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Synthesis and study of a new mesomorphic series: p-(p'-n-Alkoxy cinnamoyloxy) β-benzoyl styrene

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ABSTRACT

Homologous series p-(p/-n-alkoxy Cinnamoyloxy) β-benzoyl Styrene is synthesized and studied with a view to understand and to established the relation between molecular structure and liquid crystal property. Homologues are synthesized by reacting p-n-alkoxy cinnamoyl chlorides with p-hydroxy β–benzoyl styrene. Totally twelve homologues are synthesized. Methyl to pentyl homologues are nonmesomorphic while, hexyl to octyl, decyl, dodecyl, tetradecyl and hexadecyl homologues are only nematogenic without exhibition of any smectogenic character even in the monotropic condition. Transition temperatures of the homologues are determined from hot stage polarizing microscope. Solid-isotropic / nematic transition curve in a phase diagram follows a zigzag path of rising and falling and shows overall falling tendency as series is ascended in usual manner. Nematic-isotropic transition curve adopt a descending tendency as series is ascended and behaves in normal manner without showing up of odd-even effect. Melting temperatures are varied between 104.0^{0C} and 179.0^{0C}. Mesomorphic range and nematic-isotropic thermal stability are 6.0^{0C} to 47.0^{0C} and 144.5^{0C} respectively. Analytical data support the structures of molecules. The texture of nematic mesophase is of threaded type as determined by miscibility method. Thus, series under investigation is entirely nematogenic with middle ordered melting type and short range of liquid crystallinity. Mesomorphic properties are compared with structurally similar other homologous series.

INTRODUCTION

Number of homologous series with two similar or desimilar central bridges linking three phenyl rings or laterally substituted three phenyl rings are known to under stand the effect of structure on liquid crystal properties but an ester central bridge in addition to other central bridge –

CH=CH-CO- linking three phenyl rings are hardly appeared as liquid crystal, since and before 2007 (1). Thus, present investigation is planed for the search of new liquid crystal material due to their increasing utility in various fields of applications like medical, analytical, electronic, defence, drugs and chemical analysis, conventional unconventional and general display devices etc.

MATERIALS AND METHODS

Preparation of homologous series :

(a) Cis p-n-alkoxy cinnamoyl chlorides were prepared by refluxing alkoxy cinnamic acids with freshly distilled excess of thionyl chloride till the evolution of SO_2 and HCl ceased. Excess of thionyl chloride is distilled off and remainder product, acid chloride is directly treated with p-hydroxy β-benzoyl styrene by the established method (1,5).

(b) P-Hydroxy β-benzoyl styrene prepared by coupling p-hydroxy benzaldehyde and acetophenone in presence of 50% KOH solution by established method (1). The products were acidified by cold 1:1 HCl, fitered, washed with water, dried and crystallized in alcohol.

(c) The transition temperatures of homologues are observed through polarizing microscope with heating stage and recorded in table-1.

Scheme of synthetic rout is represented separately in figure-3

(d) Structures of some selected representative homologues are confirmed by analytical data viz; Elemental analysis, ^{1}HNMR and IR spectra. The enthalpy (ΔH) and entropy (ΔS) concept related to interstate transitions discussed qualitatively, instead of determing a value of enthalpy from peak value of transition temperature in D.S.C. scan and, thereby calculating corresponding entropy value, due to inadequate facility available at the sources.

(e) Textures of some homologue are confirmed by miscibility method.

Table- 1 : Transition Temperatures in ^{0}C

Sr. No.	R= n-alkyl group C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	162.0
2	Ethyl	-	-	172.0
3	Propyl	-	-	133.0
4	Butyl	-	-	135.0
5	Pentyl	-	-	172.0
6	Hexyl	-	164.0	179.0
7	Heptyl	-	170.0	178.0
8	Octyl	-	168.0	174.0
9	Decyl	-	115.0	145.0
10	Dodecyl		75.0	122.0
11	Tetradecyl	-	78.0	109.0
12	Hexadecyl	-	80.0	104.0

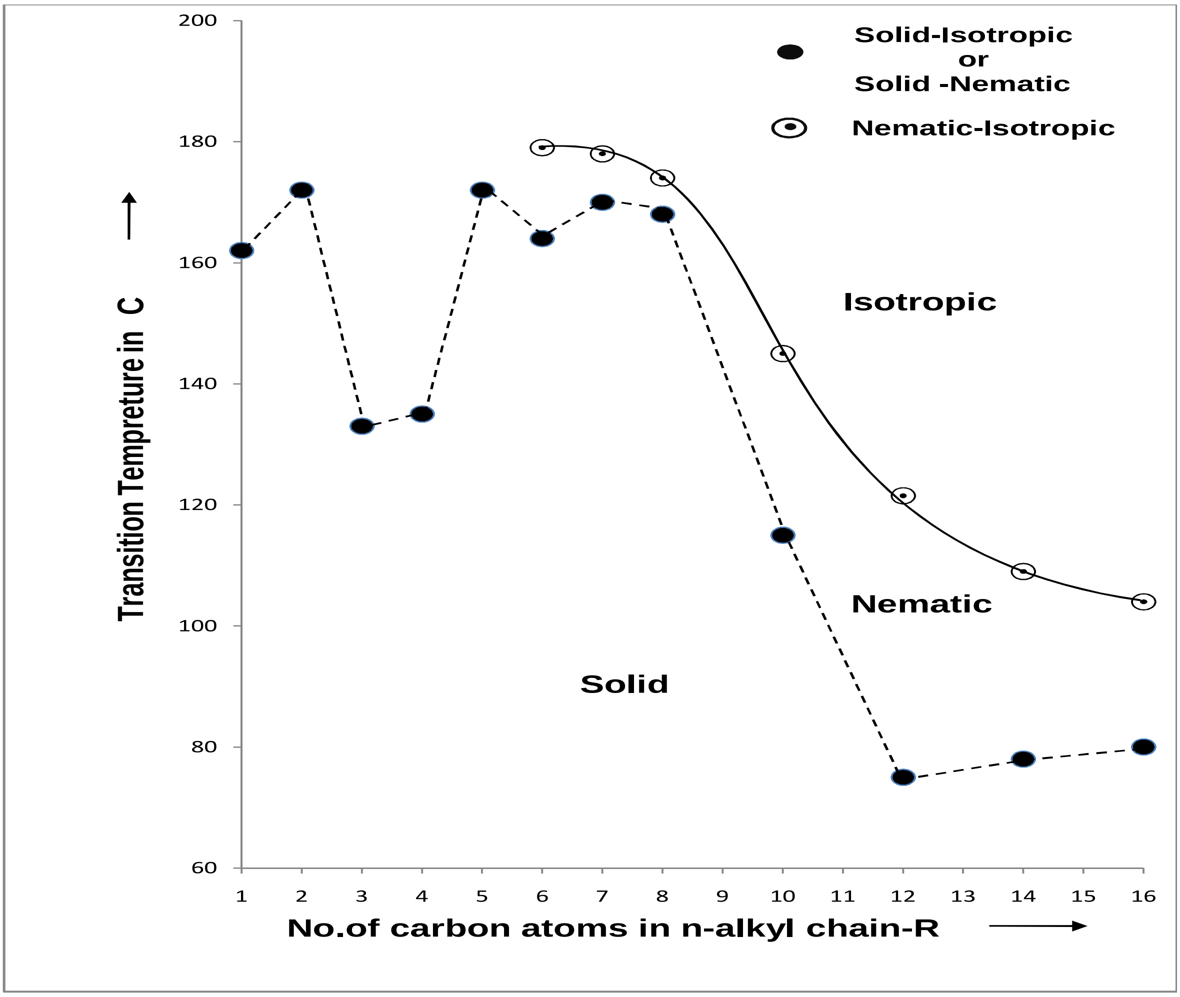


Figure – I :Series: p-[p′-n- Alkoxy Cinnamoyloxy] β-benzoyl styrene

Analytical data:

NMR: in ppm :

Octyl

0.840 →Confirms -CH_3

2.490 →Confirms- O-CH_2

3.98 →Confirms -O-CH_2 of –C_8H_{17}

4.4 and 4.0 →Confirms – CH=CH-

6.80, 6.83, 7.74 and 7.78 →Confirms P-sub.phenyl two p-sub. phenyl ring

7.24and 8.02 →Confirms P-sub.phenyl two p-sub. phenyl ring

NMR confirms the structure.

Dodecyl

0.88 →Confirms -CH_3

1.55 →Confirms -CH_2

2.40 →Confirms -OCH_2-CH_2-

3.31 →Confirms -O-CH_2 of $C_{12}H_{25}$

4.48 →Confirms- CH=CH-
6.896 and 6.925, →Confirms Two p-sub.phenyl ring
8.039 and 8.011, →Confirms Two p-sub.phenyl ring
NMR confirms the structure.

IR in cm^{-1}

Hexyl

2900.0 →Confirms alkyl group
1040,1220, & 1690 →Confirms –COO- group
660 →Confirms cis –CH=CH- group
830 →Confirms p-sub. phenyl ring
3000→ Confirms aromatic ring,=CH-
1170→ Confirms ether linkage –O-
740 →Confirms polymethylene of C_6H_{13}
IR confirms above structure

Tetradecyl

2830.0 →Confirms alkyl group
1030, 1200, & 1680 →Confirms –COO- group
660 →Confirms cis –CH=CH- group
840 →Confirms p-sub. phenyl ring
2950 →Confirms aromatic ring=CH-
1160→ Confirms ether linkage –O-
750 →Confirms polymethylene of $C_{14}H_{29}$
IR confirms above structure

Table-2: Elemental Analysis: Cis p-(p'-n-alkoxy cinnamoyloxy) β-benzoyl styrene.

Sr.No.	R=Alkyl chain C_nH_{2n+1}	Molecular formula	Calculation %		Observation %	
			C	H	C	H
1.	Methyl	$C_{25}H_{20}O_4$	78.13	5.21	78.03	4.98
2.	Propyl	$C_{27}H_{24}O_4$	78.64	5.83	78.30	5.70
3.	Butyl	$C_{28}H_{26}O_4$	78.87	6.10	78.57	6.16
4.	Pentyl	$C_{29}H_{28}O_4$	79.09	6.36	78.99	6.49
5.	Heptyl	$C_{31}H_{32}O_4$	79.49	6.84	79.56	6.62

Miscibility method: Ethyl, decyl, tetradecyl, hexadecyl.

RESULTS AND DISCUSSION

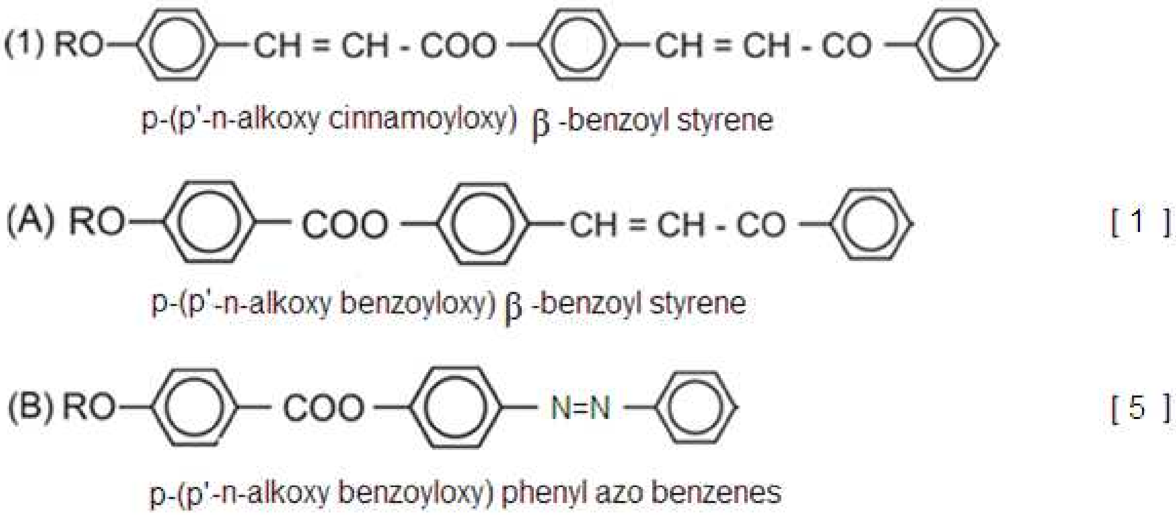
Cis p-n-alkoxy cinnamic acids and p-hydroxy – benzoyl styrene are originally nonliquid crystal in nature, however on combining them together under favourable and suitable condition, results into the new products which are homologues of this titled series, the liquidcrystal property is induced from and beyond hexyl homologue. Methyl to pentyl homologues are nonliquidcrystal in character. All the liquidcrystal homologues i.e. hexyl, heptyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives of the titled homologous series are enantiotropic nematogenic in character without exhibition of any smectic character even in the monotropic condition. Transition temperatures (table-1) of the homologues are plotted versus the number of carbon atoms presents in n- alkyl chain of left n-alkoxy group. Like points are linked and a phase diagram obtained is represented as figure-I. Careful examination of a phase diagram reveals that, the solid-isotropic or solid-nematic transition curve follows a zigzag path of rising and falling throughout the series with one or two exceptions, otherwise curve shows overall decending tendency as series is ascended and behaves in usual expected manner. Nematic-isotropic transition curve exhibits descending tendency as series is ascended and curve behaves in normal manner without showing up of odd-even effect, because, transition temperatures do not alternate in regular manner as well as nematogenic mesomorphism commences late, i.e.from and beyond sixth homologue. The mesomorphic properties of a homologous series are compared with structurally similar homologous series (A) and (B) as shown in figure-II.

The nonmesomorphic behavior of methyl to pentyl homologues observed is due to the high crystallizing tendency of the molecules which arises due to the intermolecular forces occurred between the molecules are not anisotropic and of suitable magnitude to keep molecules in proper alignment under the influence of heat from surrounding to system. Thermodynamically stable state achived by all the homologue substance (system) by exchanging energy (ΔH) from surrounding (Rest of universe other than a system) to system or vice versa. Now a thermodynamically stable unlayered substance is supplied heat i.e. heat is supplied from surrounding to system, the molecules of a homologue substance under the influence of heat start to pass from transitional motion to vibrational motion through rotational motion. Thus, vibrating molecules may or may not resist the thermal vibrations exposed upon them. If the victim vibrating molecules are unable to resist applied thermal vibrations, such molecules exhibit disaligned position on the plane of the surface with high entropy ($\Delta S=\Delta H/T$) or randomness or high order of disorder at higher temperature. Under this situation molecules of a sample homologue under examination are restricted to maintain statistically parallel orientations of molecules in floating condition due to insufficient intermolecular forces of end to end and lateral attractions occurred as a consequence of molecular rigidity and flexibility. Thus, molecules of methyl to pentyl homologues are directly converted from solid to isotropic state without passing through an intermediate state of existence, called liquid crystal state or mesomorphic state or nonamphiphilic state or mesogenic state. Thus, interstate transition of first five homologues takes place in titled homologous series, without formation of either nematogenic or smectogenic mesophase.

However the vibrating molecules resist the thermal vibrations exposed upon them from the heat supplied from surroundings, the molecules of the molecular system under examination has intermolecular lateral and end to end attractions are stronger enough to withstand the effect of exposed heat. Therefore molecules of a homologue are not disaligned i.e. molecules of a homologue make an angle less than 90^0 with the plane of the surface. Such molecular system which maintains net intermolecular anisotropic forces of attractions of suitable magnitude caused by the favourable molecular rigidity and flexibility. Thus, in such case, the statistically parallel orientations of molecules are not restricted to form nematic mesophase in floating condition in absence of sliding layered arrangement of molecules under identical condition. Hence under such situation, hexyl to hexadecyl homologues exhibit only nematic mesophase without exhibition of smectic mesophase in case of homologous series under discussion. Absence of odd-even effect in nematic-isotropic transition curve is attributed to the late commencement of mesophase i.e. mesophase appears from and beyond sixth homologue and it is a known fact that, n-alkyl chain of left n-alkoxy terminal of higher homologues may be coupled or coiled to lie on the line with major axis of the core. Thus, effect due to odd and even homologues diminishes i.e. end to end contact would then ultimately be the same for odd and even homologues.

The variation in mesomorphic properties from series to series for same homologue keeping molecular part unchanged except right terminal end group. The variation of right terminal end groups of series (1), (A) and (B) causes difference in mesomorphic properties due to diffence in molecular length, polarity of right terminal end group, molecular polarizability, rigidity, flexibility etc. The variation in mesomorphic properties among the molecules of homologues in the same series occurs due to sequencially and progressively added methylene unit at the left n-alkoxy terminal keeping right terminal intact viz; phenyl ring. Thus, varying part of the molecules causes variation in mesomorphic properties. The nematic-isotropic transition temperature maximum is 179.0^{0C} at the hexyl homologue and minimum is 104.0^{0C} at the hexadecyl homologue, varying mesomorphic range minimum of 6.0^{0C} at the octyl derivative of the series to maximum 47.0^{0C} at the dodecyl homologue. Thus, series (1) under discussion is entirely nematogenic with middle ordered melting type and of short rang liquid crystallinity.

The average thermal stability and other liquid crystal properties of structurally similar homologous series (A) and (B) are compared with titled homologous series (1) as under in table-3 from the figure –II.



p-(p'-n-alkoxy cinnamoyloxy) β -benzoyl styrene

p-(p'-n-alkoxy benzoyloxy) β -benzoyl styrene

p-(p'-n-alkoxy benzoyloxy) phenyl azo benzenes

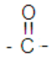
Figure-II

The molecular geometry of the homologous series (1), (A) and (B) is common with respect to three phenyl rings, left n-alkoxy terminal and without right terminal (terminal-H) but, they differ in central bridges –COO-, -CH=CH-COO-, -N=N- and –CH=CH-CO-. Homologous series (1) and (A) under comparison resemble with eacher except a central bridge –CH=CH-COO- and –COO-, linking first and second phenyl rings while, series (B)differs from series (1) in respect of both central bridges. However series (A) and (B) differs from each other with respect to central bridge –N=N- linking second and third phenylrings. Thus, the aromaticity left n-alkoxy terminal and right –H terminal and only one or both central bridge or bridges differ.

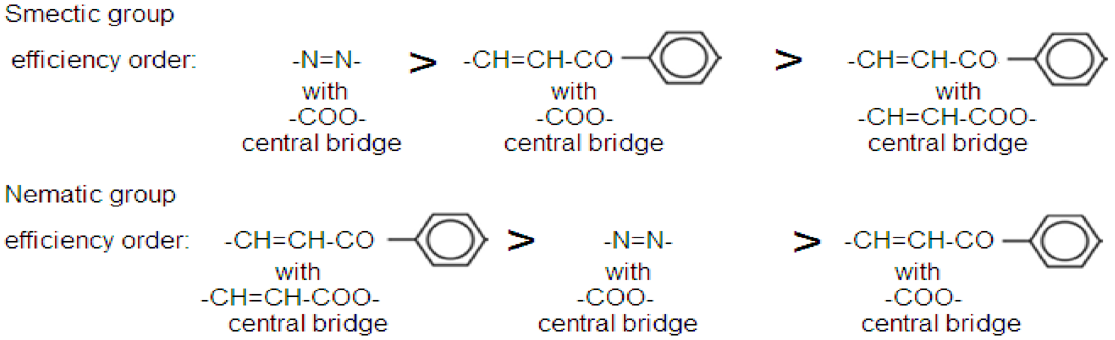
Table 3 Average thermal stability:carbon of

Series	**(1)**	**(A)**	**(B)**
Smetic – isotropic or smectic-nematic	-	106.66 (C_{10} – C_{14})	114.0 (C_{10}-C_{16})
Commencement of smetic phase	-	C_{10}	C_{10}
Nematic - Isotropic	144.5 (C_6-C_{16})	119.8 (C_8 – C_{16})	138.54 (C_1-C_{16})
Commencement of nematic phase	C_6	C_8	C_1

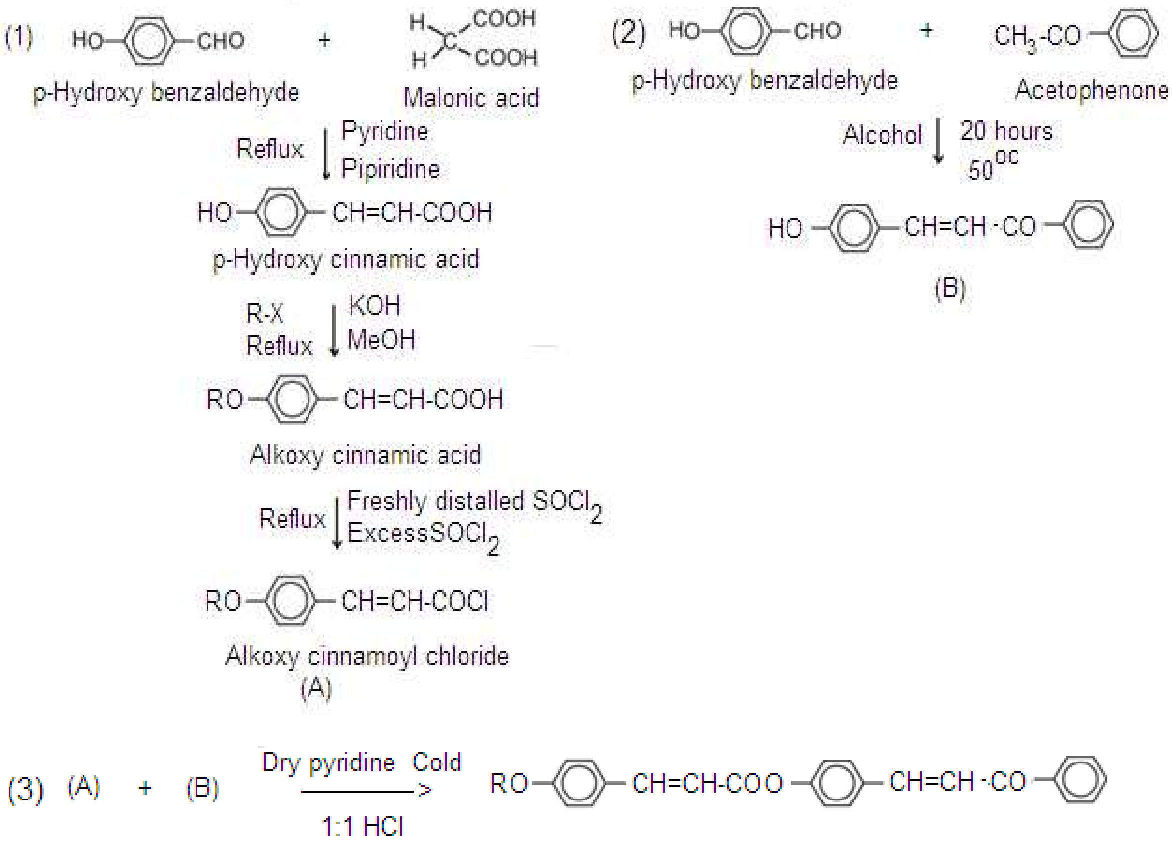
Therefore the variation in the mesomorphic properties and degree of mesomorphism depend upon the changing part of the molecules. Thus, intermolecular net isotropic or anisotropic forces of attractions vary according to resultant effect caused by overall aromaticity, polarity, polarizability, length to breadth ratio, molecular planarity, molecular rigidity and flexibility, conjugated double bond etc. The smectic-isotropic thermal stability of series (1) is zero or smectic mesophase is not exhibited by homologous series (1) or the lowest among the series under comparison, but, only nematic mesophase is exhibited by the series (1). Therefore nematic-isotropic thermal stability of series (1) is the highest among the series (1), (A) and (B). The presence of –CH=CH- unit at the both central bridges increases molecular rigiditry in addition to molecular length in case of series (1) as compared to series (A) and (B) (which contains only one double bond). This, suggests that intermolecular anisotropic forces of attraction due to end to end and lateral cohesion which are relatively higher for series (1) as compared to series (A) and (B). The electronagativity of nitrogen is more than the carbon but presence of only one double bond between two nitroges i.e. –N=N- while series (1) involve two –CH=CH- units in a molecules. Therefore molecular rigidity of series (1) due to two vinyl linkages surpasses the rigidity possessed by series (B) because of electronic interactions.

The early or late commencement of a smectic mesophase depend upon extent of noncoplanarity (12) caused by the molecule. Less extent of noncoplanarity causes early commencement of smectic mesophase. Vinyl carboxy central bridge is relatively longer than –COO-. Therefore ester groups –CH=CH-COO- causes more noncoplanarity than –COO- due to a twist obtained as the oxygen atoms of the vinyl carboxy or carboxy group bump into the nonbonded adjacent hydrogen atoms of the aromatic rings causing considerable strain on the molecule. Therefore the twist around C-O bond forces the phenyl ring out of the plane relatively more incase of –CH=CH-COO- than –COO-. Thus, the noncoplanarity of the molecule is reduced to some extent in case of series (A) and (B) involving -COO- as central bridge and noncoplanarity extended by the molecules of series (1) which will be more than the series (A) and (B). Moreover SP^2 carbon of third phenyl ring is linked directly with  $-\overset{O}{\overset{\|}{C}}-$ part of the molecule in case of series (1) and (A) while SP^2 carbon of third phenyl ring in series(B) is linked with –N=N-, in which electronegativity of nitrogen is more than a carbon. On account of these differences, smectic mesophase commemces from decyl homologue of the series (A) and (B), but it does not commence to appear till the hexadecyl homologue of the series (1), as the molecules of a series (1) involve two –CH=CH- unit while only one –CH=CH- is contained by the molecules of the series (A) and series (B) involve –N=N- unit under comparison.

Thus, group efficiency order derived on the basis of thermal stability for smectic and nematic are as under.



Scheme of Synthesis:



CONCLUSION

Titled homologous series is entirely nematogenic without exhibition of any smectogenic property with middle ordered melting type with low mesomorphic range.

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