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Physical synthesis and study of new mesomorphic series of benzoate esters: 4-Propyloxy phenyl-4'-n-alkoxy benzoates

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ABSTRACT

Benzoate esters homologous series of liquid crystals [LC] is synthesized and studied, with a view to understand and establish the relation between molecular structure and liquid crystal behavior. Totally nine homologues, viz; Methyl to hexyl, octyl, decyl and dodecyl derivatives of the series are synthesized. Methyl and propyl derivatives of the series are nonmesomorphic, while, rest of the homologue derivatives are monotropically or enantiotropically mesomorphic. All the mesomorphic homologues exhibit nematogenic character except decyl and dodecyl homologues. Smectic mesophase commences from octyl derivative. Clear cut odd-even effect is not observed for nematic-isotropic transition (or vice versa) curve in a phase diagram plot. Solid-isotropic or nematic transition curve and smectic- nematic or isotropic transition curves behaves in normal manner. Series is predominantly nematogenic and partly smectogenic. Nematogenic mesophase is of threaded or schlieren texture and that of smectic mesophase is focalconic fan shaped of Sm-A type as determined from hot stage polarizing microscope. Analytical data support the structure of molecules. Mesomorphic properties are compared with structurally similar series.

Keywords: Liquid crystal, Smectic, Nematic, Mesomorphic, Monotropy.

INTRODUCTION

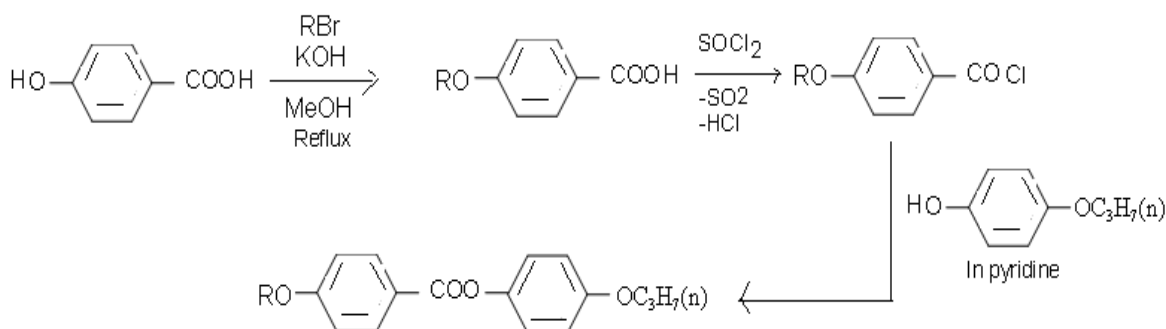
Liquid crystal materials are being useful in variety of fields like electronic display devices, medical field, biological application, pharmaceutical preparation, analytical work etc. Looking to the utility demands of LC materials in present and future, it is necessary to produce new liquid

crystal substances to maintain equilibrium between utility demand and availability or supply of material, at economical cost. New materials with liquid crystal property within definite range of temperature are planned to synthesize by changing molecular shape, size, moiety, by changing central terminal, lateral groups and number of phenyl rings so as to vary rigid and flexible molecular part or parts. Presently two phenyl rings are bridged through carboxy group is a rigid core and flexible parts are left n-alkoxy varying terminal keeping intact $-\text{OC}_3\text{H}_7(n)$ right terminal without any lateral substitution. Thus, intermolecular anisotropic forces of attractions of suitable magnitude are generated to achieve the goal of giving birth to the new LC material.

MATERIALS AND METHODS

Experimental:

Synthesis 4-n-Alkoxy benzoic acids and 4-n-alkoxy benzoyl chlorides were synthesized by modified method of Dave and Vora [3]. 4-Propyloxy phenol was prepared by the method of Mouthner and Mehta [4]. The nine esters were prepared by condensing equimolar proportion of 4-n-alkoxy benzoyl chloride with 4-propyloxy phenol in pyridine. Final product esters were purified by alcohol till constant transition temperatures obtained. 4-Hydroxy benzoic acid, n-alkyl halides, thionyl chloride, pyridine, KOH, CH_3OH were used as received. The synthetic route to the series is mentioned below as Scheme-1.



Where $R = \text{C}_n\text{H}_{2n+1}$, $n = 1$ to $6, 8, 10, 12$.

SCHEME-1: Synthetic route to the series.

Characterization:

Characterization of selected homologues were carried out by IR spectra and elemental analysis. Enthalpy (ΔH) and entropy (ΔS) with reference to thermal stability are qualitative discussed without practical performance of DSC scan. Mesomorphic properties were investigated by using polarizing microscope with heating stage.

Analytical data:

TABLE:1 Elemental Analysis for Ethoxy, Hexyloxy and Dodecyloxy derivatives.

Sr.No.	Molecular formula	Elements % found (% calculated)	
		C	H
1.	$\text{C}_{18}\text{H}_{20}\text{O}_4$	71.8 (72.0)	6.61 (6.66)
2.	$\text{C}_{22}\text{H}_{28}\text{O}_4$	74.11 (74.15)	7.81 (7.86)
3.	$\text{C}_{28}\text{H}_{40}\text{O}_4$	76.32 (76.36)	9.00 (9.08)

IR Spectra in cm^{-1} for n-Butyloxy and n-Decyloxy Derivatives**n-Butyloxy derivative**

825-p-sub phenyl ring, 1060- ether linkage, 1090 - C=O of alkoxy, 1215 C=O bending, 1460,1489,1505,1605 of aromatic -C=H-, 1750, C=O of ester, 2889- p- sub. Of alkyl group, 3080- aromatic -C=H-.

n-Decyloxy Derivative

720-polymethylene of $\text{C}_{10}\text{H}_{21}$, 830 p-sub. Phenyl ring, 1080 ether linkage 1110 C=O of alkoxy, 1240 C=O bending 1465, 1490, 1515, 1585 aromatic C=O, 1805 C=O of ester, 1890 of sub. C-H of alkyl, 3105 aromatic -C=H-.

RESULTS AND DISCUSSION

Homologous series 4-propyloxy phenyl-4'-n-alkoxy benzoates consists of nine homologues of which seven members of the series are liquid crystals and two members viz; Methyl and Propyl derivatives are non-liquid crystals. Ethyl and butyl derivatives are monotropic nematic while rest of the mesomorphic derivatives are enantiotropic nematic with or without smectic character. Smectic character commences from octyl derivatives and continue to appear upto last member of the series with nematic character in case of octyl homologue and without nematic character (only smectogenic) in case of decyl and dodecyl derivative. Nematic mesophase is of threaded or schlieren texture and smectogenic mesophase is of the focal conic fan shaped with type-A as determined by miscibility method observed under hot stage polarizing microscope. Microscopic observation of transition temperatures of the series under investigation are recorded in table-2. Transition temperatures are plotted versus the number of the carbon atoms in n-alkyl chain of left n-alkoxy terminal. A phase diagram is obtained showing phase behavior of homologues, are shown in figure-1 from table-2. Solid-isotropic or mesomorphic transition curve follows zigzag path of rising and falling manner with overall descending tendency as series is ascended. Nematic isotropic or vice versa transition curve and smectic-nematic or isotropic transition curves behaves in normal manner without showing up proper odd-even effect. Higher homologues, decyl and dodecyl derivatives are only smectogenic, suggesting that the higher homologues beyond dodecyl derivative is smectogenic only.

TABLE 2

Comp. No.	R= $\text{C}_n\text{H}_{2n+1}$ (n)	Sm	Nm	Isotropic
1.	1.	-	-	102.0
2.	2.	-	(92.0)	109.0
3.	3.	-	-	97.0
4.	4.	-	(83.0)	90.0
5.	5.	-	106.0	122.0
6.	6.	-	98.0	103.0
7.	8.	59.0	87.0	97.5
8.	10.	94.0	-	103.0
9.	12.	90.0	-	96.0

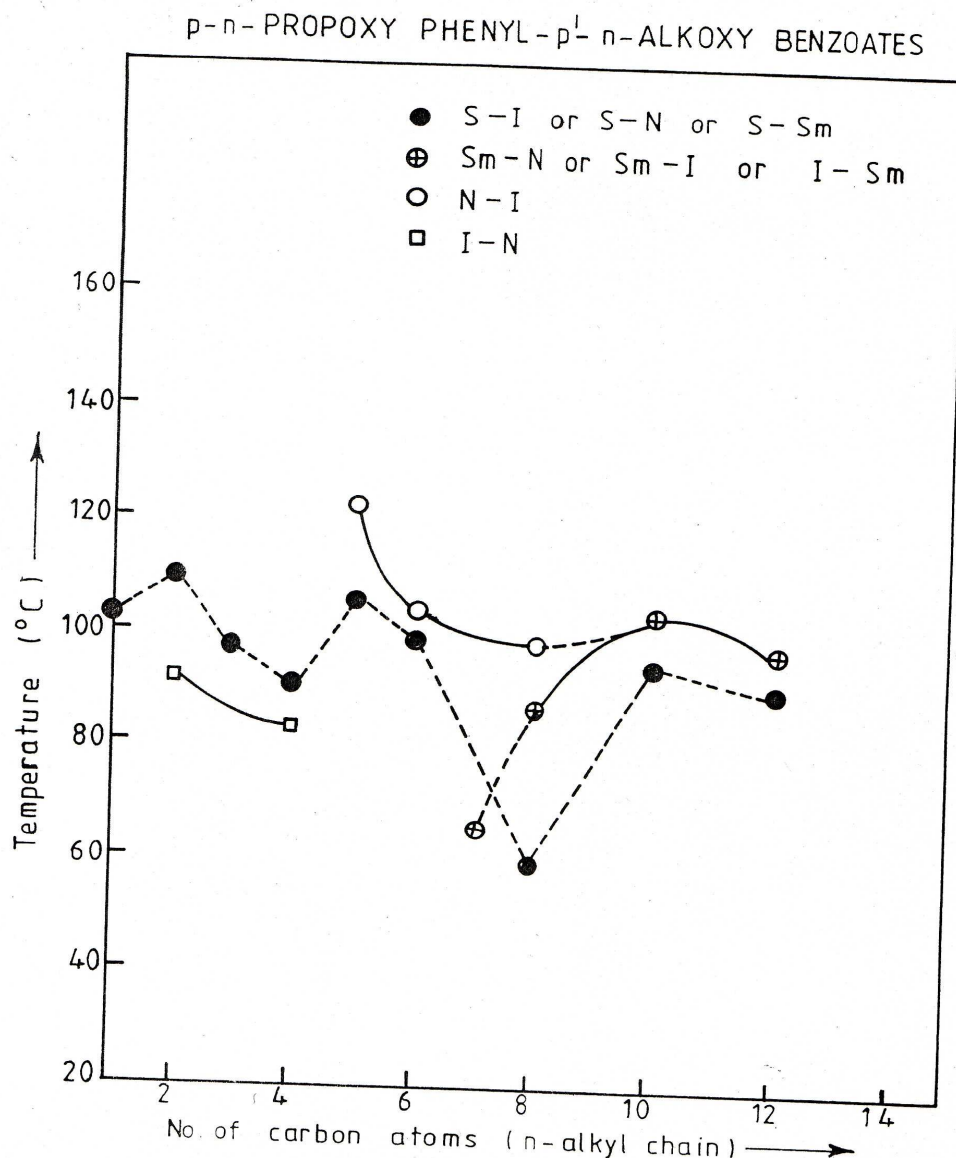


FIGURE-1 Phase behaviour of the series.

4-Propoxy phenol is a nonmesomorphic compound, but on linking it with n-alkoxy benzoic acids give rise to the formation of liquid crystal ester homologues of lower transitions, because hydrogen bonding between two phenyl rings of dimerised n-alkoxy benzoic acid disappears on esterification. Uncleared odd-even effect appeared in nematic isotropic (or vice versa) transition curve is attributed to the sequentially added methylene units at the left n- alkoxy terminal end group. Table-3 summarises average thermal stability and molecular structure of the present series-1 and other structurally similar series-A [6] and series-B [5(i)] chosen for comparative study as shown in figure-2.

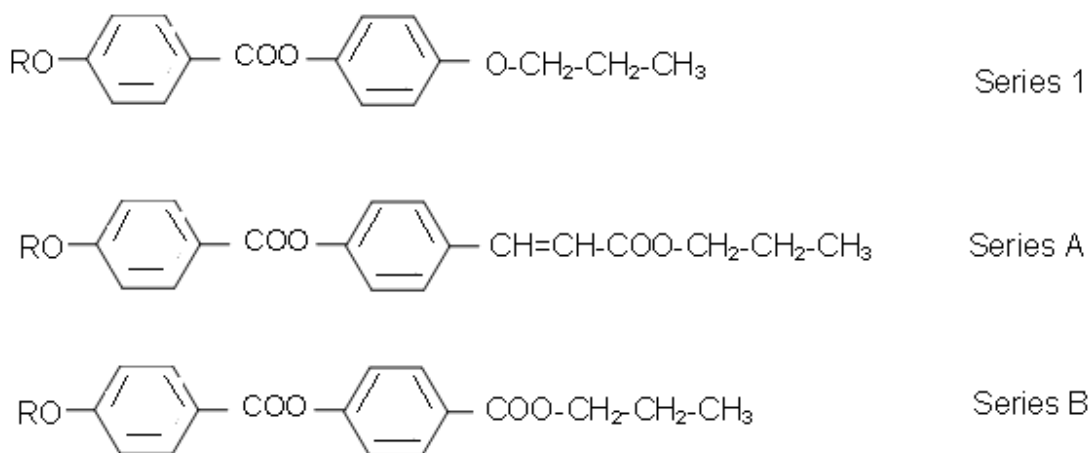


FIGURE-2

Geometrically the homologous series chosen for comparison of their mesomorphic behavior are identical in linear shape. Two phenyl rings bridged through $-\text{COO}-$ central bridge and left n-alkoxy terminal groups which are common identical parts of all the series-1, A and B. They differ only in respect of right terminals of different polarity, and polarizability causing difference in molecular length. Thus, observed difference in mesomorphic properties for same homologue from series to series is attributed to the varying right terminal end group, but variation in mesomorphic properties of homologue to homologue in same series is attributed to the varying left n-alkoxy terminals keeping right terminal end group intact.

TABLE 3: Average thermal stability in $^{\circ}\text{C}$.

Series \rightarrow	1	A	B
Smectic nematic or isotropic	96.0 ($\text{C}_8\text{-C}_{12}$)	107.5 ($\text{C}_8\text{-C}_{10}$)	78.1 ($\text{C}_8\text{-C}_{16}$)
Nematic- isotropic or isotropic-nematic	99.5 ($\text{C}_2\text{-C}_8$)	121.0 ($\text{C}_6\text{-C}_{16}$)	-
Commencement of smectic mesophase	C_8	C_8	C_6

Table-3 indicate that, smectic thermal stability of present series-1 is lower than the series-A and higher than series B. The difference in smectic thermal stability is attributed to the difference in polarity, polarizability and molecular length of right terminal $-\text{OC}_3\text{H}_7$, $-\text{CH}=\text{CH}-\text{COO}-\text{C}_3\text{H}_7$ and $-\text{COO}-\text{C}_3\text{H}_7$ which are directly related to cause intermolecular attractions and magnitude of it.

Phenyl ring is directly linked with $-\text{O}-$ in series-1 but, the same $-\text{O}-$ is linked with phenyl ring through $-\text{CH}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-$ and $-\overset{\text{O}}{\parallel}{\text{C}}-$ in series -A and series-B respectively. Polarizable terminal end groups $-\text{OC}_3\text{H}_7$ and $-\text{CH}=\text{CH}-\text{COOC}_3\text{H}_7$ allows formation of nematic mesophase in addition to formation of smectic mesophase but, $-\text{COOC}_3\text{H}_7$ stabilizes only smectic mesophase without stabilization of nematic mesophase i.e. all the homologous series under comparison, possess the intermolecular anisotropic forces of suitable magnitude as a consequence of their rigidity and flexibility allows lamellar packing of molecules in their crystal lattices required for the formation of smectic mesophase but statistically parallel orientational order of molecules in floating condition is restricted by the molecules of series- B required to form nematic mesophase while it does, in case of series -1 and A due to direct linking of $-\text{O}-$

with phenyl ring (series-1) and presence of $-\text{CH}=\text{CH}-$ unit (series-A). Thus, statistically parallel orientations are hindered by $-\text{COOC}_3\text{H}_7$, terminal relatively more than terminal $-\text{OC}_3\text{H}_7$ and $-\text{CH}=\text{CH}-\text{COOC}_3\text{H}_7$ while formation of lamellar packing of molecules in crystal lattices facilitated more by terminal $-\text{COOC}_3\text{H}_7$, than $-\text{CH}=\text{CH}-\text{COOC}_3\text{H}_7$ and $-\text{OC}_3\text{H}_7$. The late commencement of smectic mesophase in present series-1 and series—A as compared to series-B is attributed to the more extent of noncoplanarity caused by the molecules of series-1 and series-A. Interstate transition temperatures required to rupture crystal structure and to stabilize smectic and/ or nematic phase is depended upon amount of energy evolve or absorbed from and to system to surrounding or vice versa during formation of substance, called a system. The energy stored in a system at constant pressure is called enthalpy $[\Delta H]$. On raising temperature i.e. amount of heat supplied from surrounding to system, which acts against intermolecular attractive forces and causes molecular disruption inducing molecular disorder or randomness which increase with increasing temperature called entropy $= \Delta S = \Delta H / T$. The molecules of homologue which resist thermal vibrations exposed upon them and are restricted to disalign on the plane of surface, induces mesophase but the molecules which do not resist thermal vibrations exposed upon them and disalign on the plane of the surface give rise to form nonmesomorphic homologue as observed in case of methyl and propyl derivatives of the present series-1. Present series is predominantly nematogenic and partly smectogenic with short range of liquid crystallinity and middle ordered melting type. Mesomorphic range varies minimum from 5°C at hexyl derivative to maximum of 38.5°C at the octyl derivative.

CONCLUSION

Mesomorphic thermal stability can be varied by changing rigid core and/ or flexible molecular part at lateral and/ or terminal position. Intermolecular anisotropic forces of attractions of suitable magnitude causes formation of mesophase with short mesophase length in presence of terminal end group like $-\text{OCH}_2-\text{CH}_2-\text{CH}_3$.

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