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Der Pharma Chemica, 2011, 3(1): 72-82
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ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis and Study of Mesogenic Material Through Homologous Series: *n*-pentyl-*p*-(*p*'-*n*-alkoxy cinnamoyloxy) Cinnamates

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ABSTRACT

The titled new homologous series of twelve mesogens is synthesized by usual established method with, a view to understand and establish the relation between mesogenic properties of the substances and their molecular structure. Methyl to butyl derivatives of the homologous series are nonmesogenic, while pentyl, hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives are enantiotropically mesogenic in character. Pentyl, tetradecyl, hexadecyl derivatives are nematogenic only, while, hexyl to dodecyl derivatives are polymesomorphic i.e. smectic and nematic, both mesophases are exhibited enantiotropically by hexyl to dodecyl homologues. Transitions and melting temperatures of homologues are determined by the polarizing microscope with heating stage. Transition temperatures are plotted versus number of carbon atoms in *n*-alkyl chain of left *n*-alkoxy terminal end group. A phase diagram is obtained by joining like points. Solid-mesomorphic or solid-isotropic transition curve initially follows zigzag path of rising and falling upto butyl homologue and then falls gradually upto decyl homologue and again rises steeply to a hexadecyl homologue in a rounded shape from decyl to hexadecyl derivative of the series. Smectic-nematic transition curve, behaves in normal manner and merges solid-mesomorphic / isotropic transition curve at the tetradecyl derivative of homologue, with showing up of odd-even effect. Nematic-isotropic transition curve wonderfully show rising tendency as series is ascended with alternation of transition temperatures, showing odd-even effect. Texture of nematic mesophase is of threaded type and that of smectic mesophase is focal conic fan shaped of the type-A. Analytical data support the structure of the molecules.

Keywords : Liquid crystals, Mesophase, Smectic, Nematic, Mesogen.

INTRODUCTION

The liquid crystal materials are used in various fields of applications like medical field, manufacture of electronic display devices, chromatography, analysis of chemicals and drugs, hot spot identification, or to locate cancerous area of tissues and many other applications. The present investigation is planned to make available mesogenic material at economical cost through

synthesis of new mesogenic homologous series by structural variation. Thus, simultaneously the effect of structural variation can be co-related with mesogenic properties.

MATERIALS AND METHODS

Material :

(I) *p*-Hydroxy cinnamic acid :

p-Hydroxy cinnamic acid prepared from *p*-hydroxy benzaldehyde (0.15 mole) and malonic acid (0.375 mole) in presence of few drops of piperidine in pyridine (50 ml) by refluxing reaction mixture, till rapid evolution of CO₂ ceased (9, 10). Product decomposed by excess of water containing hydrochloric acid. The resultant product filtered, washed, dried, and crystallised from alcohol. M. P. 214^{0C}, yield is 70.0 %.

(ii) *p*-*n*-Alkoxy cinnamoyl chloride :

The reaction mixture of *p*-hydroxy cinnamic acid and corresponding *n*-alkyl halide reacted to yield *p*-*n*-alkoxy cinnamic acids (9, 10) by modified method of Dave and Vora (3). Purified form of *n*-alkoxy cinnamic acid is treated with excess of freshly distilled thionyl chloride by refluxing reaction mixture for three to four hours till evolution of SO₂ gas ceased. Excess of thionyl chloride is distilled off and acid chloride used as it is, for further reaction without purification. The acid chloride yielded was preserved in moisture free atmosphere for further reaction (5).

(iii) *Synthesis of p*-hydroxy *n*-pentyl cinnamate:

Equimolar proportion of *n*-pentyl alcohol and *p*-hydroxy cinnamic acid refluxed for three to four hours in presence of two milliliter conc. H₂SO₄. The reaction mixture poured in excess quantity of ice cold water to decompose the product after reflux. Solid product filtered, dried, washed and crystallised in alcohol. M. P. 122.0^{0C}, yield is 58.7 %.

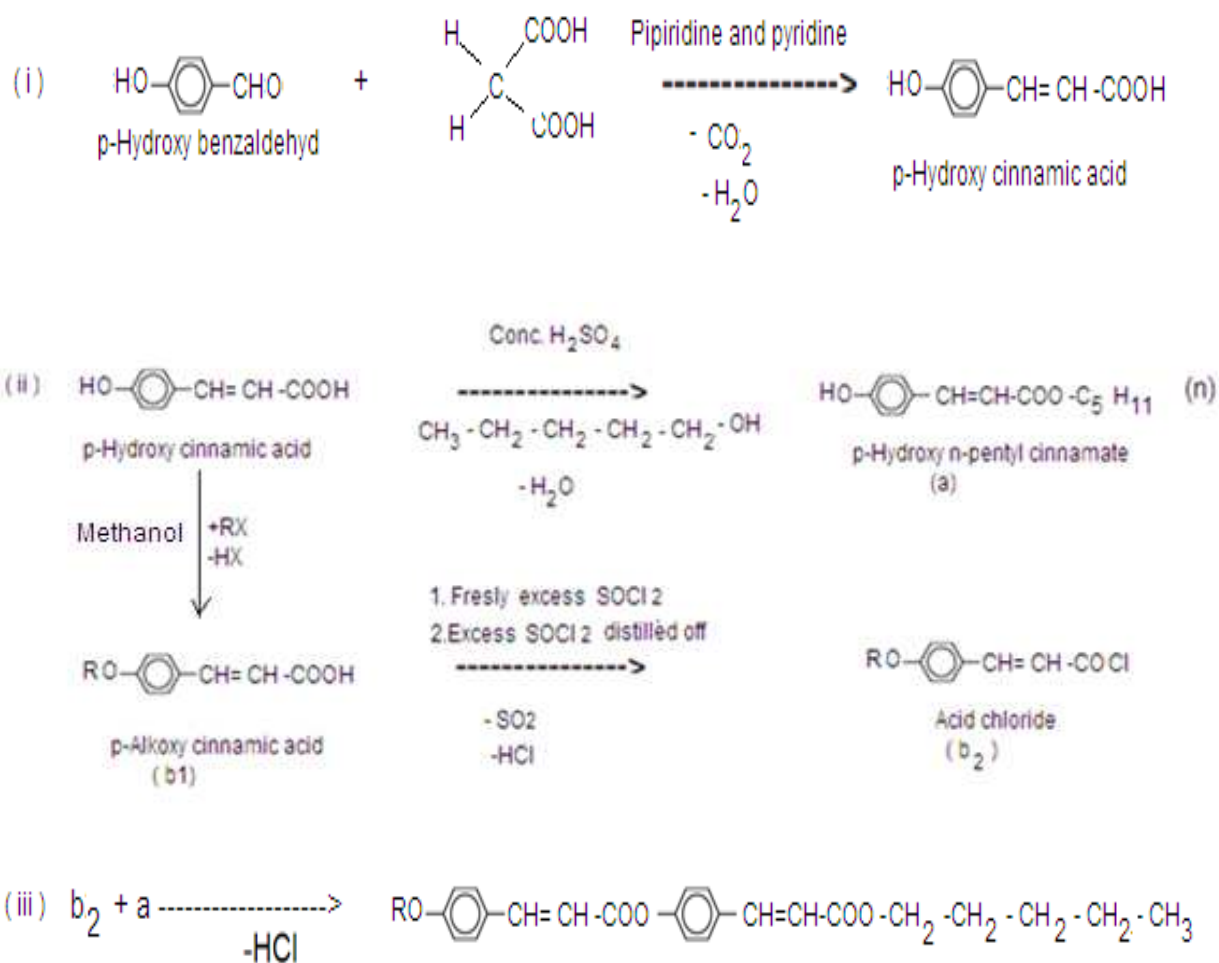
(iv) *Synthesis of n*-pentyl-*p*-(-*p*/*n*-alkoxy cinnamoyloxy) cinnamates :

p-*n*-Alkoxy cinnamoyl chloride (ii) condensed with ice cooled solution of *p*-hydroxy *n*-pentyl cinnamate (iii) in pyridine cautiously, by usual established method. (5- (iv), (v)). Products were purified by alcohol. Schematic chart of synthetic rout is separately mentioned in figure-III.

(v) *Methods and characterization* :

Transition temperatures and melting temperatures are observed through hot stage polarizing microscope as recorded in table-1. The phase diagram obtained for the series is shown in the figure –I. Some selected homologues are characterized by I R, ¹H N M R spectra and elemental analysis. Attempt is made to determine enthalpy change (ΔH) and entropy change (ΔS) from the peak value of D.S.C. scan. But, due to some difficulty of standard laboratory, providing analytical services could not allow to get it done. The type of textures of smectogenic material is confirmed by miscibility method.

Scheme of Synthesis :



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

Analytical data :**NMR: in ppm :****Hexyl**

0.83 – -CH₃; 2.49 – O-CH₂; 4.01 – O-CH₂ of O-CH₂-CH₂-CH₃; 4.44 and 4.02 – CH=CH- 6.89, 6.83, 7.75 and 7.78 – P-sub.phenyl two p-sub.benzene; 7.24 and 8.02 – P-sub.phenyl two p-sub. Benzene.

Tetradecyl

0.876 – -CH₃; 1.25 – -CH₂ ; 2.49- -OCH₂-CH₂-; 4.00– O-CH₂ of -COOC₄H₉; 3.31-O-CH₂ of C₁₄H₂₉; 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} **Hexadecyl**

2850.0 Confirms alkyl group; 1080, 1150, & 1700 Confirms –COO- group; 660 Confirms cis –CH=CH- group; 860 Confirms p-sub. phenyl ring; 3000 Confirms aromatic ring; 750 Confirms polymethylene of $\text{C}_{16}\text{H}_{33}$

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

Sr.no	R= n-alkyl group	Transition temperatures in $^{\circ}\text{C}$		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	174.0
2	Ethyl	-	-	170.0
3	Propyl	-	-	178.0
4	Butyl	-	-	168.0
5	Pentyl	-	135.0	156.0
6	Hexyl	124.0	133.0	150.0
7	Heptyl	119.0	139.0	164.0
8	Octyl	114.0	135.0	166.0
9	Decyl	110.0	135.0	163.0
10	Dodecyl	125.0	147.0	176.0
11	Tetradecyl	-	153.0	180.0
12	Hexadecyl	-	177.0	200.0

Octyl

2900.0 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_8H_{17}

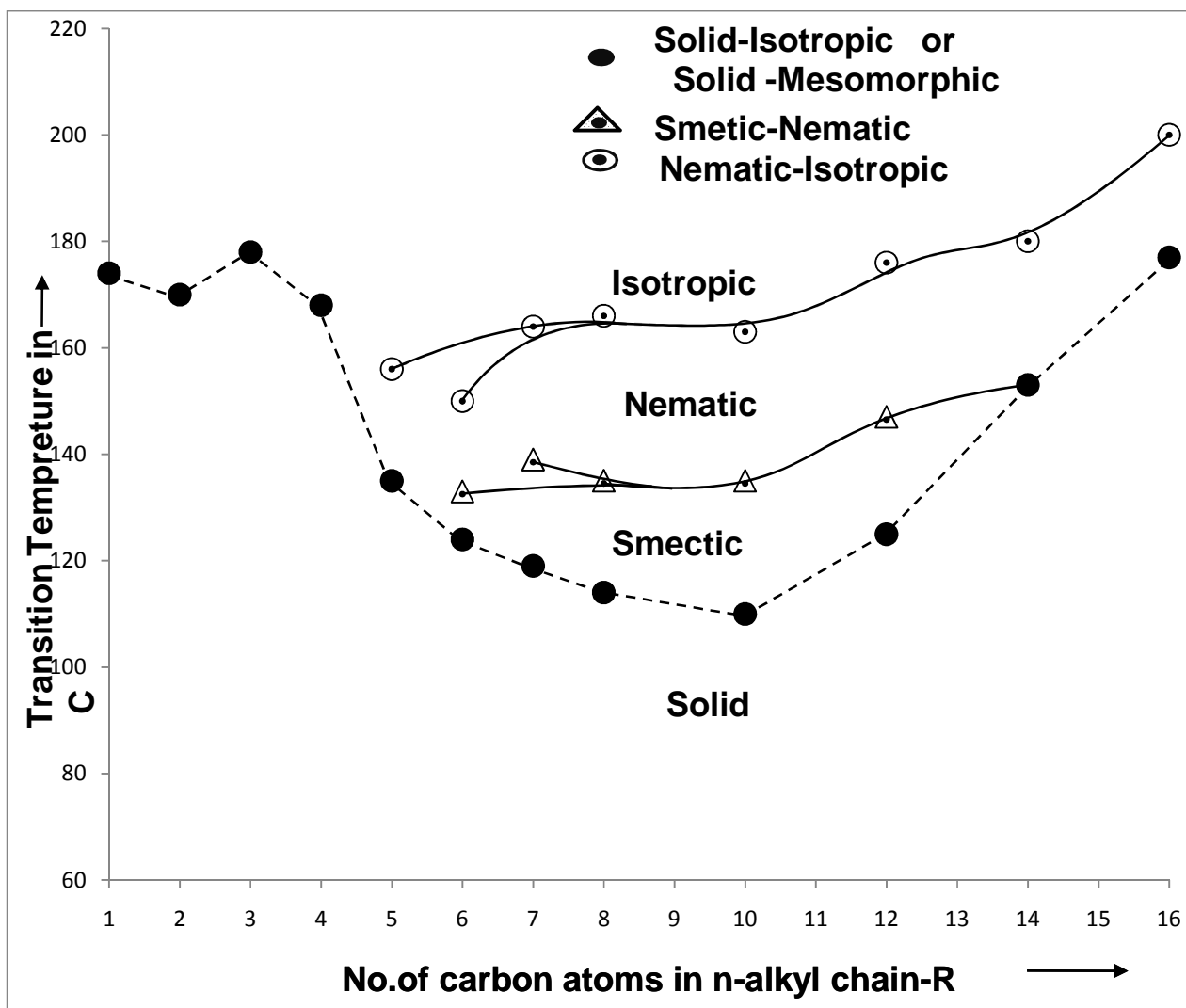
Miscibility method:

The texture of smectogenic homologues are of the type smectic –A.

Table-2: Elemental Analysis

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1.	Methyl	$\text{C}_{24}\text{H}_{26}\text{O}_5$	73.10	6.60	73.18	6.53
2.	Propyl	$\text{C}_{26}\text{H}_{30}\text{O}_5$	73.93	7.11	73.84	7.31
3.	Heptyl	$\text{C}_{30}\text{H}_{38}\text{O}_5$	75.25	7.95	75.16	8.02
4.	Dodecyl	$\text{C}_{35}\text{H}_{48}\text{O}_5$	76.64	8.76	76.50	8.96

Figure – 1 n-pentyl-p-[p'-n – alkoxy cinnamoyloxy] cinnamates



RESULTS AND DISCUSSION

The final products i.e. ester homologues of the series under discussion are *cis* isomers as determined from IR spectra. *n*-Alkoxy cinnamic acids are being dimeric, their dimerization disappears on linking them with *p*-hydroxy *n*-pentyl cinnamate due to breaking of hydrogen bonding through esterification. The esters formed are mesomorphic in nature except methyl to butyl homologues. Methyl to butyl homologues are unable to resist thermal vibrations and melts sharply at their melting point from crystalline solid state to isotropic liquid state without passing through mesogenic state. Transition temperatures are determined by hot stage polarizing microscope as recorded in table –I. Pentyl, tetradecyl and hexadecyl derivatives of homologues are only nematogenic, while, hexyl, octyl, decyl and dodecyl derivatives are poly mesomorphic i.e. smectic and nematic mesophases are exhibited by these homologues of the series. Texture of smectogenic homologues are of the type smectic -A, as determined by miscibility method and

also judged directly from field of view of microscope. Texture of nematic mesophase is of the threaded type. None of the mesomorphic homologues show monotropic mesophase exhibition. Transition temperatures (table-1) are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group. Like points are linked and a phase diagram obtained is shown in the figure-I.

A careful examination of a phase diagram (figure-I) indicate that, solid-isotropic or solid-mesophase transition curve follow a zigzag path of rising and falling from methyl to butyl homologue. Then it steeply falls to decyl homologue at the minima and again steeply rises to hexadecyl homologue making its overall rounded shape. The smectic-nematic transition curve rises to decyl homologue and then its extension merges to tetradecyl derivative, at solid-nematic point of solid mesomorphic curve. Thus, theoretically a smectic mesophase should disappear in tetradecyl derivative and really disappears practically also for tetradecyl homologue. Thus, smectic-nematic transition curve behaves in normal manner showing minima instead of maxima. Nematic-isotropic transition curve rises from pentyl to hexadecyl derivative of homologues in serpentine shape and behaves in normal manner without showing descending tendency as series is ascended and with alternation of transition temperatures. Odd-even effect is observed in solid-smectic transition curve and nematic-isotropic transition curve. Transition curves for odd and even homologues merges into decyl and octyl homologues for smectic-nematic and nematic-isotropic transition curve respectively. Mesogenic range which ranges minimum of 21.0^{0C} at the pentyl homologue to maximum of 53.0^{0C} at the decyl homologue. Thus, mesomorphic range is enough and series is of middle ordered melting type.

The nonmesogenic behavior of methyl to butyl derivative of the homologues is attributed to their high crystallizing tendency which arises from stronger intermolecular forces of attractions, which are not anisotropic and the magnitude of which correspond to amount of energy (ΔH) released from system (Formation of homologue) to surrounding (Rest of the univers other than system). According to third law of thermodynamics, the entropy (ΔS) (i.e. randomness or disorder) of perfectly crystalline substance is zero at absolute zero degree Kelvin (-273^{0C}). Therefore as heat energy (ΔH) is supplied to a sample substance from external source [i.e. from surrounding to system], the applied heat energy tend to break crystal structure and sample substance acquire disruption to move towards higher or less stable state of existence. n-Alkyl chains of left n-alkoxy terminals from methyl to n-butyl caused, stronger intermolecular forces of attractions which required relatively higher amount of energy to undergo interstate transformation. But molecules are disaligned under cohesive forces which are not anisotropic from ordered arrangement, preventing parallel orientations or sliding layered arrangement of molecules in floating condition. Thus, molecules of substance from methyl to butyl homologues at required high temperature are unable to resist thermal vibrations in bearable regular manner to have in controlled motion and sharply passes into isotropic liquid state from crystalline solid state without passing through an intermediate state of existence called mesogenic state. The uncontrolled motion or Brownian motion of molecules at their melting point causes high order of molecular disorder; i.e. the entropy change (ΔS) causes to occur high level of randomness or disorder amongst the randomly oriented disaligned molecules of a sample homologue, as transformed directly into isotropic liquid. Thus, high order of disorder or randomness or entropy (ΔS) resulted from the combine effects of molecular rigidity, flexibility and bending of molecule which disturbed alignments of molecules causing generation of intermolecular cohesion which is not anisotropic and of suitable magnitude which restricts mesophase formation.

As n-alkyl chain of left n-alkoxy terminal increase their length by sequential addition of methylene unit, crystallinity of a sample homologues gradually diminishes and amorphous character rises, introducing mesogenic character favourably. The amount of energy released (ΔH) during their formation of stable solid crystal structure, which on heating tend to destabilize require heat energy which correspond to such a magnitude of randomness or entropy change (ΔS) that, molecules of pentyl to hexadecyl derivatives of the series are able to resist thermal vibrations imposed upon them, due to generation of anisotropic intermolecular forces of adhesion by suitable combination of effects caused by molecular rigidity, by flexibility and molecular bending. As a result of this, two dimensional array of molecules is maintained in floating condition. i.e. Lamellar molecular packing and hence the sliding layered arrangement of molecules in floating condition of hexyl, heptyl, octyl, decyl and dodecyl homologues give rise to smectic-A mesophase formation, while, pentyl, tetradecyl, hexadecyl, hexyl, heptyl, octyl, and decyl derivatives of homologues acquiring balanced anisotropic intermolecular cohesive forces of suitable magnitude emerging from molecular rigidity, molecular bending or flexibility without restricting statistically parallel orientational order of molecules in floating condition which gives rise to the formation of nematogenic mesophase. Thus, hexyl, heptyl, octyl, decyl and dodecyl homologues show smectic and nematic mesophases one after another enantiotropically while, pentyl, tetradecyl and hexadecyl derivatives show only enantiotropic nematic mesophase formation.

The abnormal behavior of solid-isotropic or solid-mesomorphic transition curve from pentyl to hexadecyl homologue is attributed to the presence of highly polarisable two $-\text{CH}=\text{CH}-$ units in central and terminal group of homologues which cause dipole-dipole interactions. Similarly, the nematic-isotropic transition curve normally rises and after passing through maxima, falls as series is ascended. However in case of present investigation nematic-isotropic transition curve rises only without passing through maxima due to late shift of maxima as series is ascended. This apparently seen absence of early maxima considering abnormal behavior is attributed to the heat absorption by sample substances in presence of conjugation of polarisable $-\text{CH}=\text{CH}-$ unit of central and terminal cinnamoyl and cinnamate groups of molecule respectively under investigation. Odd-even effect observed in smectic-nematic transition curve and nematic-isotropic transition curve is attributed to the odd and even numbered methylene units present in left n-alkyl chain of n-alkoxy group which may be coiled or coupled to lie in the line with major axis of core, for higher homologues. Thus, end to end contacts would than ultimately be the same for odd and even homologue. Thus, length to breadth ratio and hence the intermolecular anisotropic forces of attractions of suitable magnitude depending upon unexpected flexibility of n-alkyl chain of n-alkoxy terminal of higher homologues are responsible for behavior of smectic-nematic or nematic-isotropic transition curves.

Nematic-isotropic transition curve normally show descending tendency as series is ascended or the nematic-isotropic transition temperatures rise to maxima before its fall or rise progressively over an extended series (14). The position of maxima may shift to any homologue (15) of the series or may shift to a position after the last homologue of the series. Therefore, in such case of a homologous series where (a) initial maxima may be absent or (b) the maxima does not appear due to its late shift till the last homologue or (c) it may shift to any early or late or middle homologue before falling. It is not necessarily be universally accepted conclusion that, nematic-isotropic transition curve should always have descending or ascending tendency as series is ascended, but, it may fall or rise with or without maxima as series is ascended, provided,

homologues of the homologous series be absolutely pure, so far as purity is concern (16). There is no maxima in nematic-isotropic transition curve of the possible only one cis isomer of each homologue of the series (figure –III) under discussion till the last homologue. Therefore nematic-isotropic transition temperatures rises and solid-smectic transition temperatures beyond rises decyloxy derivative. Thus, the statement that (17,18), nematic- isotropic transition curve should show always descending tendency as series is ascended is not an universally acceptable truth or doubting of purity of a sample substance which may be only an assumption and may not be real.

The mesogenic properties of titled homologous series (1) are compared with structurally similar homologous series (A), (B) and (C) as under.

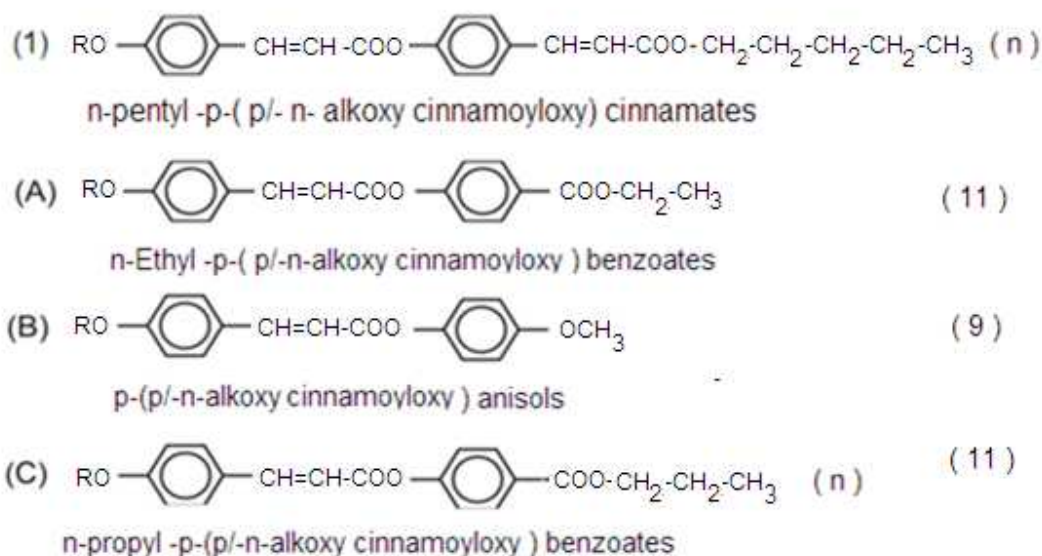


Figure-II

The net intermolecular forces of attractions depend upon shape, size, linearity, aromaticity, polarity, dipole-dipole interaction, polarizability and many other factors operating stability and liquid crystallinity of a molecule. All the homologous series under comparison possess two phenyl rings bridged through $-\text{CH}=\text{CH}-\text{COO}-$ central bridge, left *n*-alkoxy terminal end groups and aromaticity which are common identical features for series (1), (A), (B) and (C). The uncommon part amongst the above series under comparison is their right terminal end groups. Therefore the difference in liquid crystal properties and extent of liquid crystallinity will depend upon the difference of polarity of right handed terminally situated end groups viz; $-\text{CH}=\text{CH}-\text{COOC}_5\text{H}_{11}$ (*n*), $-\text{COO}-\text{C}_2\text{H}_5$, $-\text{OCH}_3$ and $-\text{COO}-\text{C}_3\text{H}_7$ (*n*). Therefore the molecular polarisability and molecular length to breadth ratio of molecules of same homologue from series to series varies with polarity of terminal end groups. The variation of mesogenic properties among the homologues of the same series will vary with the number of methylene units linked in *n*-alkyl chain increasing molecular length of left *n*-alkoxy terminal, as right handed terminal end group remains unchanged, for same series.

Table- 3: Average thermal stability

Series	(1)	(A)	(B)	(C)
Smectic – nematic Smectic-isotropic	118.5 (C ₆ – C ₁₂)	120.75 (C ₇ – C ₁₂)	95.5 (C ₁₂ – C ₁₈)	118.0 (C ₆ -C ₁₂)
Commencement of smectic mesophase	C ₆	C ₂	C ₈ -	C ₂
Nematic - Isotropic	169.3 (C ₅ -C ₁₆)	119.7 (C ₅ – C ₆)	123.5 (C ₁ -C ₁₄)	115.7 (C ₃ -C ₆)
Commencement of Nematic mesophase	C ₅	C ₁	C ₁	C ₁

Careful observation of table-3 of average thermal stability of mesophase for the series under comparison reveals that, the smectic thermal stability of series (1), (A) and (C) are almost nearer or say, equivalent and more than series (B). Obviously, the dipolemoments acting across the long molecular axis of ring–COOR bond, and phenyl ring–CH=CH–COOR terminal end groups strongly favour smectic behavior (19). But the phenyl ring –substituent bond Ph–OCH₃ is highly dipolar, in homologous series (B) which decreases the smectic thermal stability. Thus, at the cost of smectic thermal stability, nematic thermal stability increases as observed for series (B) relative to series (1), (A) and (C).

The nematic isotropic thermal stability of titled homologous series (1) is the highest among the homologous series under comparison i. e. of series (A), (B) and (C). In spite of having similar central bridge and other parts of molecules similar, the right terminal end group –CH=CH–COOC₅H₁₁ (n) differs by the additional conjugative linkage –CH=CH– in series (1) while, it is absent in the right terminal end groups of series (A), (B) and (C). Thus, the presence of conjugative –CH=CH– unit at the right terminal end group of series (1) increases molecular rigidity and contributes more to the thermal stability for nematic mesophase. The nematic thermal stability of series (B) is more than series (A) and (C) but, less than series (1) because, molecular length of a molecule containing –CH=CH– COO–C₅H₁₁ (n) terminal is more than a molecule containing highly polarizable terminal end group –OCH₃. Thus, length to breadth ratio and conjugation through double bond increases intermolecular attractions, –OCH₃ being a highly polarizable terminal, in which phenyl ring bonded through oxygen atom contributes less to smectic character due to poor lateral attraction. Thus, presence of phenyl ring –OCH₃ always strongly enhance the nematic thermal stability and diminishes, smectic thermal stability of its own homologues of homologous series as observed in table-3 of average thermal stabilities. Moreover it is also possible that, the phenyl ring –OCH₃ dipole may have quite a different orientation viz; if rotation about phenyl ring–O– bond is relatively unrestricted, or the –OCH₃ group may interact with rest of the molecule. (20)

The early or late commencement of smectic mesophase depend upon the extent of non-co-planarity (12) caused by the molecule. Smectic mesophase commences from sixth member of the series (1) and second member of the series (A) and (C) respectively, while, it commences from the eighth member of series (B). The extent of non-co-planarity caused by the molecules, depending upon lamellar packing with layered lattices which requires a suitably high ratio of lateral to terminal intermolecular attractions due to dispersion forces, induced dipole interaction and dipole-dipole interactions (5,8) etc, operating co-planarity of molecules and results into early or late commencement of smectic mesophase of a substance under investigation. Presence of

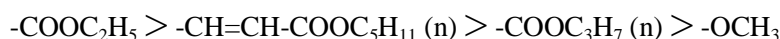
highly polarizable terminal end group $-OCH_3$ satisfy above discussed criteria for emergence of smectic mesophase latter (from eight homologue) in series (B) while, other terminal end groups of series (A), (C) and (1) satisfy above cited criteria earlier. i. e. from second and sixth homologues, respectively.

Thus, group efficiency order derived on the bases of average thermal stabilities in terms of terminal end groups are as under.

Nematic group efficiency order :



Smectic group efficiency order :



CONCLUSION

The titled homologous series is predominantly nematogenic and partly smectogenic in character.

Acknowledgement :

Authors acknowledge the thanks to the H.O.D. Dr.Nimesh Vyas and his subordinates, Dr. Mukesh Chauhan and Dr. Vipul Patel (Chemistry deptt.S. P. T. Arts and Science College Godhra) for their valuable co-operation and support in the work. Authors are also thankful to Uma laboratory,vadodra and Vaibhav laboratory,Ahmedabad and CSMCRI Bhavnagar for the analytical services.

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