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A Novel Mesomorphic Homologous Series of Ester Derivatives p(p'-n-Alkoxy Benzoyloxy) *β*-Phenyl Ethyl Benzoates

[a]Pandya Shilpa N. and [*]Chauhan M. L.

**Chemistry Dept.; Sheth P. T. Arts & Science College, Godhra –389 001, Gujarat University, Gujarat, India*
[a]Pacific Academy Of Higher Education And Research University, Udaipur

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ABSTRACT

A novel homologous series of 11 ester derivatives has been synthesized and evaluated for mesogenic behaviour. The methoxy to butyloxy homologues are nonmesomorphic, whereas the pentyloxy to hexadecyloxy derivatives are enantiotropically mesomorphic in character. The hexyloxy to dodecyloxy homologues exhibit smectogenic and nematogenic both character but pentyloxy, tetradecyloxy and hexadecyloxy homologues exhibit only nematogenic character .An odd–even effect is not observed N-I transition curves. The average smectic and nematic thermal stabilities are 194.5 ºC and 197.1ºC, respectively. Smectogenic phase lengths vary from 17 ºC(C_{12}) to29 ºC(C_8) and the nematogenic phase lengths vary from 10 ºC(C_{16}) to 27 ºC(C_6) . The series is predominantly nematogenic and partly smectogenic with considerable mesophase length and a middle-ordered melting type. The liquid crystal properties of the novel series are compared with other structurally similar Series. The texture of the nematic phase is a threaded or Schlieren type, and that of smectic phase shows the smectic A type as determined by optical polarizing microscopy. Analytical data support the molecular structures in all cases.

Keywords: Mesomorphism; nematic; smectic, Liquid Crystals, Enantiotropy.

INTRODUCTION

The exhibition of liquid crystal (LC) [1] properties requires suitable magnitudes of anisotropic intermolecular forces of attraction. These attractions are as a consequence of favorable molecular rigidity and flexibility [2–4] resulting from the molecular structure of a substance by appropriate substitution of lateral, terminal, and central groups with phenyl rings. The LC state is exploited in a number of electro-optic, biological, and thermo graphic applications, hence the synthesize of novel LC substances needed. The present work is aimed to understand of effects of molecular structure on LC properties, or synthesis novel compounds, which exhibit liquid crystalline properties. The novel molecules are constructed with three phenyl rings bridged through –COO- and Phenyl ring as a rigid core, and n-alkoxy(OR) group as a flexible core. Thus, the combined effect of the two highly polar alkoxy and phenyl groups on LC properties with the variation of the number of carbon atoms in the right and left terminal chain can be studied and evaluated. Proposed investigation will include synthesis, characterization, results and comparative study of present novel series with structurally similar series.

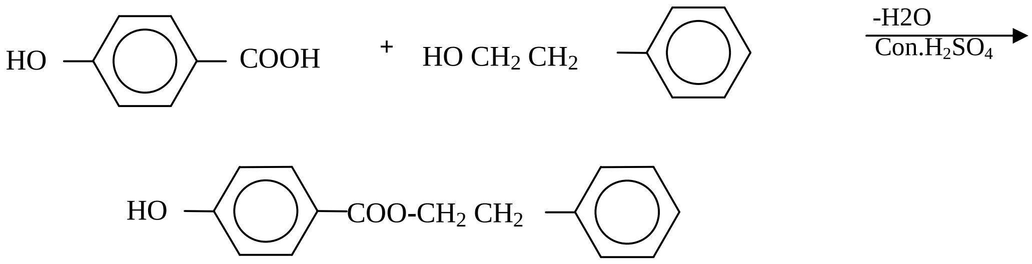
MATERIALS AND METHODS

Experimental :

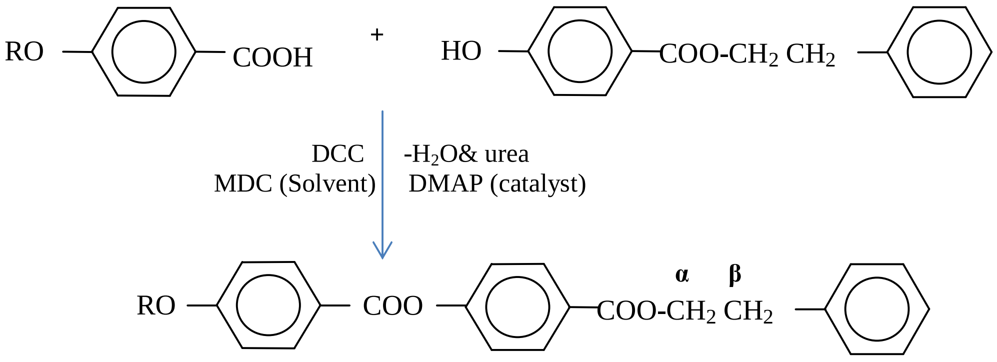
Synthesis Experimental :

(a) p-n-alkoxy benzoic acids were prepared by the method of Gray and Winsor (4),Vora and Dave [5], Vogel [6].
(b) p – Hydroxy β-phenyl ethyl benzoate is prepared by reacting p-hydroxy benzoic acid with corresponding freshly distilled 2-phenyl ethanol in presence of concentrated sulphuric acid mixture.
(c) p-n-alkoxy benzoic acids dissolved in MDC withp – Hydroxy β-phenyl ethyl benzoate is in portions with DCC & DMAP as catalyst by stirring reaction mixture. [7,8,9] Products were decomposed ,filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy benzoic acid, alkyl halides (R-X),β -phenyl ethanol, KOH, DCC,DMAP, MDC etc. required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below in **Scheme -1**

(1) p – Hydroxy β-phenyl ethyl benzoate



(2) p -(p′-n-alkoxy benzoyloxy) β-phenyl ethyl benzoates.



Scheme -1

Characterization

Some homologs as representative members of the series were selected for characterization of their structures by IR and H^1NMR techniques. IR spectra were recorded on Perkin Elmer spectrum GX and NMR were recorded using $CDCl_3$ as solvent. Microanalysis was performed on Perkin Elmer PE 2400 CHN analyzer. Transition and melting temperatures and liquid crystal properties were investigated by using optical polarizing microscopy.

Table 1.Elemental analysis for some derivatives

Sr. No.	R = n-alkyl chain	Molecular *Formula*	Calculated %		Observed %	
			C	H	C	H
1	Propyl	$C_{25}H_{24}O_5$	74.25	5.94	74.09	6.12
2	Octyl	$C_{30}H_{34}O_5$	75.94	7.17	75.18	7.49
3	Decyl	$C_{32}H_{38}O_5$	76.49	7.56	77.01	8.00

Analytical DataH^{1}NMR: in ppm. Butyl. 1.01 &0.98 – CH3, 3.98 – $OCH_{2,}$ 4.01 – OCH2 of-OCH_2 of -$C_4H_{9,}$ 6.89, 6.92,mono-sub. phenyl 8.10, and 8.03 –p-sub. phenyl two p-sub .benzene, 7.24 and 8.02 – p-sub phenyl two p-sub benzene,

Decyl. 0.88-CH_3, 1.21 -CH_2, 2.49-CH_2ph., 3.5 , 3.31 – O CH_2 of- $C_{10}H_{21,}$, 6.80 and 6.83 two p-sub phenyl ring, 7.75 and 7.78, two p-sub phenyl ring.

IR in cm−1.Octyl. 2880 alkyl group, 1080,1180, and 1680,1720 –COO- group, 1580,1450 Aromatic ring, 3000 aromatic ring, , 860 p-sub phenyl ring , 670, mono sub phenyl ring 720 polymethylene of C_8H_{17}

Dodecyl. 2840.0 alkyl group, 1050,1200, and 1710 -COO group, 3080 aromatic ring , 1550,1480 phenyl ring,660 mono sub. phenyl ring,850 p-subphenyl ring, 760 polymethylene of -$C_{12}H_{25}$,

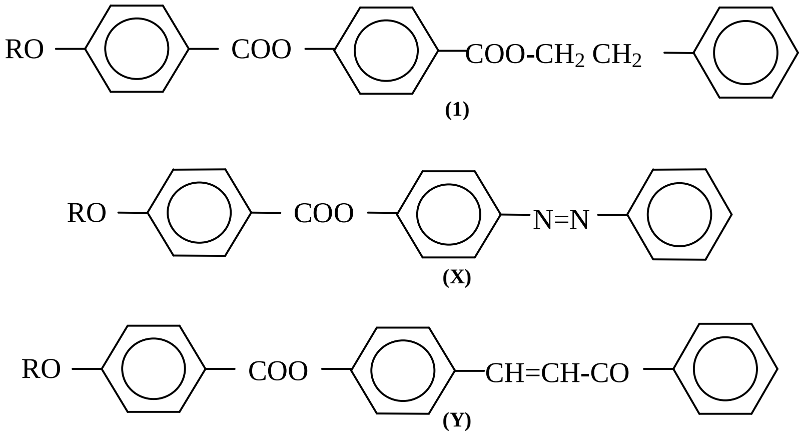
Table : 2 Transition temperatures

Sr. No.	R = n-alkyl group	Transition temperature in °C		
		Smectic	Nematic	Isotropic
1.	Methyl	-	-	192
2.	Ethyl	-	-	172
3.	Propyl	-	-	182
4.	Butyl	-	-	174
5.	Pentyl	-	142	160
6.	Hexyl	162	180	207
7.	Octyl	173	202	215
8.	Decyl	172	200	213
9.	Dodecyl	179	196	209
10.	Tetradecyl	-	172	196
11.	Hexadecyl	-	170	180

RESULTS AND DISCUSSION

Dimerization of 4-*n*-alkoxybenzoic acids disappears on the esterification process. Phenyl ethyl benzoate homologue derivative is not liquid crystalline. However, on linking it with n-alkoxy benzoic acid , the resultant product exhibits LC properties from the Pentyl to the hexadecyl homologues, while the methyl to butyl homologues do not exhibit LC properties **(Table 2).** A plot in a phase diagram of the transition temperature versus the number of carbon atoms present in *n*-alkyl terminal chain consists of three transition curves,(**Fig. 1)** solid isotropic or mesomorphic curve,(Cr-I/M)smectic–nematic curve (Sm-N), and nematic–isotropic curve (N-I),as shown in **Fig. 1**. The solid–isotropic or mesomorphic transition curve(Cr-M/I)rises and fallsas the series is ascended in a zigzag manner with an overall descending tendency. The smectic–nematic transition curve initially rises from the hexyl homologue and then passes from a maxima at the octyl derivative and then falls up to the dodecyl derivative of the series. This curve is extrapolated to the tetradecyl homologue and it merges into a point where the smectic phase ceases to appear and only the nematic phase appears. Thus, the smectogenic property is exhibited by the hexyl to the dodecyl homologues of the novel series. The nematic–isotropic transition curve initially rises and then descends as the series is ascended without the exhibition of an odd–even effect. Thus, all three transition curves of the phasediagram **(Fig. 1)** behave in the usual established manner. The mesomorphic phase length ranges from minimum to maximum 10 ºC to 45 ºC at the Hexadecyl and hexyl homologues. The series is partly smectogenic and predominantly nematogenic with a middle-ordered melting type. The mesomorphic properties vary from homologue to homologue in the same series with different magnitudes of phase length including smectic and nematic phase lengths. An odd–even effect is absent in the smectic–nematic transition curve but observed for nematic–isotropic transition curves. The smectic mesophase commences from the hexyl homologue **(Table 2).** All the mesogenic members of the series are enantiotropic mesomorphic. The breaking of hydrogen bonding due to the esterification process gives rise to esters with lower transitions than the corresponding alkoxy acids. Even membered N-I transition curve is extrapolated to C_5 member of a series which merges into isotropic point C_5 indicating impossibility of mesophase formation.

However, the addition of a third phenyl ring bonded through a –COO-CH_2CH_2-Phcentral group increases molecular rigidity and flexibility and raises transition temperatures. Non-mesomorphic behavior of the methyl to the butyl homologue derivatives is attributed to their high crystallizing tendency due to their relatively short alkyl chain- R or –OR group. Hence, the corresponding homologue molecules are unable to resist exposed thermal vibrations, which results in the sudden breaking of the crystal structure and converts the substance sharply into isotropic liquid state from solid state without exhibition of a liquid crystalline mesophase. Such a situation also arises for amesomorphic (LC) substance from and beyond the mesomorphic–isotropic transition temperature. The exhibition of mesogenic properties from the Pentyl to the hexadecyl homologues is attributed to the suitable magnitudes ofanisotropic intermolecular forces (4) of attraction caused by favorable molecular polarity and polarizability, Aromaticity, electronic–electronic interactions, length-to-breadth ratio, and the ratio of the polarity to polarizability as a consequence of the resultant molecular rigidity and flexibility (1–3). The exhibition of only nematogenic character by the Pentyl, tetradecyl, and hexadecyl homologues, or in addition to smectogenic character by the hexyl to the dodecyl homologues, is attributed to the statistically parallel orientational order of molecules in a floating condition due to favorable intermolecular end-to-end adhesion inwhich molecules appear to lie at an angle less than 90° on the plane of a floating surface, with the thermal vibration resisting under the influence of applied heat within definite temperature range. The exhibition of smectogenic character by the hexyl to dodecyl homologues is due to the presence of lamellar packing of the molecules in their crystal lattices which on heating gradually yield a sliding layered arrangement of molecules in a floating condition resisting thermal vibrations within a definite range of temperature. Thus, the presently investigated homologous series is predominantly nematogenic and partly smectogenic without showing an odd–even effect. The absence of an odd–even effect in either of the curves in the phase diagram **(Fig. 1)** is due to the absence of mesophase formation by the shorter n- alkyl homologue of the series. The disappearance of the smectogenic character in the tetradecyl and hexadecyl homologues indicates the absence of lamellar molecular packing due to the longer terminal chains, which may coil, bend, flex, or couple to lie with the major axis of the core adversely affecting the molecular rigidity and flexibility (1–3), which hinders lamellar molecular packing. The variation of mesogenic properties from homologue to homologuein the same series is due to the sequential addition of methylene unit (4) in the terminal alkoxy chain, which causes variation in molecular polarity and polarizability affecting the intermolecular attractions. Mesomorphic properties of present novel series-1 are compared structurally similar series-X and Y as under in **figure-2.**



(1)

(X)

(Y)

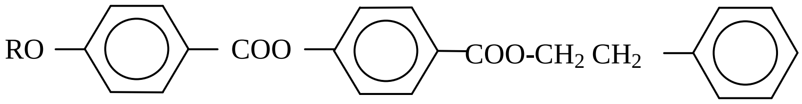
Fig. 2. Structurally Similar Series

Table-(3) Thermal stabilities in °C

Series ⟶	1	X	Y
Smectic – isotropic or smectic-nematic	194.50 (C_6 – C_{12})	114.0 (C_{10} – C_{16})	106.66 (C_{10}-C_{14})
Commencement of smactic phase	C_6	C_{10}	C_{10}
Nematic - Isotropic	197.14 (C_5–C_{16})	138.54 (C_1 – C_{16})	119.8 (C_8 – C_{16}))
Commencement of nematic phase	C_5	C_1	C_8

Figure-2 shows structurally similar homologous series with minor variations in their central bridge linking the third and middle phenyl rings. Such variations cause a difference in the mesomorphic behavior in terms of the commencement of the smectic and/or nematic phase, transition temperatures, magnitudes of intermolecular anisotropic forces of adhesion, thermal stabilities, etc., as recorded in **Table 3**. The homologous Series 1 of the present investigation and Series X and Series-Y differ in their central bridge, viz.,-COO-CH_2-CH_2, –N=N-and –CH=CH–CO– linking the third and middle phenyl rings. The ethyl carboxylate-COO-CH_2-CH_2- group is relatively longer than the -N=N-and -CH=CH–CO-except conjugated double bond. Homologous Series-1, X and Y are identical in all respect except their central bridges linking, middle and third phenyl ring. The polarity due to the three phenyl ring central groups - COO-and terminal end group are the same, but their molecular polarity and polarizability varies with the central bridge, which is reflected in the magnitudes and degree of mesomorphism due to intermolecular distance. **Table 3** indicates that the smectic–nematic thermal stability is highest of Series-1 in comparison with Series-X and Y chosen for comparison. Series-1 and Series X contains the –N=N- and -COO-CH_2-CH_2-central group, which increases the molecular length in comparison with the –CH=CH-CO-central bridge. Hence, the length to breadth ratio and the molecular polarizability of the molecules of Series-1 and X are greater than the molecules of Series Y. Thus, suitable magnitudes of anisotropic intermolecular forces of adhesion are higher in Series -1 than in Series X and Y, and this reflects the smectic–nematic thermal stability of Series-1 and X. The smectic–nematic thermal stability of Series –Y is also lower than the molecules of Series -1. This is because the molecules of Series -Y are lathlike while the molecules of its isomeric Series-1 of present investigation are nonlinear and broader than the Series -Y. Broadening of a molecule raises the intermolecular attractions by polarizability factor. But at the same time, broadening of a molecule reduces intermolecular attractions due to increase in the intermolecular distance. Thus, two opposite effects due to molecular broadening operate at a time [4] in case of Series Y. The net resultant effect of intermolecular attractions depends upon the predominating effect out of two opposing effects operating at a time. The second effect, i.e., the reduction in intermolecular attractions due to broadening of a molecule, predominates in case of Series-Y, while closer packing of molecules of Series-1 strengthens the suitable magnitudes of anisotropic intermolecular forces of attractions in comparison to Series-Y of present investigation. Therefore, the smectic–nematic thermal stability of Series-1 is higher than for Series Y. Similarly, the nematic–isotropic thermal stabilities of Series-X and Y are lower than that of Series-1of present investigation. The commencement of the smectic mesophase takes place from fifth or sixth member of the series, which indicates that the flexible identical molecular part, viz., the -COO-CH_2-CH_2-central bridge groups, causes an almost equivalent extent of molecular non-coplanarity of Series-1, X, and Y. Similarly, the magnitudes of the end to-end intermolecular attractions result in the formation of the nematogenic mesophase irrespective of the differing features of the central group or the linearity of a molecule. Thus, the variation in mesomorphic properties for the same homologue from series to series is attributed to varying features due to central group linking first and middle phenyl ring and the molecular shape or linearity.

Homologous Series :**p(p'-n-Alkoxy Benzoyloxy) *β*-Phenyl Ethyl Benzoates**



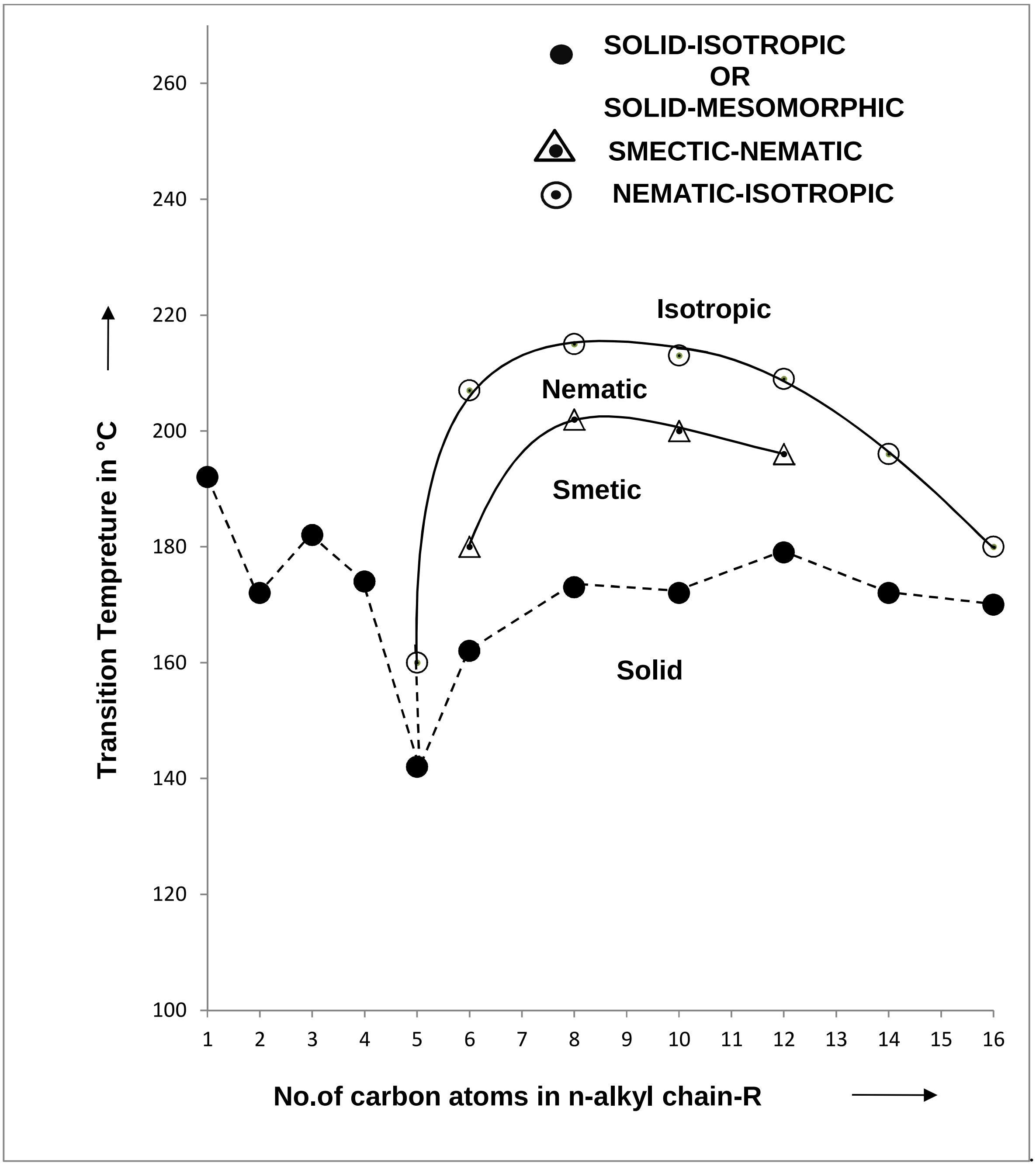


Figure :1 Phase Behavior of Series

CONCLUSION

1. Group efficiency order derived on the basis of
(a) Thermal stability is:
For smectic: -COO-CH_2-CH_2->–N=N->–CH=CH–CO–
For nematic: -COO-CH_2-CH_2->–N=N-> –CH=CH–CO–
(b) Early commencement of:
For smectic: -COO-CH_2-CH_2->–N=N-= –CH=CH–CO–
For nematic: –N=N->-COO-CH_2-CH_2- >–CH=CH–CO–

2. The novel homologous series is predominantly nematogenic and partly smectogenic.

3. Variations in mesomorphic properties from homologue to homologue in the same series and from series to series for the same homologue depend upon sequential addition of a methylene unit and varying with the central bridge linking middle and last phenyl ring the terminal end group of fixed polarities respectively.

4. Extension of a phenyl ring (Aromaticity) enhances the mesogenic tendency and the early commencement of the mesophase.

5. Favorable molecular rigidity and flexibility facilitate suitable magnitudes of anisotropic intermolecular forces of attractions.
6. Molecular rigidity and flexibility determines the formation of the liquid crystalline

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