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Synthesis and Study of Novel Homologous Series of Mesogens; α-4-[4'-n-Alkoxy Cinnamoyloxy] Benzoyl-β-3"-Nitro phenyl Ethylenes.

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ABSTRACT

Titled novel homologous series of mesogenic character viz. α-4-[4'-n-Alkoxy- Cinnamoyloxy] Benzoyl-β-3" Nitrophenyl ethylenes is synthesized and studied with a view to understand its liquid crystal (LC) properties. There are seven homologues from n-pentyl to n-hexadecyl derivatives of the series which are mesogenic. Rest of the homologues are nonmsogenic. n-pentyl to n-decyl homologues are polymesogenic, n- Dodecyl ,n-tetradecyl and n-hexadecyl derivatives of the series are only nematogenic without exhibition of smectic character. All mesogenic homologues are enantiotropically, smectogenic and/or nemetogenic. Transition and melting temperatures are observed on polarising microscope with heating stage. Phase diagram drawn on the basis of microscopic observations. The novel series is predominantly nematogenic and partly smectogenic with middle ordered melting type. Analytical data support the structures of molecules. Mesogenic properties of titled series are compared with structurally similar other homologous series.

KEY WORDS : Liquid Crystal, Mesomorphic, Mesogenic, Smectic, Nematic.

INTRODUCTION

Liquid crystal state of a material possess number of applications in the manufacture of electronic display devices like T.V., Mobile, Calculator ,electronic curtain, screens etc.[7]. Also, substances involving vinyl carboxylate and –CO-CH=CH-group are bioactive materials which may be useful in pharmaceutical preparations. Therefore present investigation is planed to synthesize new substances of liquid crystal characteristics and to study understand and determine, data mainly from the point of view of liquid crystal behavior of new substances, with variation of molecular rigidity and flexibility.

MATERIALS AND METHODS

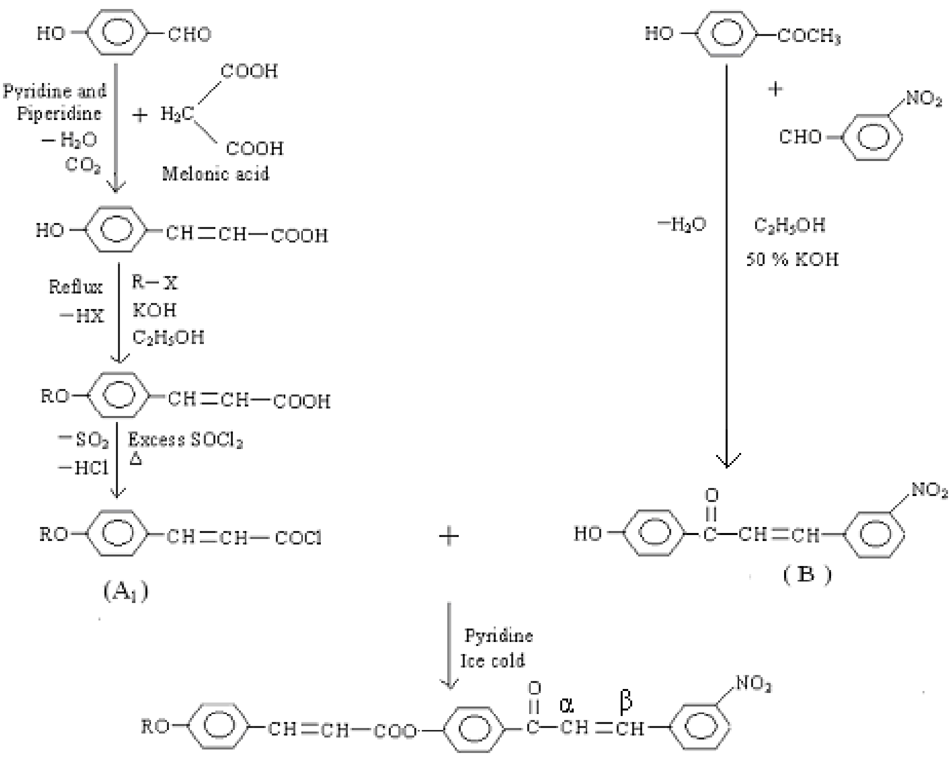
Characterization:

Representative members of the series were characterized by IR spectra, ^{1}H NMR spectra. NMR spectra were recorded using $CDCl_3$ as solvent. C,H,N analysis was performed on C,H,N analyzer. Data are recorded in Table-1.

Transition and melting temperatures are observed through hot stage polarising microscope as recorded in Table-2. Types of smectic and nematic mesophases textures are decided using miscibility method. Thermodynamic quantities enthalpy (ΔH) and entropy [ΔS] are discussed qualitatively instead of DSC Scane.

Synthesis:

4-Hydroxy cinnamic acid was synthesized by the method of Patel and Doshi [10] from p-hydroxy benzaldehyde and Malonic acid in pyridine. Hydroxy group of acid was alkylated by suitable alkylating agent by the method of Dave and Vora [5a].Alkoxy acids were converted to corresponding acid chloride(A_1) by treatment of acid with freshly distilled Thionyl chloride.α-p-Hydroxy benzoyl β-m'-Nitro phenyl ethylene(B) was prepared by the reaction between p-Hydroxy acetophenon and m-Nitro benzaldehyed by usual established method [5,10] Constituent reacting substances were used as received. The synthetic route to the series is shown as under in scheme-1.Final products were decomposed, dried and purified by alcohol.



α-4-[4'- n-Alkoxy- Cinnamoyloxy] Benzoyl-β-3" Nitro phenyl Ethylenes.
Where R= C_nH_{2n+1} *n =1,2,3,4,5,6,8,10,12,14,16*

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Scheme-1: Synthetic Route to the Series

Analytical Data:

TABLE: 1 Elemental analysis for methoxy, butyloxy, octyloxy and tetradecyloxy derivatives

Sr. No	Molecular formula	Elements % found (% Calculated)		
		C	H	N
1	$C_{25}H_{19}NO_6$	69.98 (69.93)	4.45 (4.43)	3.28 (3.26)
2	$C_{28}H_{25}NO_6$	71.30 (71.34)	5.29 (5.31)	2.94 (2.97)
3	$C_{32}H_{33}NO_6$	72.91 (72.87)	6.29 (6.27)	2.68 (2.65)
4	$C_{38}H_{45}NO_6$	74.60 (74.63)	7.32 (7.36)	2.27 (2.29)

NMR in ppm for Decyloxy derivative:
1.272 ($-CH_2-$ of $OC_{10}H_{21}$ group), 0.880 ($-CH_3$ of of $OC_{10}H_{21}$ group), 1.80 ($-O-CH_2-CH_2-$), 4.01 ($-O-CH_2-$ group), 6.93&8.05 (p-substituted phenyl ring), 7.26 (m- substituted phenyl ring). NMR confirms the structure.

IR in cm^{-1} for Hexyloxy derivative:
695,750 cm^{-1} (m-substituted benzene ring), 810 cm^{-1} (p- substituted benzene ring), 1020,1250&1700 (--COO ester group), 1270 cm^{-1} (>C=O of OC_6H_{13}group).IR confirms the structure.

Texture of Mesophase by miscibility Method: Dodecyloxy homologue: Threaded Nematic and pentyloxy homologue : Smectic-A Type.

RESULTS AND DISCUSSION

Cis-p-n-Alkoxy cinnamic acids (A_1) and α-p-hydroxy benzoyl-β-3'-Nitrophenyl ethylene (B) are nonmesogenic and melt sharply at their melting points. However on linking acid chloride(A_1) with component,(B) gives rise to form series of products from corresponding n-alkoxy acids; some of which are mesogenic in character except first four homologues of the series.i.e. Methyl to butyl derivatives of the series are nonmesogenic, while rest of the homologues are mesogenic. Pentyl, hexyl, octyl and decyl derivatives are enantiotropically smectogenic in combination with nematogenic character. Dodecyl, tetradecyl and hexadecyl derivatives are only nematogenic without exhibition of any smectic property even in the monotropic condition. Transition temperatures (Table-2) of the homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal as recorded in Table-2.

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

Compound No.	R=C_nH_{2n+1} (n)	Sm	Nm	Isotropic
1	1	-	-	172.0
2	2	-	-	166.0
3	3	-	-	180.0
4	4	-	-	171.0
5	5	128.0	134.0	144.0
6	6	136.0	150.0	158.0
7	8	130.0	151.0	166.0
8	10	116.0	129.0	152.0
9	12	-	142.0	156.0
10	14	-	143.0	162.0
11	16	-	145.0	154.0

Sm= Smectic; Nm= Nematic.

The phase behavior of the series is discussed as under. Solid-isotropic or mesomorphic transition curve adopt a zigzag path of rising and falling and behaves in normal manner.Smectic-nematic transition curve gradually rises from n-pentyloxy to n-octyloxy derivatives of the series and then smoothly falls to the n-decyloxy derivative of the series. Thus smectic-nematic transition curve behaves in usual expected manner. Nematic-isotropic transition curve partly behaves in normal manner upto n-decyloxy derivative i.e. curve rises from n-pentyloxy derivative and then adopt descending tendancy as series is ascended up to n-decyloxy homologue.But then curve abnormally behaves i.e. it rises instead of falling in case of dodecyloxy and tetra decyloxy derivatives. Odd-even effect is absent for Smectic-Nematic and Nematic-isotropic transition curves as mesophase commences from and beyond pentyloxy derivative. Smectogenic phase length and nematogenic phase length ranges from 6.0^0 C to 21.0^0 C and 8.0^0 C to 23.0^0 C respectively. Total mesophase length vary minimum 09.0^{0}C at hexadecyloxy homologue to maximum of 36.0^{0}C at n-octyloxy and n-decyloxy homologues. Series under discussion is predominantly nematogenic and partly smectogenic.

Nonmesogenic constituent components A_1 and B from which final benzoylester derivatives of the series formed induces mesophase formation. It happened due to linking of more number of phenyl rings causing increase of molecular length and aromaticity which results suitable magnitude of molecular rigidity and flexibility,molecular polarity/ polarizability as well as length to breadth ratio. Thus, intermolecular anisotropic forces of attractions are suitable and capable enough to manage two dimensional array of molecules in floating condition. Methoxy to n-butyloxy homologues are nonmesogenic due to their high crystallizing tendency arising from imbalanced and unsuitable magnitude of intermolecular forces of attractions as a consequence of undesired molecular rigidity and flexibility [1,2,3]. Thus , molecules of first four homologues are disaligned on the plane of the surface under the influence of applied heat from surroundings. As a result of this, molecules under microscopic examination are unable to resist thermal vibrations and sharply passes directly into isotropic state from solid state without passing through an intermediate state of existences called as mesogenic or mesomorphic or liquid crystal state. Rest of the molecules of homologues from and beyond n-pentyloxy derives are compitant enough to resist thermal vibrations exposed upon them under the influence of applied heat from thermodynamic surroundings; due to suitable magnitude of forces of attractions, resulting into emergence of smectic and/ or nematic mesophase. Pentyloxy to Octyloxy derivatives bear lamellar arrangement of molecules in their crystal lattices which on heating adopt sliding layered arrangements of molecules, maintaining two dimensional array of molecules in floating condition, inducing smectic mesophase. Still on raising the temperature after acquiring smectic mesophase, molecules are capable enough to resist thermal vibrations but molecular layered arrangement of molecules disappears and molecules are disaligned on the plane of the surface at an angle less than 90^0 in parallel manner i.e. statically parallel orientational order of molecules is maintained giving rise to nematic mesophase formation in addition to layered molecular arrangement. Thus, nematic mesophase occurs after smectic mesophase. Similarly dodecyl, tetradecyl and hexadecyl homologues derivatives emerges only nematic mesophase without exhibition of smectogenic mesophase. Disappearance of odd-even effect is attributed to the absence of mesophase formation by early member of the series. Variation of mesogenic behavior from homologue to homologue in same series is attributed to the progressively added methylene unit in left n-alkoxy group. Abnormal behavior of nematic-isotropic transition curve for higher member of series is attributed to the longer left n-alkyl chain which may coil, bend or flex in irregular manner,[6,7,8] inducing irregularity in molecular rigidity and flexibility. Such probability has direct effect on molecular polarity and polarizability as well as intermolecular attractions. Table-3 summarizes average thermal stability and commencement of mesophase formation. Figure-2 represents molecular structures of structurally similar homologous series-S_2 for the comparison of mesogenic properties of presently investigated series-1.

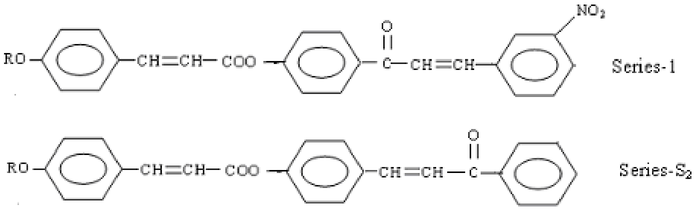

FIGURE-2. Structurally Similar Homologous Series

Both homologous series-1 and S_2 [10,11] are identical in size, shape, aromaticity central and left n-alkoxy terminal groups. But they differ in their molecular structure with respect to last phenyl ring which replaces -H of series-1 by –NO_2 group at the meta position from second central group. Moreover >C=O group is linked directly with middle phenyl ring while it links with last phenyl ring in case of series-S_2. Therefore in case of presently investigated series-1, differs from series-S_2 with respect to lateral substitution [width], keeping molecular length unchanged and positional variation of >C=O group in addition to difference caused by varying inductive and steric effects of -H and -NO_2. Thus, variation in thermal stabilities and commencement of smectic and / or nematic mesophase as well as other related mesogenic or thermodynamic properties undergo variation. Above discussed variations results into varied length to breadth ratio, molecular polarizability intermolecular distance and hence, the suitable magnitude of intermolecular forces of attractions and molecular arrangements in floating condition variation accordingly.

TABLE-3: Average Thermal stability

Series→	1	S_2
Smectic-Nematic	141.0 (C_5—C_{10})	—
Nematic-Isotropic	156.0 (C_5—C_{16})	144.5 (C_6—C_{16})
Commencement Of Smectic mesophase	C_5	—

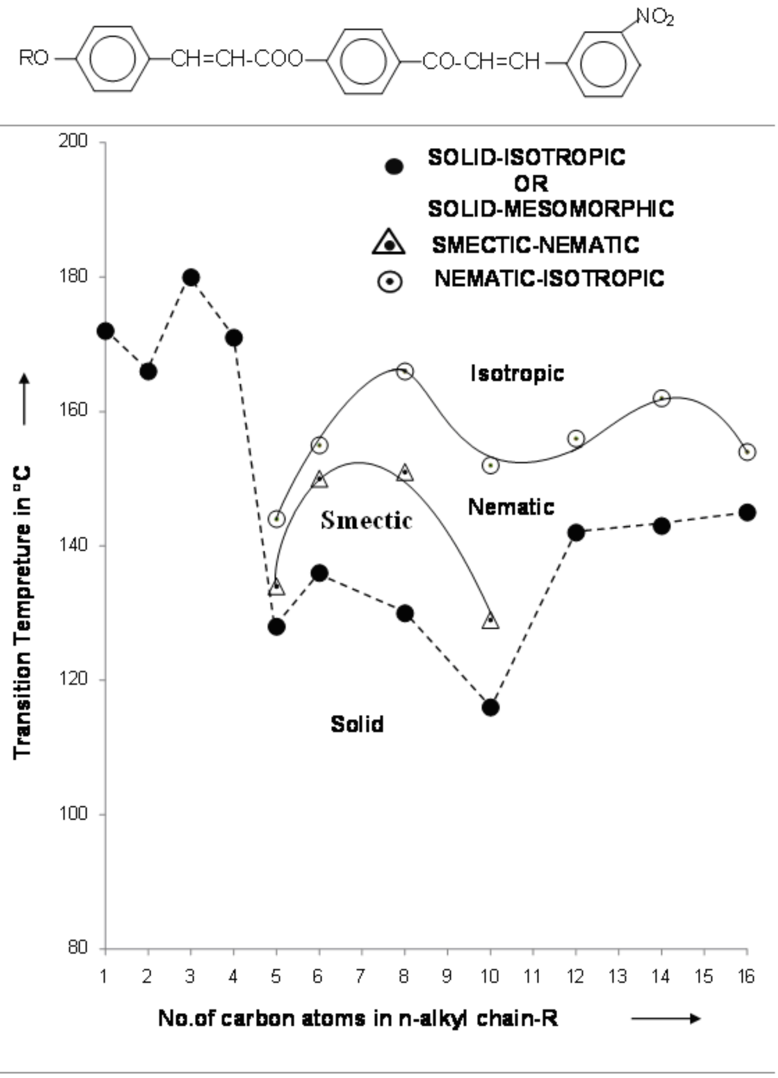

Figure :1 Phase Behavior of Series

From the table-3, it is clear that, average thermal stability for Smectic is 141.0 while that of Series-S_2 is 00.0. Secondly nematic thermal stability for series-1 is higher than the Series-S_2 under comparison. Series-1 being nonlinear due to presence of electron widrawing group–NO_2 which widraws electrons from third phenyl ring. Therefore, molecular polarity and polarizability are strengthened as compared to –H of series-S_2. Thus, thermal stability which depend upon enthalpy [ΔH] and entropy value [ΔS] of homologue as system at a given temperature. On raising temperature of a thermodynamic system [Homologue] from surroundings, the molecules under examination starts dancing or moving and fighting against intermolecular forces of internal attractions with the help of external force i.e. thermal energy supplied. Thus, molecular randomness or say entropy or molecular disorder increases at a given temperature T_1 at which mesophase commences to appear and continue up to higher temperature T_2. From and beyond T_2, the entropy or molecular randomness reaches to the extent that, high order of molecular disorder occur and a sample homologue acquires isotropic state from mesogenic state. (T_2-T_1) is called phase length of a homologue concern. Values of enthalpy and entropy are determined from the maxima observed in DSC Scane. Commencement of smectic mesophase depend upon the extent of noncoplanarity caused by the molecule. The extent of noncoplanarity is relatively more of series-1 in combination with higher magnitudes of inter molecular attractions as compared to series-S_2 due to presence of meta substituted $-NO_2$ group. Therefore smectic mesophase commences from fifth homologue in series-1 while it does not occur till the last hexadecyloxy derivative of the series-S_2.

CONCLUSION

Presently investigated novel series is predominantly nematogenic and partly smectogenic of middle ordered melting type and short phase length. Variation in mesogenic properties can be brought about by varying molecular rigidity and flexibility.

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