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## Synthesis and study of new mesogens : p-(p'-n-Alkoxy benzoxy)ter- butyl benzoates

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### ABSTRACT

A homologous series with carboxy (-COO-) as central group and -COOC<sub>4</sub>H<sub>9</sub>(ter.) as terminal end group have been synthesized by treating p-p'-n-alkoxy benzoic acid with p-hydroxy ter-butyl Benzoate. Pentyl to Hexadecyl homologues of the series are mesomorphic in nature. First, fore members of the series are non-mesomorphic. Pentyl, Hexyl, Octyl, decyl, dodecyl and tetradecyl derivatives are enantiotropically nematogenic. Smectogenic character is totally absent. Phase behavior of a phase diagram is normal for transition curves. Odd-even effect is observed for nematic-isotropic transition curve. Transition temperatures of the homologues are determined by an optical polarizing microscope, equipped with a heating stage. Analytical data supported the structures of molecules. Liquid crystal properties of the titled series are compared with structurally similar homologous series. Thermal stabilities and other mesogenic characteristics are compared with other structurally similar homologous series. Textures of the nematic phase are threaded or schlieren. Thermal stability for nematic is 190.57 C° and the degree of mesomorphism vary from 10.0 C° to 22.0 C° at the C<sub>5</sub> and C<sub>10</sub> homologue respectively. It is a middle ordered melting type series, whose relative group efficiency order for nematic derived.

**Keywords** Liquid crystals; mesomorphic; nematic.

### INTRODUCTION

The number of liquid crystals compounds consisted of rigid part as two or three phenyl rings bridged through central bridge or bridges and flexible part as varying left polar terminal, alkyl or alkoxy (1–12) end group keeping right terminal end group intact of fix polarity with or without lateral substitution. In continuation of the same, presently a homologous series with two phenyl rings bridged through carboxylate linkage and ter-butyl carboxylate fixed end group with n-alkoxy as left terminal end group, is synthesized to investigate the effect of varying molecular structure by varying molecular rigidity and flexibility on mesogenic property. The present investigation is planned with a view to establish and to understand the effect of molecular structure on liquid crystalline behavior of a substance. (13-17)

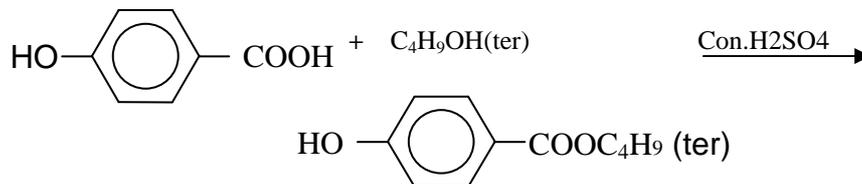
### MATERIALS AND METHODS

#### Synthesis Experimental :

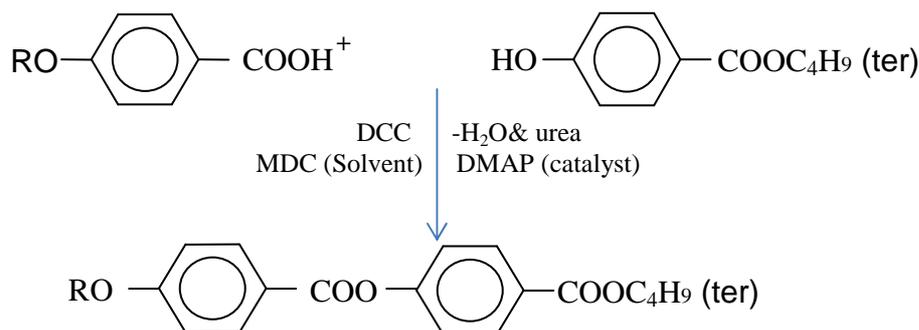
- p-n-alkoxy benzoic acids were prepared by the method of Gray and Winsor [18], Vora and Dave [19], Vogel [20].
- p-hydroxyter-butyl benzoate is prepared by reacting p-hydroxy benzoic acid with corresponding freshly distilled ter-butyl alcohol in presence of concentrated sulphuric acid mixture.
- p-n-alkoxy benzoic acids dissolved in MDC with p-hydroxy ter-butyl benzoate is in portions with DCC & DMAP as catalyst by stirring reaction mixture. [21-23] Products were decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy benzoic acid, alkyl halides (R-X), ter-

butanol, 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 ter-butyl benzoate



(2) p-(p'-n-alkoxy benzoyloxy) ter-butyl benzoates



R = C<sub>n</sub>H<sub>2n+1</sub> n = 1,2,3,4,5,6,8,10,12,14,16

**Scheme -1**

### Characterization

Some homologs as representative members of the series were selected for characterization of their structures by IR and <sup>1</sup>HNMR techniques. IR spectra were recorded on Perkin Elmer spectrum GX and NMR were recorded using CDCl<sub>3</sub> 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 <sub>21</sub> H <sub>24</sub> O <sub>5</sub>	70.78	6.74	69.23	6.61
2	Pentyl	C <sub>23</sub> H <sub>28</sub> O <sub>5</sub>	71.87	7.29	71.02	7.50
3	Octyl	C <sub>26</sub> H <sub>34</sub> O <sub>5</sub>	73.23	7.28	72.90	8.13
4	Decyl	C <sub>28</sub> H <sub>38</sub> O <sub>5</sub>	74.00	8.37	74.20	8.90
5	Hexadecyl	C <sub>34</sub> H <sub>50</sub> O <sub>5</sub>	75.83	9.29	76.21	9.69

### Analytical Data

**NMR: in ppm.** Hexadecyl. 1.1 – CH<sub>3</sub>, 3.98– O CH<sub>2</sub>, 4.01 – O CH<sub>2</sub> of O CH<sub>2</sub>-CH<sub>2</sub>, 4.44 and 4.02 – OCH<sub>2</sub> of C<sub>16</sub>H<sub>33</sub>, 6.89, 6.92, 8.00, –p-di-sub.phenyl 8.02 – p-di-subphenyl two p-subbenzene.

Octyl. 0.93 -CH<sub>3</sub>, 1.21 -CH<sub>2</sub>, 2.49 -OCH<sub>2</sub>- CH<sub>2</sub>, 3.5, 3.31 – O CH<sub>2</sub> of -C<sub>8</sub>H<sub>17</sub>, 6.9 and 6.8 two p-di-subphenyl ring, 7.85 and 7.98, two p-di-subphenyl ring.

**IR in cm<sup>-1</sup>.** Tetradecyl. 2850 alkyl group, 1100,1150, and 1730 COO ester group, , 860 p-subphenyl ring, 3000 aromatic ring, 750 polymethylene of C<sub>14</sub>H<sub>29</sub>

Hexyl. 2900.0 alkyl group, 1050,1150, and 1710 COO ester group, 850 p-sub phenyl ring, 3080 aromatic ring, 750 polymethylene of C<sub>6</sub>H<sub>13</sub>,

Table : 2 Transition temperatures

Sr. No.	R = n-alkyl group	Transition temperature in °C		
		Smectic	Nematic	Isotropic
1.	Methyl	-	-	210
2.	Ethyl	-	-	192
3.	Propyl	-	-	196
4.	Butyl	-	-	196
5.	Pentyl	-	176	186
6.	Hexyl	-	184	198
7.	Octyl	-	184	195
8.	Decyl	-	186	208
9.	Dodecyl	-	174	192
10.	Tetradecyl	-	175	195
11.	Hexadecyl	-	148	160

## RESULTS AND DISCUSSION

The homologous series p-(p'-n-alkoxy benzyloxy) ter-butyl benzoates is presently synthesized and studied for 11 homologs, which were evaluated for their mesomorphic characteristics. The transition temperatures of the homologous series under discussion are recorded in **Table-2**. The Pentyl to Hexadecyl members of the series showed a threaded or Schlieren texture on heating the crystalline solid reversibly on heating and cooling to isotropic liquid, while the methyl to butyl homologs are nonmesomorphic. Thus, the Pentyl to hexadecyl homologous are enantiotropically nematogenic without exhibition of any smectogenic character. **Table-2** shows the dependence of transition temperatures on the number of carbon atoms in the terminal chain. The average thermal stability and other mesomorphic behavior of titled homologous series-1 are compared with the structurally similar homologous series-A [24] as shown in **Fig. 1**. The solid-nematic or isotropic transition curve follows a zigzag path of rising and falling tendency as the series is ascended. The plot of the phase diagram (**Fig. 2**) shows the presence of the odd-even effect in the nematic-isotropic transition curve, and then it falls up to the last homologue 16<sup>th</sup>. Thus, the behavior of nematic-isotropic transition curve of the present study suggests that, enthalpy change of the homolog from fifth up to hexadecyloxy homologue decreases.

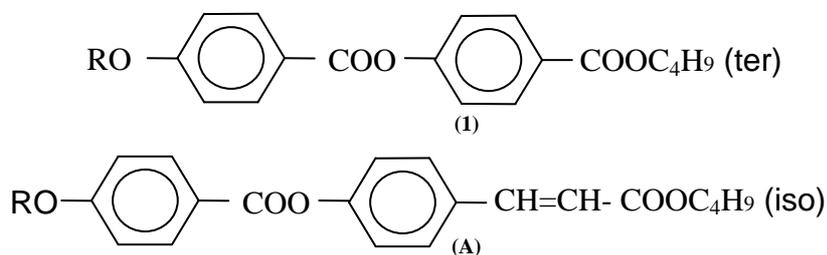


Fig. 1

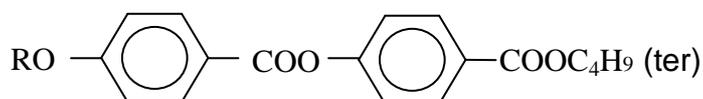
Hence, a low and a high value of enthalpy correspond to a low and a high amount of heat energy requirement (low and high temperature) from surrounding to system. The opposing effects to the molecular geometry of an ter-butyl terminal group operates (1) an effect due to widening of the molecule causing a reduction in the intermolecular adhesion by increasing the intermolecular distance and on the other hand (A) increased molecular width, increases molecular polarizability causing an increase in the intermolecular adhesion. Thus, closeness of molecular packing depends upon the net resultant intermolecular forces of attractions, which depend upon the predominating effect out of two opposing effects (1) and (A). In the present study, the latter effect is a predominating effect. **Table-3** summarizes the average thermal stabilities and molecular structure of the present series and other structurally related series A chosen for comparative study. The molecular geometry of all the homologous series under comparison consists of two phenyl rings linked through a carboxy or a vinyl carboxy ester central linkage with n-alkoxy group at the left terminus and  $-\text{CH}=\text{CH}-\text{COO}-\text{CH}_2-\text{CH}-(\text{CH}_3)_2$  (iso) and  $-\text{COO}-\text{C}-(\text{CH}_3)_3$  (ter) at the right terminus for series (1) and (A) respectively. The variation in the mesomorphic characteristics can be attributed to the combined effect of the presence of central ester and different right terminal groups, which have different molecular rigidity and flexibility related to molecular polarity and polarizability for the formation of mesophase [13,14]. On comparing the mesomorphic characteristics of series (1) with series A, it is observed that, the homologous of both the series differing in respect of central bridge only are enantiotropically nematogenic. Introduction of a polar ter-butyl group at the terminal position with  $-\text{COO}-\text{C}-(\text{CH}_3)_3$  in series-1 enable considerable and significant anisotropic (1) forces of attraction of suitable magnitude for pentyloxy to hexadecyloxy homologs, which serve to stabilize statistically parallel orientational order of molecules by end-to-end attractions conducive to the formation of a nematogenic

mesophase. This effect persists even in the homologs with long n-alkoxy groups. Comparison of series-1 with series-A indicates that the series-A has an isobutyl group at the right terminal with a vinyl carboxy central group while series-A has ter-butyl terminal group with a carboxy group. The flexible straight chained ter-butyl group with  $-\text{COO}-$  group in series -1 adds the formation of nematic mesophase due to enhanced lateral attraction in addition to terminal attractions, which facilitates lamellar packing required for the formation of higher temperature nematic mesophase (1). Thus, both series exhibits only nematogenic character. The nematic thermal stability of series-A being lower than series-1 is understandable because of the difference in terminal attractions arising from the isobutyl and ter-butyl groups.

Table-(3) Thermal stabilities in °C

Series	(1)	(A)
Smectic-isotropic	–	–
Commencement of Smectic phase	–	–
Nematic-isotropic	190.57 (C5-C16)	108.8 (C6-C14)
Commencement of Nematic-phase	C5	C6

Homologous Series: **p-(p'-n-Alkoxy Benzoyloxy) ter- ButylBanzoates.**



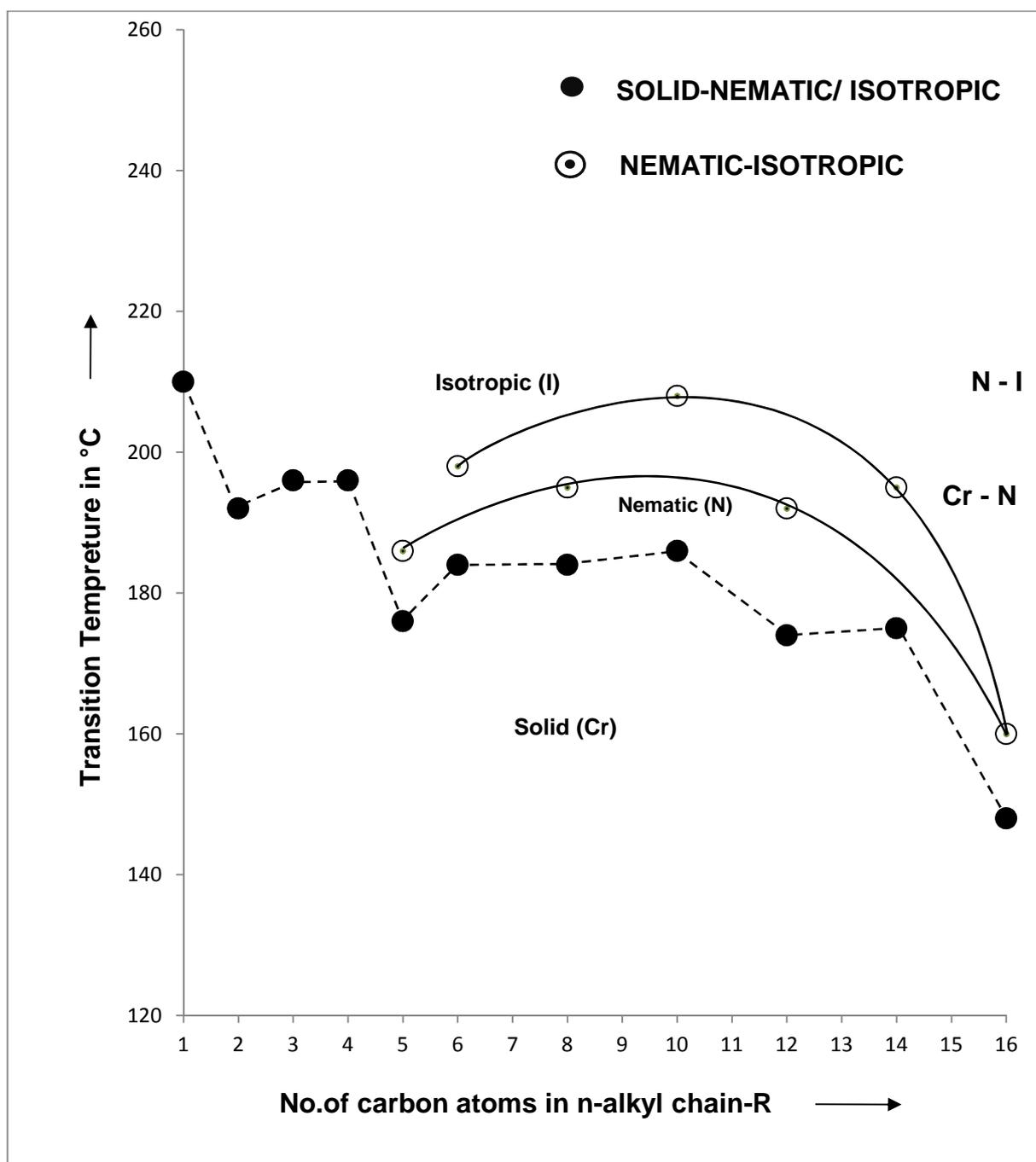


Figure : 2 Phase Behavior of Series

### CONCLUSION

The study suggests that a polar substituent at a terminal position in a homologous series with present molecular geometry gives rise to the exhibition of a nematogenic mesophase. Moreover, the presence of a vinyl carboxylate unit at a central and/or a terminal position favorably induce a lower temperature nematogenic mesophase.

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