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Synthesis and Study of Liquid Crystallinity of Benzoate Derivatives in a Laterally substituted Homologous Series: n-Propyl-o-[p'-n-alkoxy benzoyloxy] benzoates

Doshi A.V.^{*}, Joshi C.G.^a and Patel V.R.^b

^{*}Matushri Virbaima Mahila Science & Home Science College, Rajkot (Gujarat-India)

^aChemistry Deptt., M. D. Science College Porbander (Gujarat India)

^bSheth P. T. Arts & Science College, Godhra (Gujarat India)

ABSTRACT

A homologous series n-Propyl-o-[p'-n-alkoxy benzoyloxy] benzoates was synthesized and studied with a view to understand and establish the effect of benzoate derivatives on liquid crystal behaviour by n-propyl group. Ten homologues were synthesized. Eight homologues showed liquid crystal behaviour while two homologues viz. methyl and ethyl homologues escape from liquid crystal behaviour. Curves of the phase diagram drawn from transition temperatures of the homologues as determined by hot stage polarizing microscope shows normal behaviour with persistence of odd-even effect in nematic – isotropic transition curve. n – Propyl to hexyl, octyl derivatives are enantiotropic nematic, decyl derivative is enantiotropically nematic in addition to smectic character, while dodecyl and tetradecyl derivatives are only enantiotropic smectic. Analytical data support the structure. Liquid crystal properties are compared with structurally similar homologous series. Textures of nematic and smectic mesophase are threaded or schlieren and focal conic fan shaped of smectic A or C respectively.

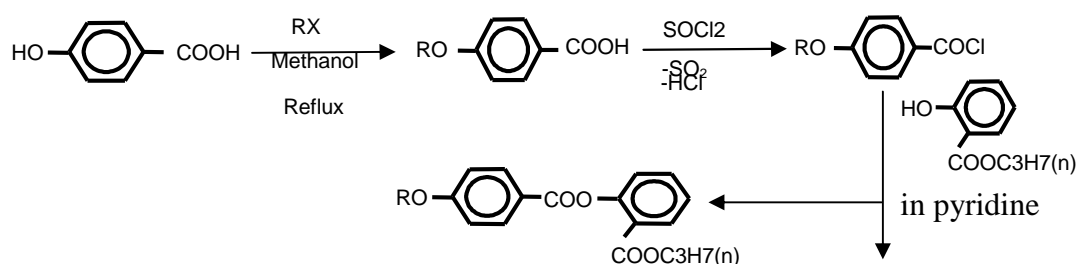
Keywords : Liquid crystal, Mesogens, Nematic, Smectic, Monotropic.

INTRODUCTION

Numbers of ester homologous series with para substituted groups are reported earlier. The effect of ortho substituted group or laterally substituted groups are less reported. Moreover, benzoate derivatives being bioactive molecules and possessing liquid crystal properties are useful in biological, pharmaceutical and analytical field as well as laterally substituted grouped homologues being expected to be of low temperature mesogenic, may be useful in nonmedical fields, like manufacture of electronic devices, conventional and unconventional LCD indicators, electronic screens etc. Keeping in view of the studying mainly the effect of molecular structure on liquid crystal property and purposes shown above, the present investigation was planned.

MATERIALS AND METHODS

Experimental: Synthesis of n-alkoxy benzoic acid and p-n- alkoxy benzoyl chlorides from p-hydroxy benzoic acid were carried out by modified method of Dace and Vora [3]. O-Hydroxy n-propyl benzoate was prepared by usual established method [4, 8]. Ten homologues of the titled homologous series were synthesized by condensing equimolecular proportion of p-n- alkoxy benzoyl chloride and n- propyl-o- hydroxy benzoate in pyridine. Ester derivative of final products were obtained after decomposition, filtration, washing, drying and purifying by alcohol till constant melting and transition points obtained. P-hydroxy benzoic acid, o-hydroxy benzoic acid, n- alkyl halides, n-propanol, methanol, pyridine, thionyl chloride, KOH, H₂SO₄, were used as received. The synthetic route to the series is mentioned below in scheme-1.



Were $R = C_nH_{2n+1}$, $n = 1$ to $6, 8, 10, 12, 14$,

SCHEME-1: Synthetic route to the series

Characterisation:

Selected members of the series were characterized by IR spectra and elemental analysis. Thermodynamic property viz. heat content, enthalpy (ΔH) and entropy (ΔS) with reference to thermal stability are qualitatively discussed instead of performing DSC scan to get entropy value from peak value of thermogram. Liquid crystal property and textures of mesophase were investigated using hot stage polarizing microscope.

Analytical data:

TABLE: 1 Elemental analysis for Pentyloxy, Octyloxy and Decyloxy Derivative.

Sr.No.	Molecular formula	Elements % Found (% Calculated)	
		C	H
1	C ₂₂ H ₂₆ O ₅	71.19 (71.35)	7.13 (7.02)
2	C ₂₅ H ₃₂ O ₅	72.93 (72.81)	7.82 (7.77)
3	C ₂₉ H ₄₀ O ₅	74.05 (74.25)	8.64 (8.55)

IR Spectra in cm⁻¹ for Propyloxy derivative

n- Butyloxy derivative: 750cm⁻¹ polymethylene, 840 cm⁻¹ p-sub. benzene ring, 1050, 1250 & 1750 cm⁻¹ ester group, 1150 cm⁻¹ alkoxy group, 2900 cm⁻¹ satu. C-H str. of alkyl, 3000 cm⁻¹ aro. =C-H str. of phenyl.

Texture of Mesophase by miscibility Method:

Hexyl derivative: Threaded texture

Tetradecyl derivative: Smectic – A

Figure-1: Phase behavior of series

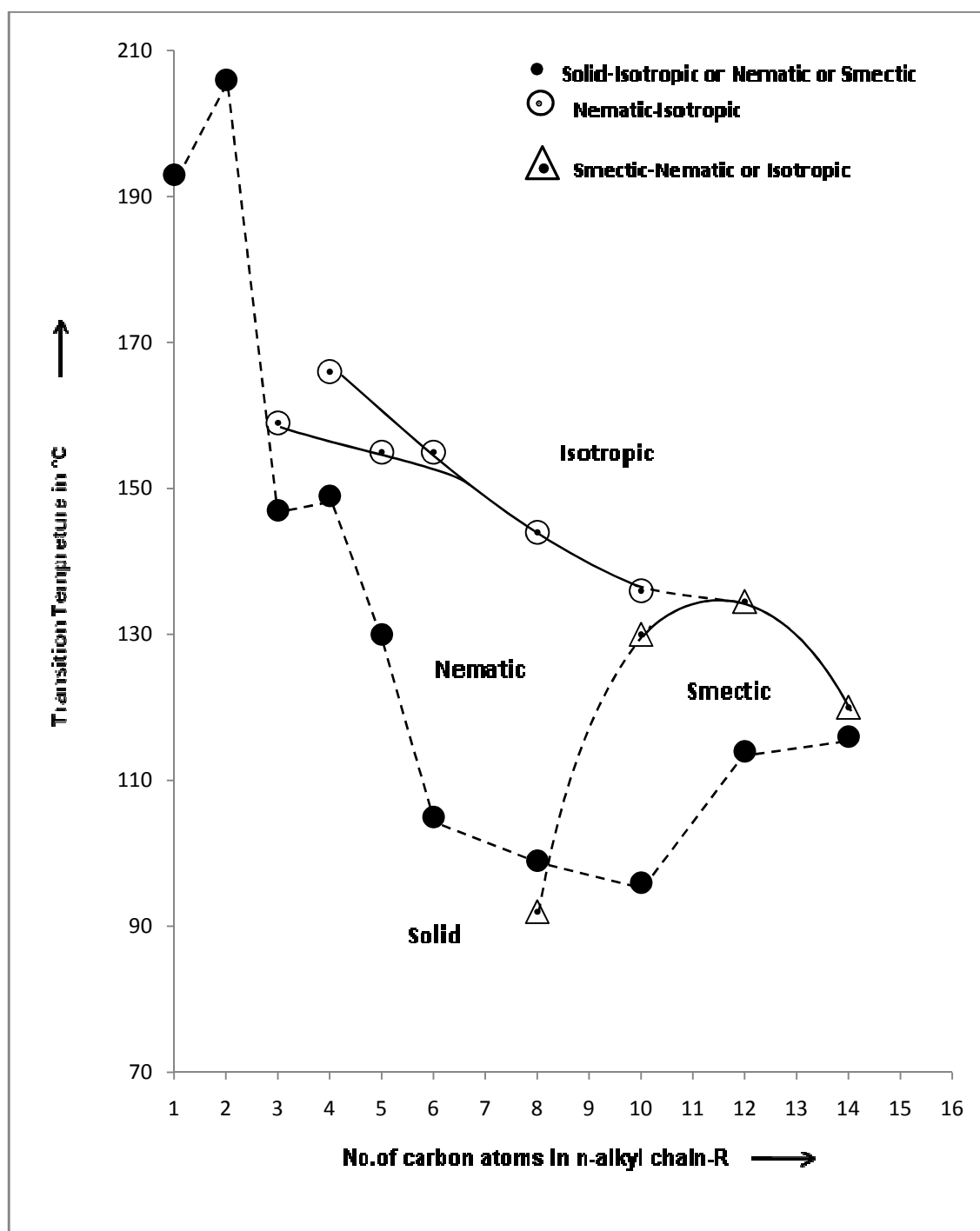


Figure:1 Series: n-propyl-o-[p'-n-alkoxy benzyloxy] benzoates

RESULTS AND DISCUSSION

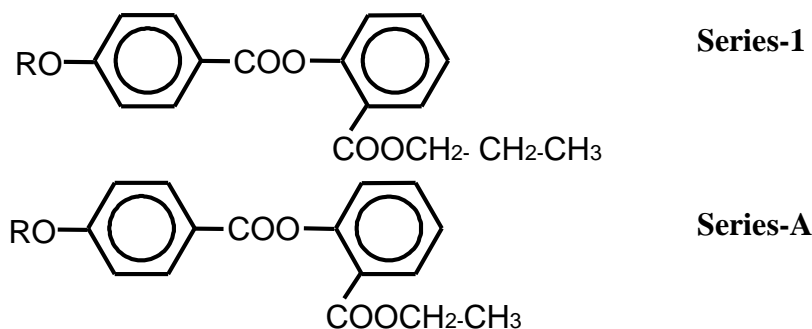
Ortho hydroxy-n-propyl benzoate [4] is nonmesomorphic substance but, on condensing it with p-n- alkoxy benzoyl chloride, prepared from dimerised p-n-alkoxy benzoic acid gives rise to new ester homologous series with mesomorphic or liquid crystal property of relatively lower transition temperatures as compared to corresponding dimerised p-n-alkoxy benzoic acids due to disappearance of hydrogen bonding on esterification. Propyloxy to hexyloxy, octyloxy

homologues are only nematogenic, decyloxy homologue is polyomesogenic (Sm & Nm) while dodecyloxy and teteradecyloxy homologues are smectogenic. Thus, series under discussion is partly smectogenic and predominantly nematogenic with middle ordered melting type. All the mesomorphic homologues are enantiotropic smectic or/and nematic. A phase diagram for the series is plotted for the phase transition temperatures of homologues as determined from hot stage polarizing microscope [Table-2] versus number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end group as shown in figure-1 from table-2. From the phase diagram, it is seen that, solid-isotropic or nematic or smectic transition curve adopt a zigzag path of rising and falling with overall descending tendency as series is ascended. Smectic –nematic or isotropic transition curve rises and falls through maxima and behave in normal manner. Curve is extrapolated to octyloxy homologue to determine monotropic smectic latent transition temperature (LTT) which comes out to be between 80 to 90 °C. Nematic-isotropic transition curve follow descending tendency as series is ascended with showing up of odd-even effect. It merges into smectic-isotropic transition curve and behave in usual expected manner.

TABLE-2 Transition temperatures in °C of series

Compound No.	R=C _n H _{2n+1} (n)	Sm	Nm	Isotropic
1	1	-	-	193.0
2	2	-	-	206.0
3	3	-	147.0	159.0
4	4	-	149.0	166.0
5	5	-	130.0	155.0
6	6	-	105.0	155.0
7	8	-	99.0	144.0
8	10	96.0	130.0	136.0
9	12	114.0	-	134.5
10	14	116.0	-	120.0

Alternation of transition temperatures of the series, appearance of odd-even effect of nematic-isotropic transition curve, variation in transition temperatures and liquid crystal property from homologue to homologue in same series is attributed to the number of methylene units, sequentially and progressively added to the left n-alkyl chain of n-alkoxy terminal end group. Nonmesomorphic behaviour of methoxy and ethoxy derivatives is attributed to their high crystallising tendency arising from their molecular rigidity and flexibility and high stability at room temperature. Table-3 summerises average thermal stability and commencement of smectic mesophase and figure-2 represents the molecular \structure of presently investigated series-1 and other structurally similar homologous series-A [8] and B[8] chosen for comparative study.



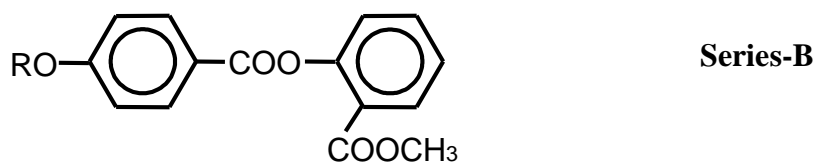


FIGURE-2

Figure-2 shows geometrical shape of series-1, A and B under comparison of liquid crystal properties. All the series are identical in their shape, size, consisted of two phenyl rings bridged through $-\text{COO}-$ central group, same aromaticity, length to breadth ratio, left n-alkoxy terminal end groups, lateral substitution $-\text{COOR}$ at ortho position to central group etc., but they differ in alkyl group $-\text{R}$ at the laterally substituted $-\text{COO}-$ unit, in which n-propyl, ethyl and methyl group are present in case of series-1, A and B respectively. Therefore variation in mesomorphic behaviour and magnitude of liquid crystal properties depend upon the effect caused by alkyl group linked to carboxy $-\text{COO}-$ unit of laterally substituted group. The length of alkyl group increases from methyl to ethyl to n-propyl unit by methylene unit which can cause different magnitude of steric hindrance. As a result of this, the ratio of the molecular polarity to polarizability also vary. Such variation can cause variations in intermolecular anisotropic forces of attractions of suitable magnitude as a consequence of varied molecular rigidity and flexibility. Hence thermal stability of different homologues of different series differ to more or less extent.

TABLE-3: Average Thermal Stability in $^{\circ}\text{C}$

Series	1	A	B
Smectic-Nematic Or Isotropic	128.0 [C ₁₀ -C ₁₄]	111.3 [C ₁₂ -C ₁₆]	110.0 [C ₁₀ -C ₁₄]
Nematic-Isotropic	152.5 [C ₃ -C ₁₀]	139.1 [C ₄ -C ₁₂]	151.1 [C ₃ -C ₁₀]
Commencement of smectic mesophase	C ₁₀	C ₁₂	C ₁₀

Table-3 indicate that, numerical values of smectic thermal stability decreases from the series

→
1 A → B i.e. from propyl → ethyl → methyl ester but values of the nematic thermal stability of ethyl ester i.e. series A is higher than the series 1 and B. Series-1 and B are ester series of propyl and methyl ester (odd number carbon) while series B i.e. ethyl being even numbered alkyl group esters. Thermodynamic thermal stability of any substance at room temperature and one atmosphere pressure is directly related to its heat content enthalpy (ΔH) value at given temperature. A sample homologue molecular thermodynamic system is supplied heat energy from the rest of the part of univers [i.e. surroundings] other than a thermodynamic system, the supplied heat will act against the intermolecular forces of attractions of suitable or unsuitable magnitudes as a consequence of molecular rigidity and flexibility depending upon molecular geometry and polar or nonpolar groups attached at lateral or terminal position of a molecule. If temperature is raised, the intermolecular distance of a thermodynamic system increases or vice versa and molecules tend to move from stabilized state to destabilized state. The value of heat content ΔH vary with temperature. Molecules of a system homologue start dancing and orienting at a given temperature on gaining heat and disalign or align on the plane of a surface or may acquire molecular disalignment at an angle less than 90° and if intermolecular anisotropic force of attraction value reaches to suitable magnitude and maintain either statistically parallel orientational molecular order (end to end attraction) to show nematic mesophase or sliding layered (lateral attractions) molecular arrangement may cause to show smectic mesophase, between two temperatures T_1 and T_2 . The difference of temperature T_2-T_1 is

called liquid crystal mesophase length or range of liquid crystallinity of a sample homologue thermodynamic system as observed for the homologues propyl to tetradecyl derivative of the presently investigated series. But if the molecules of sample substance randomly orient and move in all possible direction without any control, acquiring molecular alignment on the plane of the surface under the influence of unsuitable magnitude of heat, the high order of molecular disorder occurs, called as entropy $\Delta S = \Delta H/T$ at which mesophase or liquid crystal phase does not appear [$T_2 - T_1 = 0$] and a sample substance directly passes from crystalline state to isotropic state without passing through liquid crystal state, as observed in case of methyl and ethyl derivatives of the present series. The late commencement of the smectic phase in a homologues series A chosen for comparison is attributed to the extent of noncoplanarity caused more by the molecule of the series A as compared to series 1 and B. Thus, molecular coplanarity is directly related to early or late commencement of smectic mesophase. Series 1 and B shows commencement of smectic mesophase from octyloxy derivative, while it commences from dodecyloxy derivative in case of series A.

CONCLUSION

Laterally substituted -COOR group containing molecules of the ester homologous series exhibit liquid crystal property with medium range liquid crystallinity and melts relatively at low temperature. Such series are predominantly nematogenic and partly smectogenic. Thermal stability rises as methylene unit added to R of the lateral -COOR group.

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