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Synthesis and Study of Ester Homologous Series of Mesogenic Characteristics : p-Isobutyloxy Phenyl-p'-n-alkoxy benzoates

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ABSTRACT

Titled homologous series of mesogens: p-Isobutyloxy Phenyl-p'-n-alkoxy benzoates consisted of ten members of a series is synthesized with a view to understand the effect of structure on mesomorphic properties . Methyloxy and ethoxy homologues are nonmesogenic, propyloxy to octyloxy homologues are only nematogenic and decyloxy, dodecyloxy as well as tetradecyloxy derivatives of the series are monotropcally smectogenic in addition to enantiotropically nematogenic. Thus, series under investigation is predominantly nematogenic and partly smectogenic. Analytical data support the structure of molecules. Series is middle ordered melting type and its mesogenic properties are compared with structurally similar homologous series. Texture of smectic mesophase are focalconic fan shaped and that of nematic mesophase is threaded or schlieren type.

Keywords: Nematic, Smectic, Liquid crystals, mesogen, monotropy.

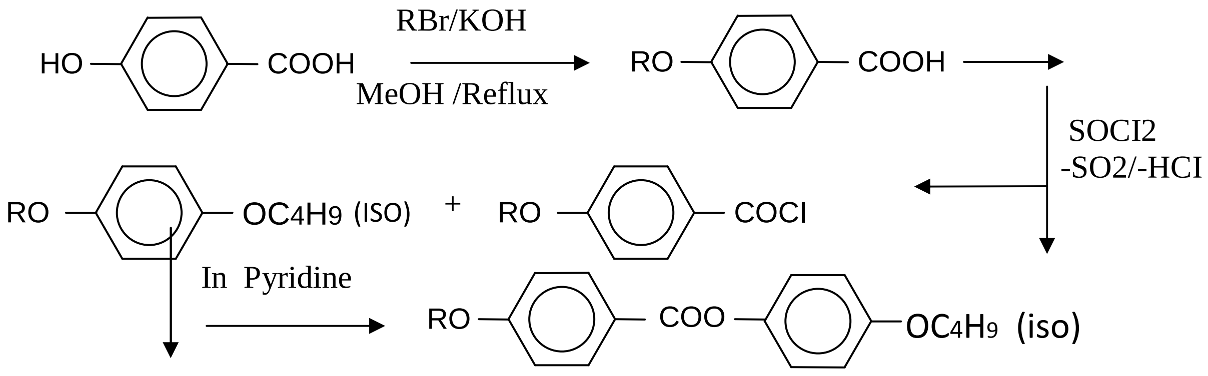
INTRODUCTION

Mesogenic material [LC] is useful for various purposes of applications based on their molecular structure. Cinnamates and benzoates derivatives being biologically and pharmaceutically active materials are planned to synthesize and to study the effect of molecular stucture on mesomorphic properties which may be useful for the groups of researchers studying the application part in the electronic display devices, medical field, analytical field etc.

MATERIALS AND METHODS

Experimental

p-n-alkoxy benzoic acids and p-n-alkoxy benzoyl chlorides were synthesized by modified method of Dave and Vora [3]. p-isobutyloxy phenol was prepared by the method of Mouthner and Mehta [4]. The ten homoiogues of the series of esters were synthesized by condensing equimolar proportion of p-n-alkoxy benzoyl chloride with p- isobutyloxy phenol in pyridine. All the members of the series were purified after decomposition, filteration and drying by alcohol till constant transition temperatures obtained . p- Hydroxy benzoic acid , Alkyl halides, thionyl chlorides, pyridine, Methanol, Potassium hydroxide, Sulphuric acid are used as received .The synthetic route to the series is mentioned below in scheme-1



Scheme-1: synthetic route to the series

Characterization:

Selected homologues of the series were characterized by IR spectra and elemental analysis. Thermodynamic quantities viz enthalpy [ΔH] and entropy [ΔS] are discussed qualitatively with reference to thermal stability of the series without practical performance of DSC scane. Mesogenic properties were investigated by polarizing microscope with heating stage.

Analytical data:

Table:1 Elemental Analysis for Propyloxy, acityioxy,and tetra decyloxy derivatives

Sr. no.	Molecular formula	Elements % found (% calculated)	
		C	H
1	$C_{20}H_{24}O_4$	73.09[73.17]	7.28[7.31]
2	$C_{25}H_{34}O_4$	75.40[75.37]	8.50[8.54]
3	$C_{31}H_{46}O_4$	77.05[77.18]	9.58[9.57]

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

Ethoxy derivative:

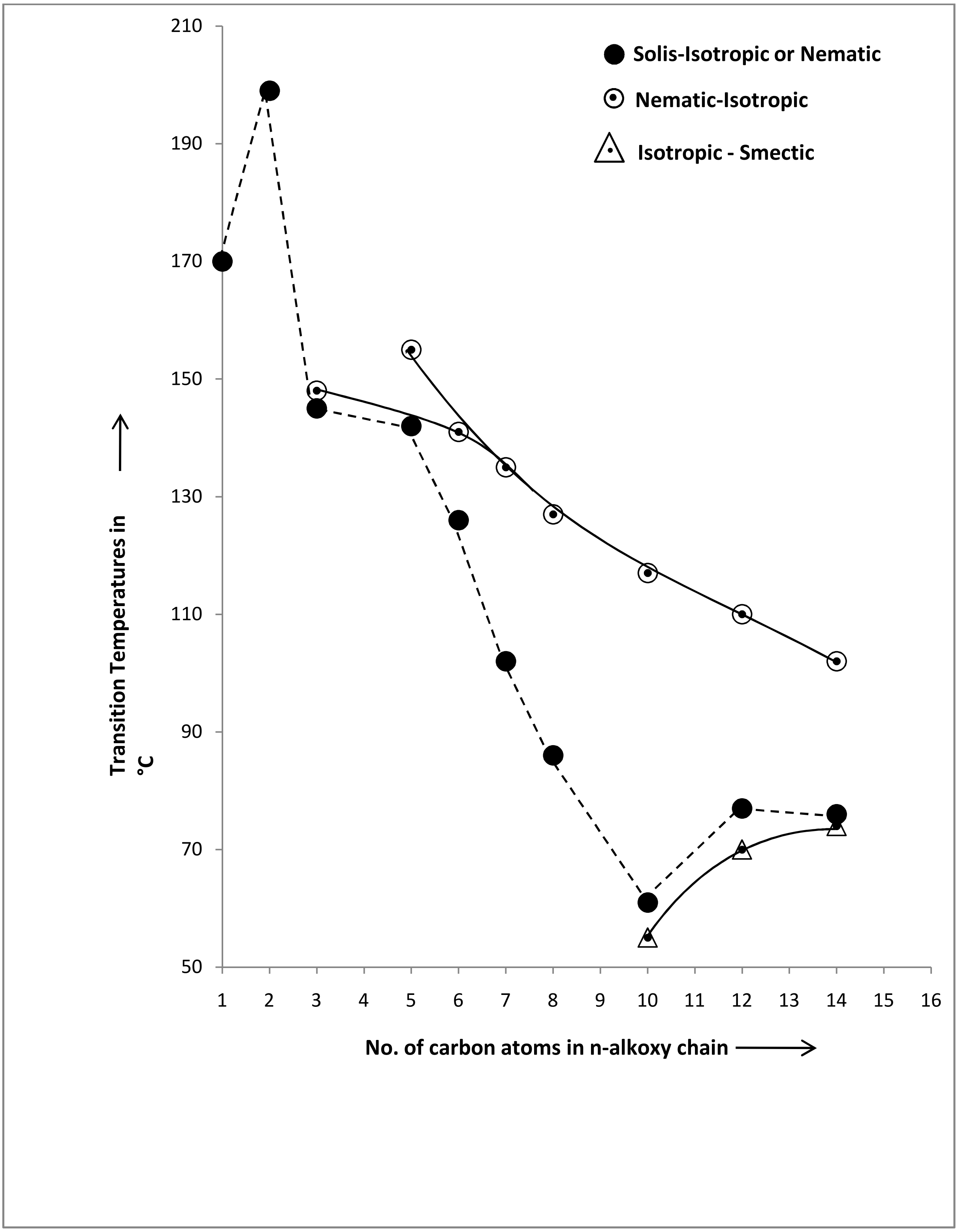
850cm^{-1} p-sub benzene ring, 1050, 1250 & 1680cm^{-1} ester group, 1150cm^{-1} alkoxy group, 1300 & 1330cm^{-1} gem-dimethyl of isobutyl, 2800cm^{-1} satu. C-H str. Of alkyl, 3000cm^{-1} aro. =C-H str. Of phenyl.

Hexyloxy derivative:

750cm^{-1} polymethylene of hexyloxy, 850cm^{-1} p-sub.benzene ring, 1150,1250 & 1680cm^{-1} ester group, 1350 & 1400cm^{-1} gem-dimethyl of isobutyl, 3000cm^{-1} aro.=C-H str. Of phenyl.

RESULTS AND DISCUSSION

Homologous series p-isobutyloxy phenyl p'-n-alkoxy benzoates consists of ten homologues. Methoxy and Ethoxy homologues are nonliquid crystal or nonmesogenic, while rest of the homologues is liquid crystals in nature. Propyloxy to hexyloxy derivatives and octyloxy derivative are enantiotropically nematogenic while, decyloxy, dodecyloxy and tetra decyloxy derivatives are monotropic smectic and enantiotropically nematic in character.



Series: p-Isobutyloxy Phenyl-p'-n-alkoxy benzoates
FIGURE : 1 Phase behavior of the series

Alkoxy benzoic acids are dimeric with high melting points but on esterification with p-isobutyloxy phenol gives rise to ester homologues relatively of lower transitions than their correspong p-n-alkoxy acids due to breaking of hydrogen bonding of dimerised alkoxy benzoic acids. The texture of nematic mesophase is of threaded or schlierens type and that of smectic mesophase is focal conic fan shaped, as judged directly from the field of view of hot stage polarising microscope. Transition temperatures from **table-2** of the homologues of the series under discussion are plotted versus the number of carbon atoms in left n-alkoxy group of the n-alkyl chain of the molecules. A phase diagram showing phase behavior is obtained is shown in **figure-1**. Phase behavior diagram of the series indicate that solid-isotropic or nematic transition curve continuously falls from ethoxy homologue to decyl homologue as series is ascended, but it rises from first to the second homologue and falls in usual manner. Then it rises from decyl to tetra-decyl derivative. Thus, it partly follows zigzag path of rising and falling. Nematic isotropic transition curve continuously shows descending tendency as series is ascended and shows expected normal behaviour. Nematic-smectic mesophase transition curve behaviour in normal manner. Odd-even effect is observed for nematic-isotropic transition curve in normal expected manner

TABLE-2 Transition Temperatures of Series

Comp. no.	R=$C_n H_{2n+1}$ [n]	Sm.	Nm.	Isotropic
1	1	-	-	170.0
2	2	-	-	199.0
3	3	-	145.0	147.0
4	4	-	142.0	155.0
5	5	-	126.0	141.0
6	6	-	102.0	135.0
7	8	-	86.0	125.0
8	10	[55.0]	61.0	117.0
9	12	[70.0]	77.0	110.0
10	14	[74.0]	76.0	102.0

[Values in the parenthesis indicate monotropy]

The nonmesogenic behaviour of Methoxy and ethoxy derivatives of the series is attributed to the high crystallizing tendency of the compounds arising due to their high level of intermolecular forces of attractions. Odd-even effect observed for the nematic isotropic transition curve is attributed to the sequentially added methylene unit in the left n-alkoxy terminal group. **Table-3** summarizes average thermal stability and molecular structure of the present series and other structurally similar homologous series A[15] and B[16] chosen for comparative study as shown in **figure-2.**

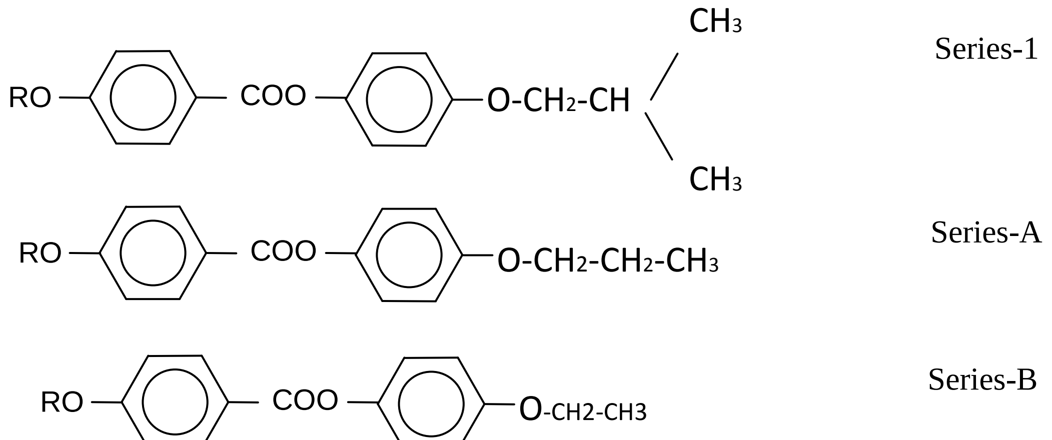


Figure-2

Mesogenic properties of a substance depends upon the intermolecular anisotropic forces of attractions of suitable magnitude as a consequence of its molecular rigidity and flexibility .The geometrical shape, size, linearity of a molecule, molecular polarity and polarizabity, aromaticity, electron density, type of laterally and terminally substituted groups and length to breadth ratio are the factors affecting magnitude of intermolecular forces of attractions. The net intermolecular anisotropic or isotropic forces of attractions depend upon the combine effect of above mentioned parameters. Homologous series A and B chosen for comparison with series-1 consist of two phenyl rings bridged through -COO- central group and left n-alkoxy terminal are common identical part of all the molecules of the series-1, A and B. They only differ with respect to right terminally situated end group. Therefore observed variation in mesogenic properties and the extent of variation in mesogenic properties can be linked with the difference in molecular polarity and polarizability varied due to varied terminal end groups viz $–OC_4H_9$ [iso], $-OC_3H_7$ [n] and $–OC_2H_5$ respectively for series 1,A and B.

TABLE-3: Average Thermal Stability in °C

Series	1	A	B
Nematic smectic or smectic isotropic	66.3 $[C_{10}-C_{14}]$	96.0 $[C_8-C_{12}]$	118.3 $[C_8-C_{12}]$
Nematic isotropic or isotropic nematic	130.25 $[C_3-C_{14}]$	99.5 $[C_2-C_8]$	119.8 $[C_5-C_{10}]$
Commencement of smectic phase	C_{10}	C_8	C_8

Careful observation of Table-3 indicate that, the Nematic-isotropic thermal stability decreases from the series containing $–OC_4H_9$ [iso] → $–OC_2H_5$ → – OC_3H_7[n] right terminal end group while smectic thermal stability increases from $–OC_4H_9$ [iso] → $–OC_3H_7$[n] → $–OC_2H_5$. i.e. smectic thermal stability can be linked with number of methylene units contained by alkyl group of riese end group bonded through oxygen atom at the phenyl ring. Thus polarity of terminal end group regulates nematic-isotropic or nematic or vice versa thermal stability of series-1 smectic-isotropic or nematic or vice versa thermal stability of series-1 is the lowest among the series under comparison because isobutyl terminal end group is nonlinear while $–OC_3H_7$[n] and $–OC_2H_5$ groups are linear. Therefore molecular polarity in addition to molecular polarizability reduces intermolecular attractions due to increase in the intermolecular distance as compared to series A and B. The variation in mesogenic properties observed from homologue to homologue for same series is attributed to the varying left n-alkyl chain in which methylene units are gradually added keeping right terminally group intact. But, variation in mesogenic properties for the same homologue from series to series is attributed to varying right terminal end group polarity and polarizability. Every homologue of the series under discussion stabilized at room temperature and under constant atmospheric pressure. Therefore a homologue substance thermodynamically can be considered as an open system and rest of the universe can be considered as surrounding. Thus exchange of energy can take place from system to surrounding or from surrounding to system**.** The energy contained by system(homologue) at constant pressure is ΔH,called as Enthalpy change at room temperature T, when a system possesses three dimensional arrangement of molecules. Now, as heat energy supplied to a system from surrounding , the supplied heat energy fights against the intermolecular attractions. As a result of this intermolecular distance increases with gradual rise of temperature. Consequently molecular randomness and hence the entropy $[\Delta S_1= \Delta H_1/T_1]$ increases at temperature T_1. Thus, molecular randomness increases and resultant intermolecular forces of attractions becomes anisotropic of suitable magnitude at temperature T_1 showing mesogenic phase. Now molecular system acquires two dimensional array of molecules in which statistically parallel oriential order of molecules maintained and/or sliding layered arrangement from lamellar arrangement of molecule emerge, causing formation of nematic and/or smectic mesophase respectively of a system. Thus, mesophase commence to appear at temperature T_1 and continue to appear up to higher or lower temperature T_2 . The difference of temperature $[T_2-T_1]$ or vice versa is called mesogenic phase length. The intermolecular forces of attractions become isotropic and a substance under investigation becomes isotropic liquid on heating and solid on cooling from and beyond temperature T_2. The value of ΔS_2 can be determined from the peak value of DSC scame of ΔH versus the temperature T thermo gram. The commencements of smectic mesophase take place from decyloxy derivative for series 1 while it take place from eights homologue in series A and B. Early or late commencement of smectic mesophase depend[B] upon the extent of noncoplanarity caused by a molecule. Isobutyl terminal is nonlinear and undergo into the influence of steric hindrance more as compared to linear propyl and ethyl group of series A and B. Thus, extent of noncoplanarity caused by the molecules of series 1 is more than the molecules differ of series A and B. Thus, smectic mesophase commences later at is from i.e, tenth homologue in series 1. The mesogenic range varies minimum from 2.0^{oc} at the third homologue to maximum of 43^{oc} at the sixth homologue .Thus mesogenic range is enough and the series is of middle ordered melting type.

CONCLUSION

The study of titled homologous series suggest that, nonlinear structured molecules of aster homologoes series with carboxy central bridge are not entirely smectogenic, but nonlinear Isobutyloxy terminal replaces smectogenic characteristic of the series to predominantly nematogenic characteristic at the cost of smectic property. Thus present study support the earlier views and raises credibility to conclusions drawn earlier[7.11].

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