

**MESOMORPHISM DEPENDENCE ON MOLECULAR RIGIDITY
FLEXIBILITY OF ESTER COMPOUNDS****Patel B. K.¹ and Chauhan M. L.*²**¹Research Scholar, Pacific Academy of Higher Education and Research University, Udaipur.²Department of Chemistry, Sheth P. T. Arts & Science College, Godhra Gujarat University,
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A Novel homologous series of mesogens have been synthesized and studied with a views to understand and establish the relations between molecular structure and liquid crystal properties of a Compounds. Totally eleven members of series synthesized. Mesogenic behaviors commences from C₆ member of a series and continued up to C₁₆ member. The rest of the members C₁ to C₅ are nonmesogenic. Mesogenic homologues (C₆ to C₁₆) are enantiotropically nematogenic. Textures of nematic phase are threaded or schlieren. Transition temperatures were determined by an optical polarizing microscopy equipped with a heating stage. Analytical and structural data confirms

the molecular structures of homologues. Thermal stability for nematic is 166.6 °C. Mesomorphic phase length range from 9.0 °C to 36.0 °C. Cr-I/N and N-I transition curves of a phase diagram behave in normal manner from C₁ to C₁₆ members. Mesogenic properties of present novel ester series are compared with the structurally similar series. Odd-even effect is missing for the N-I transition curve. Thus present series is partly nematogenic without exhibition of smectic property whose transition temperatures vary between 190 °C and 136 °C.

KEYWORDS: Liquid Crystal, Smectic, Nematic, Mesogen, Mesomorphism.**INTRODUCTION**

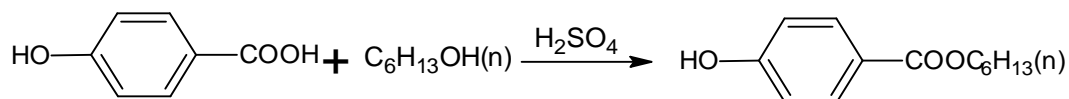
Study of liquid crystalline (LC) state^[1] has attracted to the researchers belonging to science and technology, irrespective of their specialized branch of science or technology, with different aims, objects and views^[2-5] in the benefit of mankind.^[6,11] Every researcher needs

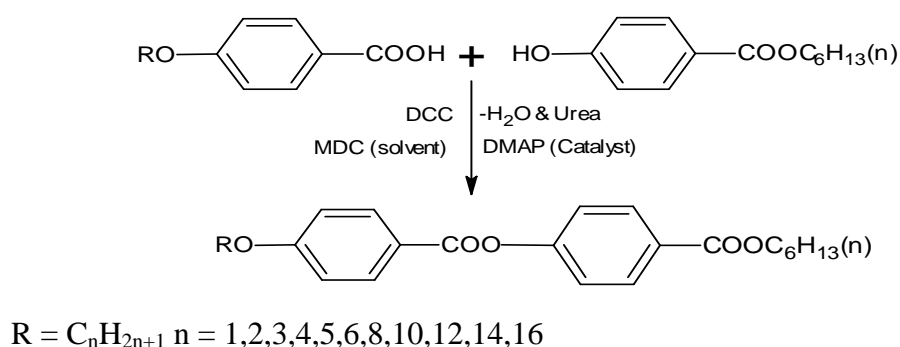
always novel substances to continue their research in their specialized objects. Therefore we being chemists decided to synthesize novel molecules which can yield novel thermotropically mesomorphic (LC) substances. Number of LC substances have been reported^[12,19] till the date. However, proposed novel investigation is planned with a view to synthesize novel substances through homologous series consisted of two phenyl rings and one of the –COO– central groups. Thus, the present study will add some novel LC substances which can be useful to the researchers working in the field of Liquid crystals with different aims and objects. Thus, present study is aimed to synthesize novel LC substances to understand and establish the effects molecular structure^[20,22] on LC properties and evaluated data; will be interpreted in terms of molecular rigidity and flexibility.^[23,26]

MATERIALS AND METHODS

- P-n-alkoxy benzoic acids were prepared by the modified method of Dave and Vora (1970)^[27] using suitable alkylating agent (R-X)
- P-Hydroxy n-Hexyl Benzoate was prepared by reacting P-Hydroxy Benzoic acid with corresponding n-Hexyl Alcohol (dissolve in Benzene) using modifying method of Doshi, Patel and Marathe through European pattern.^[28]
- Acid were directly condensed with the p-Hydroxy n-Hexyl Benzoate dissolved in MDC in portions with DCC & DMAP as catalyst by stirring reaction mixture.^[29] Products were decomposed filtered, washed, dried and purified, till the constant transition temperatures obtained. P-Hydroxy benzoic acid, alkyl halides (R-X), methanol, KOH, P-Hydroxy Benzoic acid, n-Hexyl Alcohol, con. H₂SO₄, 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

P- Hydroxy n-hexyl benzoate



P-(P'-n-alkoxy benzoyloxy) – n-hexyl Benzoate**Scheme-1: Synthetic route to the series.****Characterization****Table 1: Elemental analysis for ethyloxy, propyloxy and butyloxy derivatives.**

Sr. No.	Molecular Formula	Elements % Found (% Calculated)	
		C	H
1.	$\text{C}_{22}\text{H}_{26}\text{O}_5$	71.35 % (73%)	7.02 % (7.1%)
2.	$\text{C}_{23}\text{H}_{28}\text{O}_5$	71.87% (73%)	7.29 % (7.3%)
3.	$\text{C}_{24}\text{H}_{30}\text{O}_5$	72.36% (74%)	7.53 % (7.4%)

Spectral Data

^1H NMR in ppm for the Decyloxy derivatives: 1.2, 1.3, 1.5, 1.6 (alkyl chain H), 3.8, 3.6, 4.08 ($-\text{OCH}_2$ of $-\text{OC}_{10}\text{H}_{21}$ and $-\text{OC}_6\text{H}_{13}$), 7.2, 6.9 (p-di substituted benzene ring)

^1H NMR in ppm for the Tetradecyloxy derivatives: 1.2, 1.3, 1.5, 1.6, 2.0 (alkyl chain H) 3.9, 4.0, 4.06, ($-\text{OCH}_2$ of $-\text{OC}_6\text{H}_{13}$), 6.8, 7.2, 7.34 (p-di substituted benzene ring)

IR in cm^{-1} for Hexyloxy derivatives: 891 & 844 cm^{-1} para di substituted phenyl ring 1087, 1045, 1244, cm^{-1} ether linkage, 1438, 1512, 16025 cm^{-1} aromatic ring, 1700 cm^{-1} ester present, 2850, 2926 long chain alkane present

IR in cm^{-1} for Octyloxy derivatives: 893 & 842 cm^{-1} para di substituted phenyl ring 1008, 1207, 1271 cm^{-1} ether linkage, 1442, 1608 cm^{-1} aromatic ring, 1707 cm^{-1} ester present, 2866, 2941 long chain alkane present

Texture: by miscibility method, Threaded nematic C_6 , Schlieren nematic - C_{10} and C_{12}

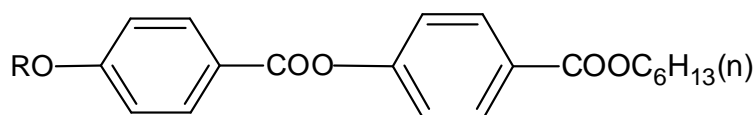
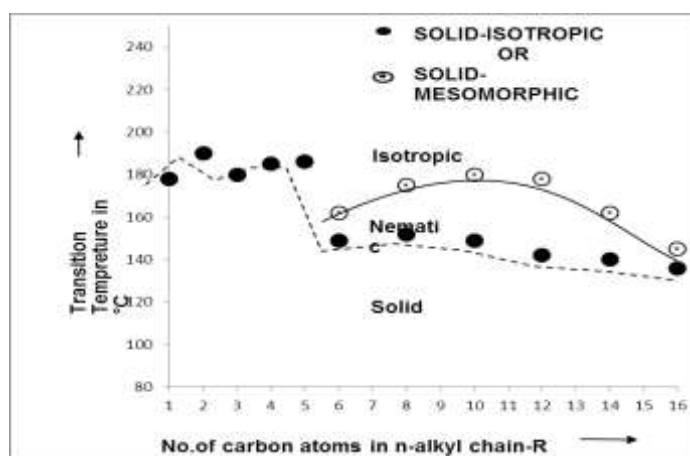


Table 2: Transition temperatures.

Sr. No.	n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	178
2	Ethyl	-	-	190
3	Propyl	-	-	180
4	Butyl	-	-	185
5	Pentyl	-	-	186
6	Hexyl	-	149	162
7	Octyl	-	152	175
8	Decyl	-	149	180
9	Dodecyl	-	142	178
10	Tetradecyl	-	140	160
11	Hexadecyl	-	136	145



RESULTS AND DISCUSSION

P- Hydroxy n-hexyl Benzoate (yield 68%) is a nonmesomorphic substance. But, on condensing it with n-alkoxy benzoic acid yielded C₆ to C₁₆ homologues as enantiotropic nematic without exhibition of smectogenic property. The rest of the homologues (C₁ to C₅) are nonmesogenic. Transition temperatures (Table -1) as determined from an optical polarizing microscopy with heating stage were plotted against the number of carbon atoms present in n-alkyl chain bonded with phenyl ring through oxygen atom of left flexible tail group. Like or related points were linked to draw Cr-I/N and N-T transition curves adopt a zigzag path of rising and falling with overall descending tendency up to C₁₀ homologue, then, it deviates at C₁₂ and C₁₆ homologues from usual expected behavior. N-I transition curve initially rises and then descended as series is ascended up to C₁₀ homologue and then deviated from normal expected behaviors. i.e. It is rising, instead of falling for C₁₆ homologue. N-I transition temperature keeping in view of the trend of a N-I transition curve. The N- I curve is extended up to Cr – I (Isotropic) transition temperature. N – I transition curve does not

exhibit odd-even effect. Mesogenic behaviors of liquid crystalline homologues vary from homologue to homologue in present series with changing number of methylene unit or units in flexible *n*- alkyl chain. Keeping alkyl tail group intact throughout the same series. The disappearance of *n*- alkoxy benzoic acids is due to the breaking of hydrogen bonding between two molecules of aromatic carboxylic acids by esterification process. The nonmesogenic property of homologues C₁ to C₅ members of a present series is attributed to their high crystalizing tendency arising from inability of respective nonmesogenic homologues to resist externally exposed thermal vibrations as a consequence of unsuitable magnitudes of molecular rigidity and flexibility induced by low dipole–dipole interactions and the low magnitude of dispersion forces by the interaction between instantaneous dipoles produce by the spontaneous oscillations of the electron clouds of the molecules which hinders the suitable magnitudes of anisotropic forces of intermolecular cohesion and disallows molecular arrangement required for definite range of temperature (i.e. zero temperature range). End to end attractions predominated more than lateral attractions. Therefore, more ordered sliding layered arrangement of molecules is less favored to facilitation formation of smectic phase against less bordered, statistically parallel orientational order of molecules in floating condition on the surface to cause nematogenic mesophase formation. Presently investigated novel series enhances nematic thermal stability and diminishes the stabilization of smectic mesophase formation. Absence of odd-even effect in N-I transition curve is attributed to the absence of mesophase forming tendency from C₁ to C₅ homologues and absence of odd-even effect for higher homologues with longer *n*- alkyl chain which can be attributed to uncertainty in the status of relatively longer *n*- alkyl chain which may coil or bend or flex or couple to lie with major axis of core structure of molecules Therefore intermolecular cohesive forces of C₁ to C₅ homologue are weakened to such an extent that, even, statically parallel orientation order of molecules C₁ to C₅ is not facilitated to cause nematic mesophase formation. Hence, reasons for nonmesomorphism character of C₁ to C₄ are different. N-I transition curve is hypothetical and not realistic. Cr-I point is real which merges into isotropic point. The observed deviation behaviors transition curves for C₁₄ and C₁₆ can be attributed to longer *n*-alkyl chain and highly polar and polarizable and flexible nitro tail group which may have enthalpy value (H) unusually higher than normal of suitable magnitudes, which can exhibit mesophase formation in the normal condition. The variation in mesogenic properties of present series from homologue to homologue is due to the sequentially or progressively added -CH₂ - unit which added molecular polarization and length or size of each homologue molecule in the same series, keeping the rest of the molecular part unchanged. Thus, a series

under discussion is partly nematogenic and partly nonmesogenic with absence of smectogenic character. The mesogenic behaviour of present series-1 are compared with structurally similar homologous series-2 [30] as shown in figure-2.

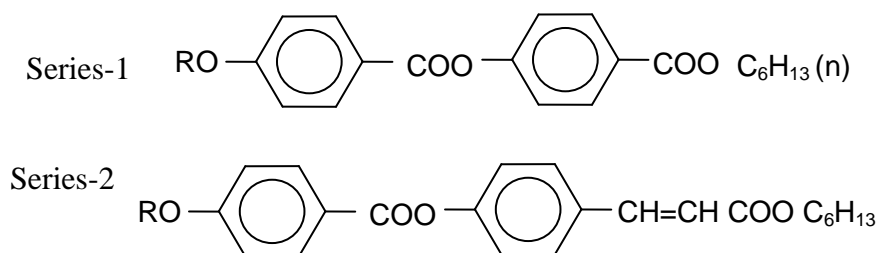


Figure: 2 Structurally Similar Series.

Novel homologous series-1 and 2 are identical with respect to two phenyl rings and central bridge linking with both phenyl ring. Moreover left n-alkoxy flexible terminal end group $\text{C}_n\text{H}_{2n+1}$ i.e. RO- are the same for the same homologue from series to series. But remaining part of each series differs with each other. i.e. series-1 and 2 differs with right side end group as and i.e. molecular rigidity differs but molecular flexibility remains unaltered. Homologous series-1 and 2 are identical with respect to central bridge linking middle and differs with respect to $-\text{COO}-$ and $-\text{CH}=\text{CH}-\text{COO}-$ respectively for the same homologue from series to series i.e. molecular flexibility is altered keeping molecular rigidity unaltered for the same homologue from series to series. Thus, variations in mesogenic properties and the degree of mesomorphism observed, are depended upon the altering magnitudes of either molecular rigidity or the molecular flexibility among the presently investigated series-1 and the homologous series - 2 chosen for comparative study. Following table-3 represents some mesogenic properties like average thermal stabilities, commencement of mesophase or mesophases, mesophase lengths etc. to indicate effect of molecular structure on liquid crystal properties in terms of or as a consequence of altering molecular rigidity or flexibility; as under.

Table 3: Average thermal stability in °C.

Series	Series - 1 -COO-C ₆ H ₁₃	Series - 2 -CH=CH-COO-C ₆ H ₁₃
Smectic -isotropic Or Smectic- nematic	-	179.4 (C ₇ -C ₁₄)
Commencement of smectic phase	-	C ₇
Nematic -isotropic	166.6 (C ₆ -C ₁₆)	190.9 (C ₆ -C ₁₄)

commencement of nematic Phase	C ₆	C ₆
Total mesophase length in °C (Nm-Iso)	9 - 36	10 - 60
Cn ₁ Cn ₂	C ₆ C ₁₆	C ₆ C ₁₄

From above table-3, it is clear that,

- Presently investigated novel series -1 only nematogenic whereas series -2 is nematogenic in addition to smectogenic
- Smectic property commences from C₇ homologue of a series -2, whereas, it does not commence till the last member of a series 2.
- Nematic mesophase commences from C₆ homologue of series-1 whereas it commences C₆ homologue of the series-2 respectively.
- Total Mesophase length range of series-1 is relatively lower than series- 2.

Mesogenic characteristics difference of a substance varies with changing structural part of molecules under comparison. The changing molecular structural part between series-1 and 2 is a right terminal end -COO-C₆H₁₃, and -CH=CH-COO-C₆H₁₃. Both central bridges contributes molecular rigidity of different magnitude though -COO- unit as commonly present in Series 1 and 2. The remaining uncommon part, other than -CH=CH- common unit for series -1 and series -2 respectively. The -CH=CH-COO-C₆H₁₃ unit of series-2 is longer than -COO-C₆H₁₃, group of series -1 which links with -COO- common unit of both series under comparison. However linking of uncommon longer unit -COO- bonded with common sp² hybridized -C₆H₁₃ unit through sp³ carbon of -CH₂, whereas the sp² carbon of shorter -COO- group of uncommon part of a central bridge of series - is bonded to a common sp² hybridized unit. Thus, longer and shorter differing units of present novel series-1 and 2 bonded with common tail unit -C₆H₁₃, through sp³ or sp² carbon respectively. Such differences induces differences into molecular polarity and polarizability as a consequence of molecular rigidity, keeping molecular flexibility unchanged for the same homologue from series-1 to series-2 which causes difference in the suitable magnitudes of anisotropic forces of intermolecular end to end attractions, commencement of mesophase, thermal stability, mesophase length range and other mesogenic properties.

CONCLUSIONS

A novel homologous series consisted of two phenyl rings and two ester right end group which acts as rigid core and contributing flexible core of the molecules, induces nematic type of mesomorphism with absence of smectic property. Series is middle ordered melting type with high thermal stability.

Group efficiency order derived on the basis of

(i) Thermal stability (ii) commencement of mesophase (iii) total mesophase length for nematic with reference to molecular rigidity/flexibility are as under

(i) Smectic:

Rigidity/Flexibility: Only -CH=CH-COO-

Nematic

Rigidity/Flexibility: -CH=CH-COO-C₆H₁₃ > -COO-C₆H₁₃

(ii) Smectic:

Rigidity/Flexibility: Only -CH=CH-COO-

Nematic

Rigidity/Flexibility: -CH=CH-COO-C₆H₁₃ > -COO-C₆H₁₃

(iii) Total (Sm+N):- (Right end group)

-CH=CH-COO-C₆H₁₃ > -COO-C₆H₁₃

Series- 2 Series -1

- Suitable magnitudes of combined effect through molecular rigidity and flexibility can induce mesomorphism.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Present novel ester compounds may be useful in the study of binary systems and agricultural field.
- Presence of vinyl group is predominantly nematogenic.

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