic-isotropic transition temperature for above set of homologues, concern with exhibition of smectic character. Intermolecular cohesive anisotropic forces are weakened to such an extent of hexadecyloxy homologue that, lamellar packing of molecules being originally present or absent in crystal lattices, the absence of sliding layered arrangement of molecules in floating conditions causes the occurance of smectic character missing. However molecules are able to resist thermal vibrations and causes to maintain statistically parallel orientational order of molecules in floating condition in absence of sliding layered arrangement of molecules. Thus, hexadecyloxy homologue exhibit only nematogenic character without exhibition of smectogenic character, while heptyloxy to tetradecyloxy homologues are smectogenic in addition to nematic character. Odd-even effect observed for nematic-isotropic transition curve is due to the sequential addition of methylene unit. Both curves for odd and even homologues merge into each other at the octyloxy homologue. Alternation of transition temperature diminishes as series is ascended for higher homologues, because 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 contacts would than ultimately be the same for odd and even homologue. Mesomorphic range varies minimum from 10.0^{0C} at the propyloxy homologue to maximum 60.0^{0C} at the tetradecyloxy homologue. Nematic-isotropic transition temperature varies between 148.0^{0C} at hexadecyl homologue and 219.0^{0C} at the octyloxy homologue. Thus, series is of low mesomorphic length and middle ordered melting type.

Mesomorphic properties like thermal stability, range of liquid crystallinity, odd-even effect, commencement of smectic and nematic mesophase, extent of noncoplanarity causing early or late commencement of smectic mesophase etc. are compared with structurally similar homologous series as under from table-3 and figure-II respectively.

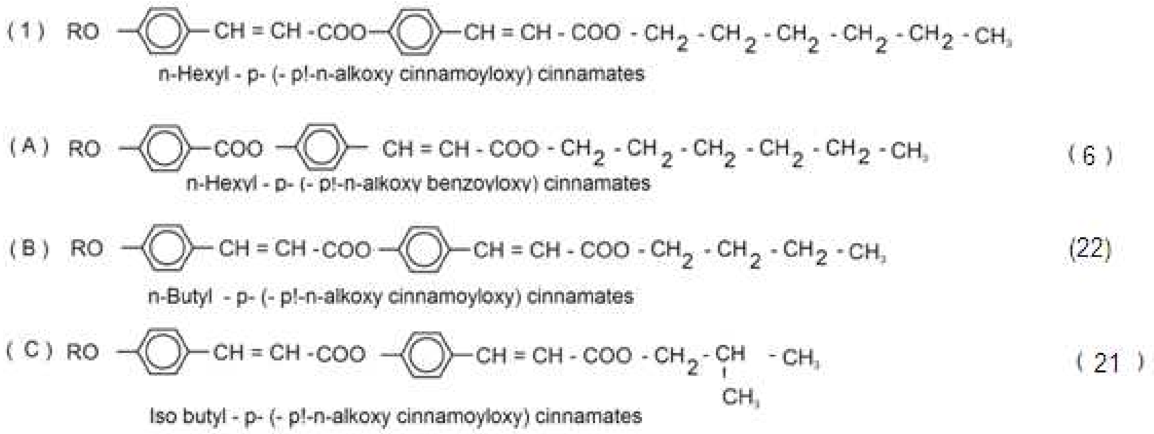


Figure-II

All the homologous series under comparision (figure-II) have two phenyl rings and left n-alkoxy terminal end group contain as common identical part, but they differ with respect to central and / or right terminal end groups without laterally substituted group. Homologous series (1) and (A) contain left and right terminal end groups and two phenyl rings as common identical part but they differ with respect to central bridges viz; vinyl carboxylate and carboxy –COO- group. Homologous series (1), (B) and (C) differ with respect to only right terminal end group keeping remaining molecular part or moity common including central bridge. Homologous series (A), (B) and (C) differ with respect to central and right terminal end group keeping remaining part viz; two phenyl rings and left n-alkoxy groups unchanged. The variation of molecular structure causes variation in molecular rigidity and molecular flexibility, molecular length, molecular dipolarity and polarizibility, intermolecular distance, length to breadth ratio, ratio of the polarity to polarizibility, intermolecular distance etc. These above factors play role differently for different homologous series (1), (A), (B) and (C) and contribute different magnitude of end to end and lateral attractions to the homologous series under comparition.

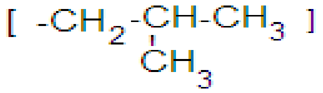
The variation in mesomorphic or liquid crystal properties from homologue to homologue in same series is occurred due to sequentially added methylene unit in n-alkyl chain of left in alkoxy terminal and any other varying molecular part, keeping right terminal two phenyl rings and central bridge intact. Similarly the variation in liquid crystal or mesomorphic properties for same homologue arises from series to series depend upon either varying terminal end group (right side) or varying central group keeping any one or both group unchanged alternatively from series to series. Thus, observed variation in mesomorphic properties for same homologue between series (1) to series (A) arise due to varying central bridge only. The variation in mesomorphic properties for same homologue among the series (1), to series (B) to series (C) arise due to varying right terminal end group –CH=CH-COOR where R= $-C_6H_{13}$, $-C_4H_9$ (n) and $–C_4H_9$ (iso) for series (1), (B) and (C) respectively.

Table- 3: Average thermal stability

Series	**(1)**	**(A)**	**(B)**	**(C)**
Smectic-isotropic or Smectic-nematic	179.6 $C_7 – C_{14}$)	93.2 ($C_8 – C_{14}$)	101.0 ($C_{10} – C_{12}$)	-
Commencement of smectic mesophase	C_7	C_8	C_{10}	-
Nematic - Isotropic	190.9 (C_3-C_{16})	136.4 ($C_6 – C_{14}$)	140.0 (C_5-C_{16})	138.5 (C_5-C_{16})
Commencement of Nematic mesophase	C_3	C_6	C_5	C_5

The nematic-isotropic thermal stability and smectic-isotropic or smectic-nematic thrmal stability of titled homologous series (1) are the highest (table-3) among the homologous series under comparison. The longest linear lath like molecular shape of series (1) causes strongest intermolecular forces of end to end and lateral attractions due to the high magnitude of molecular rigidity, flexibility and molecular length in presence of highly polarizable vinyl carboxylate as central and terminal group. Homologous series (A) having same vinyl carboxylate terminal end group but having shorter centeral group –COO- causes reduction in molecular length and length to breadth ratio and hence the intermolecular forces of adhesion as compared to series (1). Hence series (A) has lower thermal stability. The nematic-isotropic thermal stability of series (A), (B) and (C) are almost nearer or say equivalent viz. 136.4, 140.0 and 138.5^{0C} respectively. However they differ mutually in respect of smectic-isotropic thermal stabilities considerably because, smectic mesophase is not exhibited by series (C) while series (A) and (B) exhibit smectic mesophase but the values of smectic thermal stabilities are relatively much lower than series (1). Relatively shorter molecular length in combination with molecular width causing anisotropic intermolecular forces of the adhesion results into difference of smectic thermal stability and mesogenic properties, among the series under discussion.

Early or late commencement of smectic mesophase depend upon the extent of noncoplanarity caused by the molecules. According to Dave and Kurian,(12) early commencement of smectic mesophase is related with less noncoplanarity of the molecules. Homologous series (1) and (A) under comparison resemble in all respects except the central bridges which are –CH=CH-COO and –COO- respectively. Though vinyl carboxylate –CH=CH-COO- has greater length than -COO- should cause more noncoplanarity due to a twist obtained as the oxygen atoms of vinyl carboxylate group bump into the non bonded adjacent hydrogen atoms of aromatic phenyl rings, which should cause considerable strain on the molecule. Consequently a twist around C-O bond should occure forcing phenyl rings out of plane of the molecule. But from table-3, the commencement of smectic mesophase take place from seventh homologue i.e. length of central bridge seems ineffective in causing to increase of extent of noncoplanarity for series (1) as compared to series (A). But, incase of series (B) and (C), the above effect due to shorter alkyl [-C_4H_9 (n) and – C_4H_9 (iso)] chain operate effectively as compered to series (1) and (A). Thus, late commencement of smectic mesophase i.e. from tenth homologue occours in series (B) with normal linking in butyl group and effect due to the presence of isobutyl



$$[\ -CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3\ ]$$

linking as a part of–CH=CH –COO- C_4H_9 [iso] terminal end group causing steric hindrance in series (C), causes more twist, inducing some more extent of noncoplanarity than molecules of series (1), (A) and (B). Thus, smectic mesophase does not occure to appear till the last homologue of series (C) i.e. smectic mesophase is totally absent due to steric hindrance, caused more by isobutyl group than other terminal end group, viz; -C_4H_9(n) and –C_6H_{13} (n).

Thus, group efficiency order derived for smectic and nematic mesophases on the basis of thermal stabilities for terminal end groups are as under.

Smectic group efficiency order:

$-CH{=}CH{-}COOC_6H_{13}$ (n) > $CH{=}CH{-}COOC_4H_9$(n) > $-CH{=}CH{-}COOC_6H_{13}$(n) > $CH{=}CH{-}COOC_4H_9$(iso)

with vinyl carboxy central bridge	with vinyl carboxy central bridge	withcarboxy central bridge(-COO-)	with vinyl carboxyl cenral bridge

Nematic group efficiency order:

$-CH{=}CH{-}COOC_6H_{13}$ (n) > $CH{=}CH{-}COOC_4H_9$(n) > $-CH{=}CHCOOC_4H_9$(iso) > $-CH{=}CH{-}COOC_6H_{13}$(n)

with vinyl carboxyl central bridge	with vinyl carboxyl central bridge	with vinyl carboxyl central bridge	with (-COO-) central bridge

Scheme of synthesis

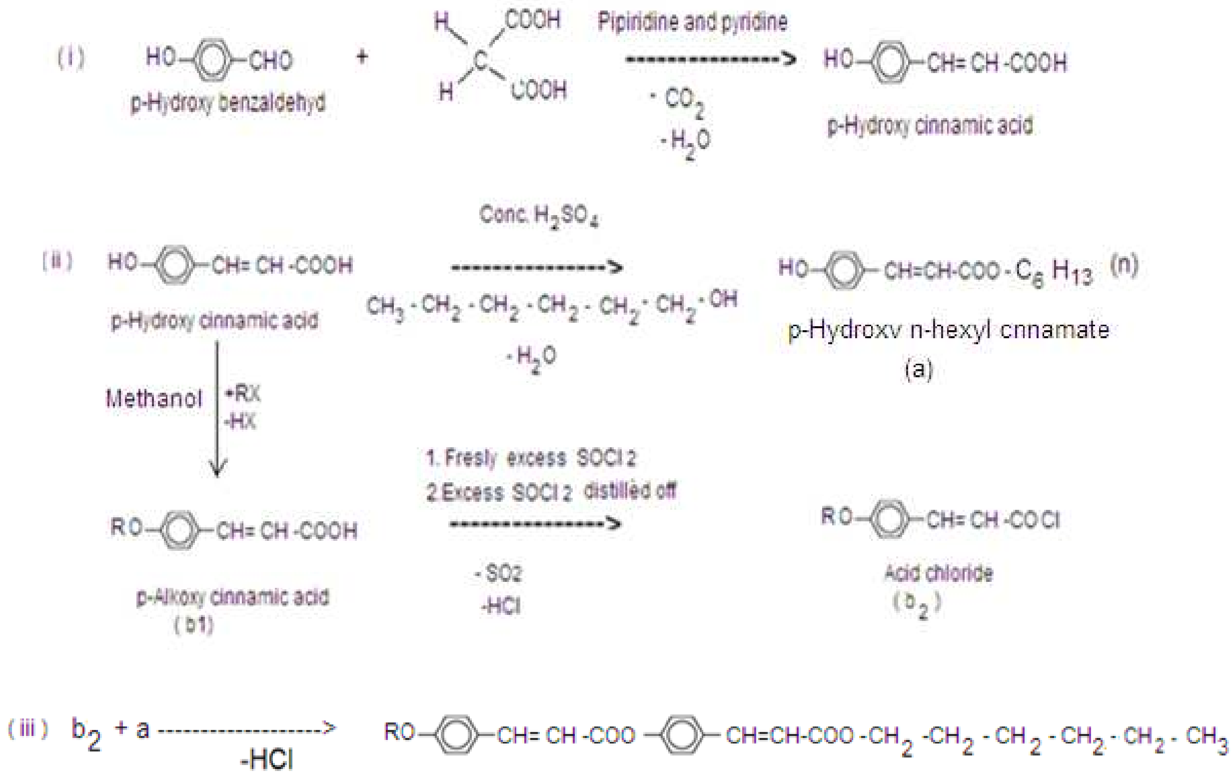


Figure – III

Where $R=C_nH_{2n+1}$ *and n= 1,2,3,4,5,6,7,8,10,12,14 and 16*

CONCLUSION

A titled new homologous series of mesogens n-hexyl-p-(p/-n-alkoxy cinnamoyloxy) cinnamates is predominantly nematogenic and partly smectogenic with middle ordered melting type and low mesopashe range supporting early views (1 to 4,8) and strengthened the credibility to the established relation between liquid crystallinity and molecular structure.

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