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Synthesis and study of the effect of positional Isomerism on Liquid Crystal Behavior of the series: Methyl-o-[p'-n-alkoxy benzoyloxy] benzoates

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ABSTRACT

Homologous series Methyl-o-[p'-n-alkoxy benzoyloxy]benzoates was synthesized with a view to understand and establish the effect of molecular structure on liquid crystal[LC] properties in positionally isomeric molecules. Totally ten homologues are synthesized. Methyl and ethyl derivatives of the series are nonliquidcrystals, propyl to hexyl and octyl derivatives are enantiotropic nematic, decyl derivative is polymesomorphic , i.e. exhibits enantiotropic nematic mesophase in addition to enantiotropic smectic mesophase as well as dodecyl and tetradecyl derivatives are enantiotropic smectic. Transition temperatures are determined by hot stage polarizing microscope. Analytical data support the structure. Texture of the nematic mesophase is threaded or schlieren type. Liquid crystal properties of titled series are compared with structurally isomeric series.

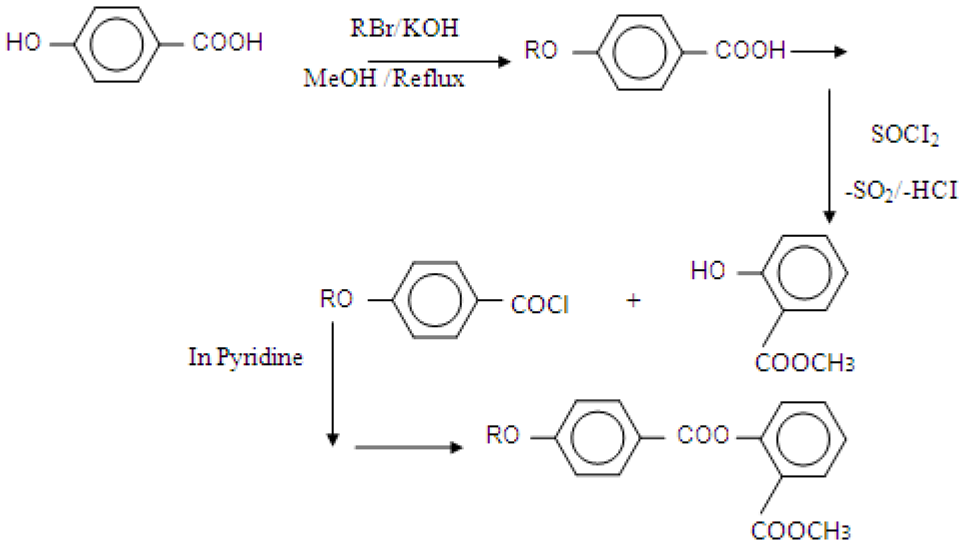
Keywords: Liquid crystal, Smectic, Nematic, Mesomorphs.

INTRODUCTION

The knowledge of relation between liquid crystal property and molecular structure to predict the liquid crystal behavior of a substance is an important part of a research work. Moreover benzoate derivatives are being biologically and pharmaceutically active, are useful from the point of view of their application in medical field and other fields of life. Present homologous series of liquid crystal was planned to synthesize, under above purposes.

MATERIALS AND METHODS

p-n-alkoxy benzoic acids and p-n-alkoxy benzoyl chlorides were prepared by modified method of alkylation of hydroxyl group of p-hydroxy benzoic acid as proposed by Dave and Vora [3]. O-Hydroxy methyl benzoate was prepared by refluxing methanol with o-hydroxy benzoic acid in presence of concentrated sulphuric acid [4]. Ten homologues of esters were synthesized by condensing equimolar proportion of p-n-alkoxy benzoyl chloride with o-hydroxy methyl benzoate in pyridine. All the ten homologues of the series were purified by alcohol till constant melting points were obtained. P-hydroxy benzoic acid, alkyle halide, salicylic acid and thionyl chloride, pyridine, methanol, potassium hydroxide, sulphuric acid and o-hydroxy benzoic acid were used as received. The synthetic route to the series is under mentioned in scheme-1



Scheme-1: synthetic route to the series

Characterization:

Some selected homologues of the series were characterized by elemental analysis, IR Spectra, Thermodynamic quantities, enthalpy[ΔH] and entropy[ΔS] discussed qualitatively, without performing D.S.C. scane. Liquid crystal properties were investigated by hot stage polarizing microscope. Smectic-A mesophase and nematic mesophase were confirmed by miscibility method.

Analytical data:

Table:1 Elemental Analysis for Butyloxy, Haxyloxy,and Dodecyloxy derivatives

Sr. no.	Molecular formula	Elements % found (% calculated)	
		C	H
1	$C_{19}H_{22}O_5$	69.47[69.51]	6.02[6.09]
2	$C_{21}H_{26}O_5$	70.52[70.78]	6.69[6.76]
3	$C_{27}H_{36}O_5$	73.61[73.64]	8.08[8.12]

IR Spectra. in cm^{-1} for Ethoxy and octyloxy derivatives.

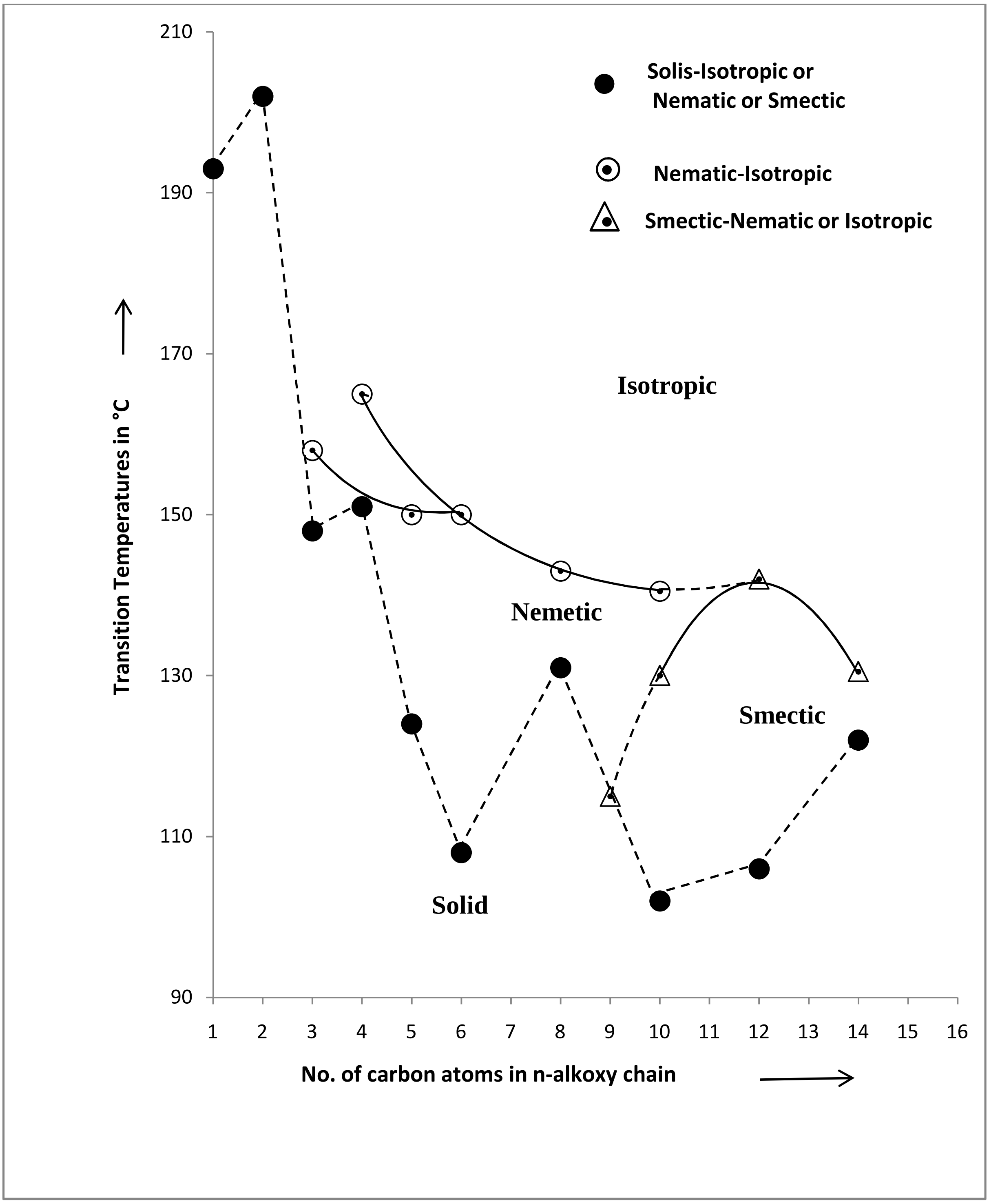
Ethoxy derivative:

850cm^{-1} p-sub benzene ring, 1050, 1250 & 1680cm^{-1} ester group, 1150cm^{-1} alkoxy group, 3000cm^{-1} aro. =C-H str. Of phenyl.

Octyloxy derivative:

750cm^{-1} polymethylene of C_8H_{17}, 820 cm^{-1} p-sub benzene ring , 1150, 125 & 1680 cm^{-1} ester group, 3000 cm^{-1} aro.=C-H str. of phenyl.

Miscibility Method:
Pentyl and Hexyl derivative: Threaded Texture
Decyl derivative: Smectic-A Texture

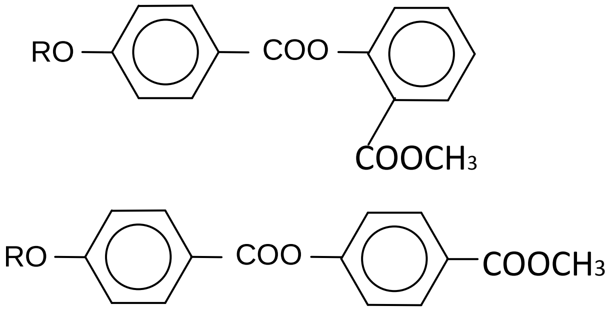


RESULTS AND DISCUSSION

Titled homologous series Methyl-o-[p'-n-alkoxy benzoyloxy] benzoates consists of ten homologues. Liquid crystal property of the series commences from propyl derivatives to tetradecyl derivatives. Methyl and ethyl homologues of the series are nonliquidcrystals and rest of the homologues propyl to hexyl and octyl derivatives are only enantiotropically nematogenic, decyl derivative exhibit enantiotropically smectogenic mesophase in addition to nematogenic character, while dodecyl and tetradecyl derivatives are entirely smectogenic. Texture of a nematic mesophase is of threaded or schlieren type and that of a smectic mesophase is of focal conic fan shaped of a smectic-A or C. The transition temperature observed through hot stage polarizing microscope are recorded in **Table-2** and plotted versus the number of carbon atoms in left n-alkyl chain of n-alkoxy terminal end group. A phase diagram for the titled homologous series is obtained : as shown in the figure-1. The phase diagram observations show that, solid-isotropic or nematic or smectic transition curve follows zigzag path of rising and falling as series is ascended in normal manner. Smectic nematic or smectic-isotropic transition curve initially rises and then falls in usual manner. Nematic-isotropic transition curve shows descending tendency as series is ascended and merges into smectic-isotropic transition curve with exhibition of odd-even effect. Smectic isotropic transition curve is extrapolated for octyloxy derivative and Latent transition temperature determined whose predicted value is more than 100°c.

TABLE-2 Transition Temperatures in °C

Comp. no.	**R=$C_n H_{2n+1}$ [n]**	**Sm.**	**Nm.**	**Isotropic**
1	1	-	-	193.0
2	2	-	-	202.0
3	3	-	148.0	158.0
4	4	-	151.0	165.0
5	5	-	124.0	150.0
6	6	-	108.0	150.0
7	8	-	131.0	143.0
8	10	102.0	130.0	140.5
9	12	106.0	-	142.0
10	14	122.0	-	130.5



Series-1

Series-A

Figure-2

Ortho hydroxy methyl benzoate is a nonmesomorphic, but, on linking it with p-n-alkoxy benzoic acid, gives eight ester homologues of lower transitions with liquid crystal property. The dimerization of alkoxy benzoic acids disappears due to breaking of hydrogen bonding on esterification. Odd-even effect and alternation of transition temperature is observed due to sequentially and progressively added methylene unit at the left n-alkoxy terminal end group. Odd-even effect diminishes as series is ascended for higher members of the series for longer n-alkyl chain because longer n-alkyl chain of n-alkoxy group may coil or bend without any contribution to odd-even effect. Nonliquid crystal behavior of methoxy and ethoxy terminal end group bearing, homologues are attributed to their high thermodynamical stability with liquid crystal range zero degree temperature. Two dimensional array of molecules in floating condition is not maintained and molecules of a sample homologue are free to move and orient randomly in all possible directions which causes high level of disordered molecular arrangement, called as high value of entropy[$\Delta S=\Delta H/T$] at their melting point. **Table-3** summarizes average thermal stability and molecular structure of present series1 and other structurally similar isomeric series-A[ ] chosen for comparison as shown in figure-2.

The magnitude of intermolecular forces of attractions of titled homologous series-1 is different than the isomeric series-A chosen for comparison of liquid crystal [LC] properties, because geometrical shape of series-1 is nonlinear and that of series-A is linear. Therefore length to breadth ratio and polarizability differs, irrespective of their same two phenyl rings with same central group and same lateral or terminal group $-COOCH_3$ as well as left n-alkoxy terminal end groups. Thus, different molecular polarizability causes difference in liquid crystal properties for the same homologue from series-1 to series-A. The variation in liquid crystal properties from homologue to homologue in the same series-1or A is attributed to the sequentially added methylene unit at the left n-alkoxy terminal end group.

TABLE-3: Average Thermal Stability in °C

Series	1	A
Smectic-Nematic or isotropic	110.0 [C_{10}-C_{14}]	109.1 [C_5-C_{16}]
Nematic isotropic or vice versa	151.1 [C_3-C_{10}]	-
Commencement of smectic mesophase	C_{10}	C_5

Careful observation of table-3 indicate that the smectic-nematic or isotropic thermal stability of series-1 and A is almost equivalent neglecting numerical different viz. 110.0 and 109.1 but nematic-isotropic thermal stability of series-1 is 151.1. Thermal stability of a series or a homologue (system) is associated with its enthalpy [ΔH] content. As heat energy is supplied from the surroundings i.e. parts of universe other than a system, the supplied heat operates against the intermolecular binding forces of attractions as a consequence of molecular rigidity and flexibility. Thermodynamic stability of system tends to destabilise leading random orientations of molecules. As, temperature rises the quantum of heat energy supplied from surrounding to system , enhances random orientational disorder of molecules acquiring definite value of molecular randomness or a thermodynamic quantity entropy [$\Delta S=\Delta H/T$] at which intermolecular forces of attractions happens to be anisotropic of suitable magnitude which maintains to float molecules of a sample substance or a system in two dimensional array, either sliding layered arrangement and/or statistically parallel orientational ordered molecular arrangement. Thus, smectic and/or nematic mesophase occurrence is practically observed within definite range of temperature called phase length. Nematic mesophase occurred in series-1 is attributed to the laterally substituted $-COOCH_3$ group in series-1 instead of it is substituted linearly as end group in case of series-A. Polarizability factor predominates in series-1, instead of polarity factor of a group $-COOCH_3$. Nematic mesophase induces at the cost of smectic mesophase in series-1. Thus, series-1 is predominantly nematogenic and partly smectogenic with middle ordered melting type whose range of liquid crystalinity ranges from 8.0°C to 42.0 °C . Series-A selected for comparative study is entirely smectogenic without exhibition of any nematic character with relatively lower transition, whose liquid crystal phase length ranges from 21.0 °C to 58.0 °C at the tetradecyl derivative of the series. The commencement of smectic mesophase takes place from decyl homologue in series-1, while it commences from fifth homologue of series-A. Early or late commencement of smectic mesophase depend [7] upon the extent of noncoplanarity caused by the molecule. Molecules of series A are less noncoplaner than the molecules of series 1, in which laterally substituted –$COOCH_3$ induces more noncaplanarity and steric hindrance. Thus, less noncoplaner molecules allows early sliding layer arrangement of the molecules from the substance which holds originally lamellar arrangement of molecules.

CONCLUSION

Laterally substituted group induces nematic mesophase at the cost of smectic mesophase, otherwise ester series are smectogenic. Polarizability induces by Ortho substituted –$COOCH_3$ is more than the same isomeric group situated at the Para position of central –COO- group. Thus, conclusions derived from present study raised the credibility to the early research work [7,11].

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