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Synthesis and Study of New Homologous Series of Mesogens: n- Butyl-p-(p/-n-alkoxy cinnamoyloxy) Cinnamates.

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ABSTRACT

Titled homologous series: n-Butyl-p-(p/-n-alkoxy cinnamoyloxy) cinnamates is synthesized and studied with a view to understand the relation between mesogenic properties of substances and their dependence on molecular structure. Methyl to pentyl homologues are nonmesogenic, while, hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl homologues are enantiotropically mesogenic with exhibition of only nematogenic character. Smectogeni character is totally absent. Phase diagram is obtained by plotting a graph using number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group,versus transition temperatures as determined from polarizing microscope with heating stage. Solid-isotropic or solid-nematic transition curve shows descending tendency without following zigzag path, irregularly up to hexyl / octyl homologue and than it follows zigzag path of rising and falling as series is ascended. Nematic – isotropic transition curve behaves in normal manner without showing up of odd-even effect. Average thermal stability is relatively higher than the structurally similar homologous series selected for comparative study. Textures of the homologues are of threaded type. Analytical data support the structures of the molecules.

Key words: liquid crystals, Nematic,Smectic,Mesogens.

INTRODUCTION

Several ester homologous series of mesogens are reported by different groups of researchers (1to16) to understand and to establish the relation between molecular structure and mesogenic properties. In continuation of the same, attempt is made to synthesise an ester homologous series with –CH=CH-COO- central bridge and –CH=CH-COOC$_4$H$_9$ (n) as a terminal end group without any lateral substitution. Increasing demand of liquid crystal materials in various fields of their applications, like medical instruments, electronic display devices etc., inspired to produce, new liquid crystal materials through synthesis of new homologous series of mesogens.

MATERIALS AND METHODS

(i) Synthesis of p-hydroxy n-butyl cinnamate:

Equimolar proportion of p-hydroxy cinnamic acid and absolute n-butylalcohol mixed and shaked well in presence of two drops of concentrated $H_2SO_4$and reaction mixture was refluxed for four hours. Then reaction mixture decomposed in ice cooled water, and allowed it to settle. Solid substance p-hydroxy n-butyl cinnamate is obtained. Product was filtered, washed, dried and then purified by alcohol. Fine crystals are obtained M.P. 126^0C, yield63.74% (6)

(ii) Preparation p-n-alkoxy cinnamoyl chloride. :

p-n-Alkoxy cinnamic acids are refluxed with excess of freshly distilled thionyl chloride till evolution of SO_2 ceases. Excess of thionyl chloride is distilled off, (1to5, and10, 13) leaving behind p-n-alkoxy cinnamoyl chloride and preserved carefully in moisture free atmosphere without furthe purification.

(iii) Synthesis of n-butyl-p-($p^/$-n-alkoxy cinnamoyloxy) cinnamates

Homologues of the titled homologous series are prepared by usual established method, by reacting carefully corresponding acid chloride (step-(ii)) with pre ice cooled solution of p-hydroxy n-butyl cinnamate (step-(i)) dissolved in pyridine drop wise and than subsequently warming the reaction mixture for half an hour after complete addition of a solution of p-hydroxy n-butyl cinnamate and further treatment followed to get final product in pure state after 24 hours.(5, 7)

(iv)Transition temperatures are determined by polarizing microscope with heating stage as recorded in table-1.

(v)Analytical data supported the structure of molecules

Table-1: Homologous series: n-Butyl-p-($p^/$-n-alkoxycinnamoyloxy) cinnamates

Sr.No.	n-alky lgroup- C_nH_{2n+1}	Transition temperatures in ^{0}C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	200.0
2	Ethyl	-	-	215.0
3	Propyl	-	-	219.0
4	Butyl	-	-	180.0
5	Pentyl	-	-	142.0
6	Hexyl	-	130.0	142.0
7	Octyl	-	122.0	160.0
8	Decyl	-	140.0	189.0
9	Dodecyl	-	135.0	222.0
10	Tetradecyl	-	160.0	236.0
11	Hexadecyl	-	152.0	220.0

Analytical data:

Table-2; Elemental Analysis Homologous series: n-Butyl-p-(p/-n-alkoxy cinnamoyloxy) cinnamates

Sr. No.	R=n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1	Methyl	$C_{23}H_{24}O_5$	72.63	6.32	72.94	6.8
2	Ethyl	$C_{24}H_{26}O_5$	73.1	6.6	73.58	7.14
3	Proxyl	$C_{25}H_{28}O_5$	73.53	6.86	73.72	7.38
4	Butyl	$C_{26}H_{30}O_5$	73.93	7.11	74.18	7.6
5	Pentyl	$C_{27}H_{32}O_5$	74.31	7.34	74.51	7.71
6	Hexyl	$C_{28}H_{34}O_5$	74.67	7.56	74.74	7.93
7	Octyl	$C_{30}H_{38}O_5$	75.31	7.95	75.54	8.64
8	Decyl	$C_{32}H_{42}O_5$	75.89	8.3	76.22	8.75
9	Dodecyl	$C_{34}H_{46}O_5$	76.4	8.61	76.39	8.96
10	Tetradecyl	$C_{36}H_{50}O_5$	76.87	8.9	76.9	9.38
11	Hexadecyl	$C_{38}H_{54}O_5$	77.29	9.42	77.12	9.42

NMR: in ppm :
Hexyl
1.25 – $-CH_3$
3.98 – $O-CH_2$
4.01 – O-CH2 of $O-CH_2-CH_2-CH_3$
4.44 and 4.02 – CH=CH-
6.89, 6.92, 8.00 and 8.03 – P-sub.phenyl two p-sub.benzene
7.24and 8.02 - P-sub.phenyl two p-sub.benzene
NMR confirms the structure.

Tetradecyl
0.83 – $-CH_3$
1.21 – $-CH_2$
2.49- $-OCH_2-CH_2-$
3.5 – $O-CH_2$ of–$COOC_4H_9$
3.31-O-CH2 of $C_{14}H_{29}$
4.41 – CH=CH-
6.80 and 6.83, – Two p-sub.phenyl ring
7.75 and 7.78, - Two p-sub.phenyl ring
NMR confirms the structure.

IR in cm^{-1}
Hexadecyl
2900.0 Confirms alkyl group
1150, 1260, & 1710 Confirms –COO- group
666 Confirms cis –CH=CH- group
840 Confirms p-sub. phenyl ring
2950 Confirms aromatic ring
740 Confirms polymethylene of $C_{16}H_{33}$
IR confirms above structure

Octyl
2850.0 Confirms alkyl group
1150,1270, & 1725 Confirms –COO- group

660 Confirms cis –CH=CH- group
830 Confirms p-sub. phenyl ring
3000 Confirms aromatic ring
740 Confirms polymethylene of C_8H_{17}
IR confirms above structure

Homologous Series: n-Butyl-p-[p′ n-alkoxy cinnamoyloky] Cinnamates.

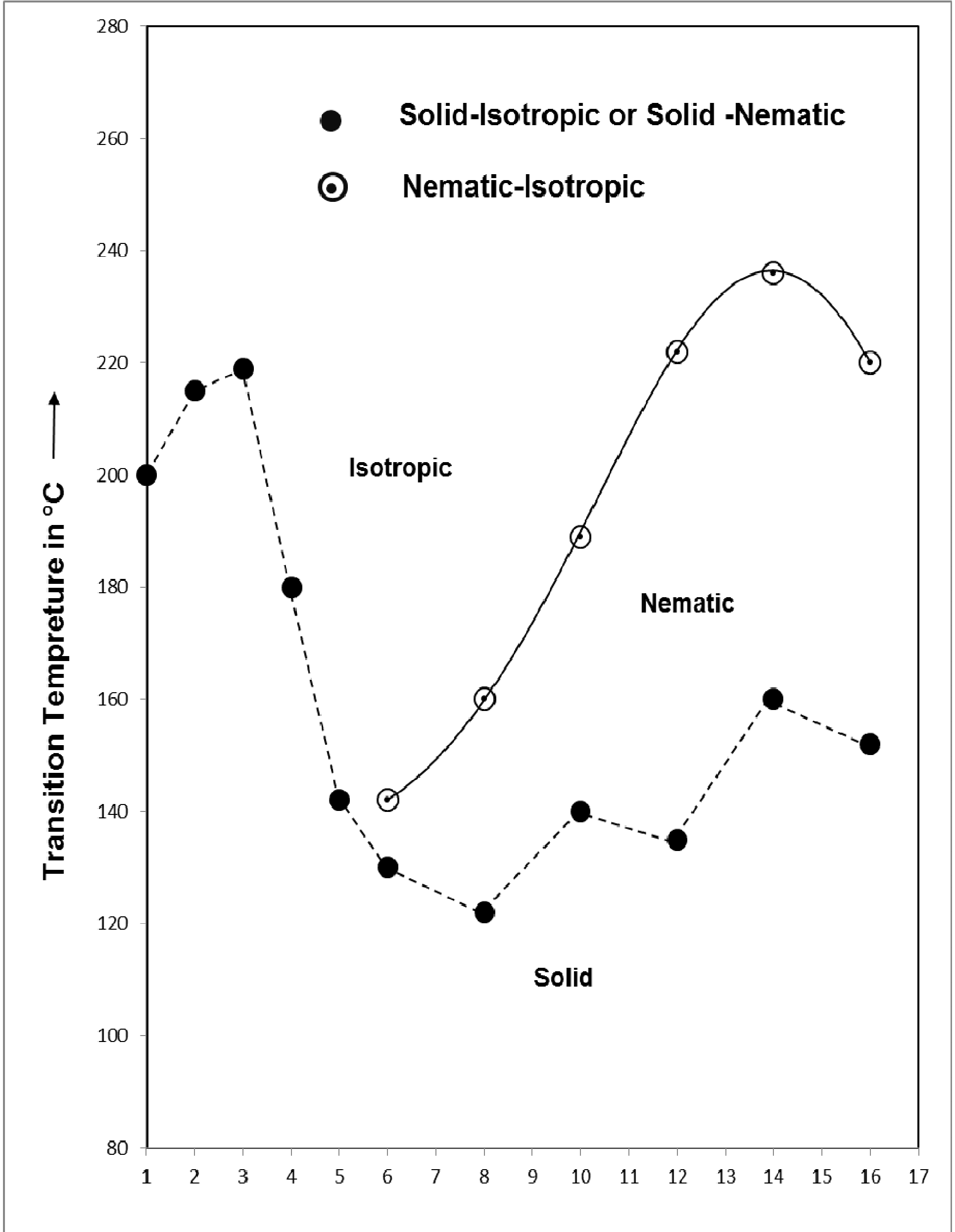

Figure-1 No.of carbon atoms in n-alkyl chain-R →

RESULTS AND DISCUSSION

On synthesis of titled homologous series, resulted eleven homologues.Microscopic examination of the homologues resulted, methyl, ethyl, n-propyl, n-buty, and n-pentyl derivatives as nonmesogenic homelogues and hexyl, octyl, decyl, dodecyl, tetradecyl and hexadecyl derivatives as mesogenic homologues. p-Hydroxy n-butyl cinnamate is nonmesogenic, but on linking it with p-n-alkoxy cinnamic acid through esterification gave mesogenic homologues from hexyl to hexadecyl derivatives. A phase diagram (Figure-I) is obtained by plotting a graph for number of carbon atoms present in n-alkyl chain of left n-alkoxy end group versus the transition temperatures of the homologues (Table-1) .Transition temperatures of homologues are determined by polarizing microscope with heating stage, as recorded in table-1. Analytical data support the structures of molecules. Texture of the nematic mesophase is of threaded type as judged directly from microscopic field of view. A nematogenic type of mesophase is exhibited by the members of the series showing mesogenic character. Smetic type of mesophase is not exhibited by any of the homologues under discussion. Careful observation of a phase diagram (Figure-I) obtained, indicate that, solid-isotropic or solid-nematic transition curve shows falling tendency as series is ascended up to octyl derivative of the series without following zigzag path of rising and falling. However from and beyond octyl derivative it follows zigzag path of rising and falling tendency upto hexadecyl derivative of series. Nematic – isotropic transition curve inially rises and than falls in a normal manner. Odd even effect is not observed for nematic-isotropic transition curve, because nematogenic character is exhibited by only even numbered homologues viz. hexyl, octyl, decyl, dodacyl, tetradecyl and hexadecyl derivatives. None of the odd numbered member of the series exhibit nematogenic character. Nematogenic mesophase length ranges from 12^0c to 87^0c in hexyl homologue and dodecyl homologue respectively. Transition and melting temperatures are relatively high. Thus, series is of high melting type with long range of nematogenic character and without exhibition of smectogenic character.

Inability for exhibition of mesogenic character by methyl,ethyl, propyl,bultyl and pentyl derivatives of titled homologous series is attributed to their high crystalisation tendency ,arising from irregular heat absorption and abrupt breaking of crystal lattices, which leads to the smooth passing of solid substance directly in to isotropic liquid without exhibition of an intermediate state of existence between solid and liquid, called liquid crystal state or mesomorphic state or mesogenic state or nonamphiphilic state at definite temperature and constant pressure. Dimerisation of p-n-alkoxy cinnamic acids disappear on esterification due to breaking of hydrogen bonding and linking of p-hydroxy n-butyl cinnamate, bridged through –CH=CH-COO- increases length of a molecule by phenyl ring and its para substituted n-butyl group. This extended molecular length, introduces mesogenic character from hexyl to hexadecyl derivatives of the series.

Homologues of titled homologous series from hexyl to hexadecyl derivatives are of enantiotropic nematogenic in character, because molecular adhering forces of attractions operated from hexyl to hexadecyl derivatives are capable enough to resist thermal vibrations and consequently molecules arrange themselves in two dimensional array in floating condition under the influence of molecular forces generated maintaing statistically paralled orientational order. Homologues from methyl to pentyl are unable to resist thermal vibrations and molecules are randomly oriented in floating condition with disordered manner. None of the homologues exhibit smectogenic character, because molecules are failed to maintain sliding layered ordered arrangemant in floating condition under the influence of thermal energy supply. Thus, extent of nematogenic high phase length (87.0^0C) occurred at the cost of eliminated smectic mesophase. Methylene unit is progressively added in n-alkyl chain of left n-alkoxy terminal end group keeping remaining part of a homologue molecule intact. This causes variation in homologue to homologue molecular length of same series. Hence, length to breadth ratio gradually varies from homologue to homologue. Consequently molecular polarity, and polarizability and hence, the intermolecular forces of attractions and molecular rigidity also undergo variation. Thus,variation in mesogenic properties arise from homologue to homologue in the same series. Mesogenic properties are compared with structurally similar homologous series as under.

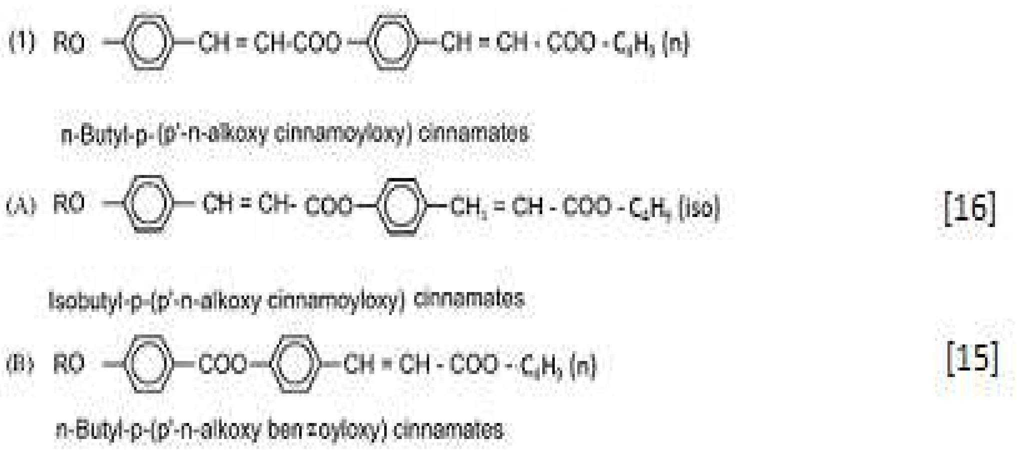

Figure:III

Average thermal stability for smectic and /or nematic and commencement of mesophase are recorded in table – 3 as under.

Table- 3 Average thermal stability:

Series □	**(1)**	**(A)**	**(B)**
Nematic – isotropic	194.8(C_6 - C_{16})	138.1(C_5 - C_6)	140.0 (C_5-C_{16})
Commencement of nematic phase	C_6	C_5	C_5
Smectic - Isotropic	-	-	101.0C_{10}-C_{12})
Commencement of Smectic phase	-	-	C_{10}

The molecular geometry of the homologous series (1), (A) and (B) are similar i.e. made up of two phenyl rings left n-alkoxy terminal end group as common identical part varying central bridge viz. -COO-and-CH=CH-COO-and right side terminal end group viz. -C_4H_9(n) and –C_4H_9(iso). Thus, variation in mesomorphic properties and the degree of mesomorphism will vary according to variation arising in molecular structure. The intermolecular forces of attraction arising out from polarity and polarizability, length to breadth ratio, pai electron density, varying structural arrangement of butyl end group and its spatial steric effect etc causes variation in the magnitude of intermolecular forces of attractions among the series (1), (A) and (B) for the same homologue from series to series and for different homologues of the same series.

Careful observation of average thermal stability in table-3 indicates that, thermal stability for nematic for the titled homologous series (1) is the highest (194.8^{0}C) while that of series (A) and (B) are 138.1^{0}C and 140.0^{0}C respectively. The highest value of thermal stability of series (1) is attributed to its long linear rod like shape which leads to the closest intermolecular paking, enhancing rigidity and compactness as compared to molecules of series (A) and (B). Iso linking –C_4H_9(iso) in series (A) increases intermolecular distance while in case of series (B) central bridge - CH=CH=COO- is replaced by – COO - .Thus, - C_4H_9(iso) linking of end group of series (A) and inspite of –C_4H_9(n) linking of end group replacement of central bridge by -COO- in series (B), reduces the intermolecular adhering forces and end to end attractions, which in turn lowers thermal stability for nematic in series (A) and (B). The values of thermal stability for nematic of series (A) and (B) is almost equivalent i.e. 138.1^{O}C and 140.0^{0}C respectively.

Thus, present investigation support the earlier views, that, central bridge is less effective than end to end attraction resulting into the nematic isotropic thermal stability. The commencement of nematic mesophase takes place from sixth, fifth and fifth member of the series (1), (A) and (B) respectively. Series (B) exhibit smectogenic character in addition to nematogenic mesophase exhibition, while series (1) and (A) are entirely nematogenic i.e. smectic mesophase does not appear till the last homologue. Early or late commencement of smectic mesophase depend upon (12, 15) the extent of noncoplanarity caused by the molecule. The extent of nonco-planarity caused by the molecules of decyl and dodecyl homologues adjust their co-planarity [series (B)] in such a way that, formation of sliding layered arrangement of molecules in crystal lattices occur in floating condition and smectic mesophase, in addition to nematic mesophase appeared. However, disappearance of smectic phase taking place in case of tetradecyl and hexadecyl homologue, of the same series (B), which may be due to disturbance of co-planarity factor by longer n-alkoxy chain which restricts, sliding layered arrangement of higher ordered two dimensional array of molecules. In case of absence of smectogonic character by series (1) and (A) is attributed to the fact that, non-coplanarity due to terminal end group –CH=CH-COO-R in combination with central bridge, -CH=CH-COO- operates in such an extent that, smectic mesophase does not commence to appear till the last homologue of the series (1) and (A).

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

Nematic group efficiency Order for
terminal end group : -CH=CH-$COOC_4H_9$(n) >-CH=CH-$COOC_4H_9$ (iso)
Smectic group efficiency Order for
terminal end group: -CH=CH-$COOC_4H_9$(iso) >-CH=CH-$COOC_4H_9$ (n)

CONCLUSION

-CH=CH-COOR terminal end group in combination with –CH=CH-COO- Central bridge induced nematogenic character more than the terminal end group –COO- in combination with –CH=CH-COO- or –COO-. -COO- group is predominantly smectogenic while –CH=CH-COO- group is predominantly nematogenic. Present investigation support earlier views, that, central bridge does have less effect on mesogenic properties as compared to terminal end group.

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