# SYNTHESIS AND STUDY OF A NEW HOMOLOGOUS SERIES OF NOVEL CHALCONE DERIVATIVE

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## ABSTRACT

A new homologous series of non-amphiphilic liquid crystals viz; p-n-alkoxy benzoic acid with α-4 Hydroxy benzoyl β -4' –n-Pentyl phenylethylene configuration is synthesized and studied with a view tounderstand the effect of molecular structure on mesomorphic properties of substances which maybe useful to the various fields of applications. Methyl to pentyl homologues arenonmesomorphic, hexyl to hexadecyl homologues are mesomorphic i.e. nematogenic in character without exhibition of any smectic character. A phase diagram is drawnfrom the transition temperatures as determined from hot stage polarizing microscope ofhomologues against the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal endgroup. Solid-isotropic or solid nematic transition temperature curve follows a zigzag path ofrising and falling throughout the series as series is ascended in normal manner. Nematic-isotropictransition curve initially rises and then, shows descending tendency as series isascended. Thus, it follows usual established trend as expected. Doesn't known odd-even effect isobserved for nematic-isotropic transition curve. Analytical data support the structures ofmolecules. The enantiotropic nematic mesophase appeared for all the homologues, is of threadedtype as determined from miscibility method. Thermal stability for nematic is 168.5°C andmesomorphic range is short which varies from 13.0°C to 30.0°C. mesomorphic properties of titled homologous series is compared with structurally similar homologous series.

**KEYWORDS:** Mesomorphism, Mesophase, Mesogen, Smectic, Nematic, Enantiotropy.

## 1. INTRODUCTION

Liquid crystalline (LC) novel homologues of chalconyl derivatives are important from the point of view of their applicability[1-6] in the manufacture of LC devices to be operated at desired or room temperature and their bioactivities to be exploited as anticancer, antimalarial, antibacterial etc in the benefit of mankind. Therefore present investigation was planned to synthesize novel chalconyl ester derivatives which can be useful to all scientific and technological research investigators working on LC state with different aims, objects and views with different angle. The present aim of investigation is fixed with a view to understand and establish the effect of molecular structure[7-10] on properties of thermotropic LC substances, which includes even a minor change in molecular structure can bring about major change in LC behaviour as a consequence of changing molecular rigidity and/or flexibility.[11-15] Numbers of chalconyl ester or azo ester or simple esters have been reported till the date.[16-20] The synthesis of novel homologous series of proposed investigation after their due characterization will be compared with other structurally similar analogous series and then group efficiency order will be derived with respect to thermal stability, early commencement of mesophase and the degree of mesomorphism.

## 2. EXPERIMENTAL

**Experimental: (Synthesis)**

- p-n-alkoxy benzoic acids (A) were prepared by the modified method of Dave and Vora (1970)[21] using suitable alkylating agent (R-X).

- n-alkoxy Benzoic acids were condensed with α-4 Hydroxy benzoyl β -4' –n-Pentyl phenylethylene[22] (B) by usual established method.

- Components (A) and (B) were condensed[23-25] to give final products. Synthetic route to series is mentioned below as **scheme-1**. Final products were individually decompose, filtered, washed, dried and purified till the constant transition temperatures obtained.

a-4-(4'-n-Alkoxybenzoyloxy)benzoyl-b-4"pentloxy phenyl ethylene
Where, R=CnH2n+1 and n = 1 to 8 and 10,12,14,16
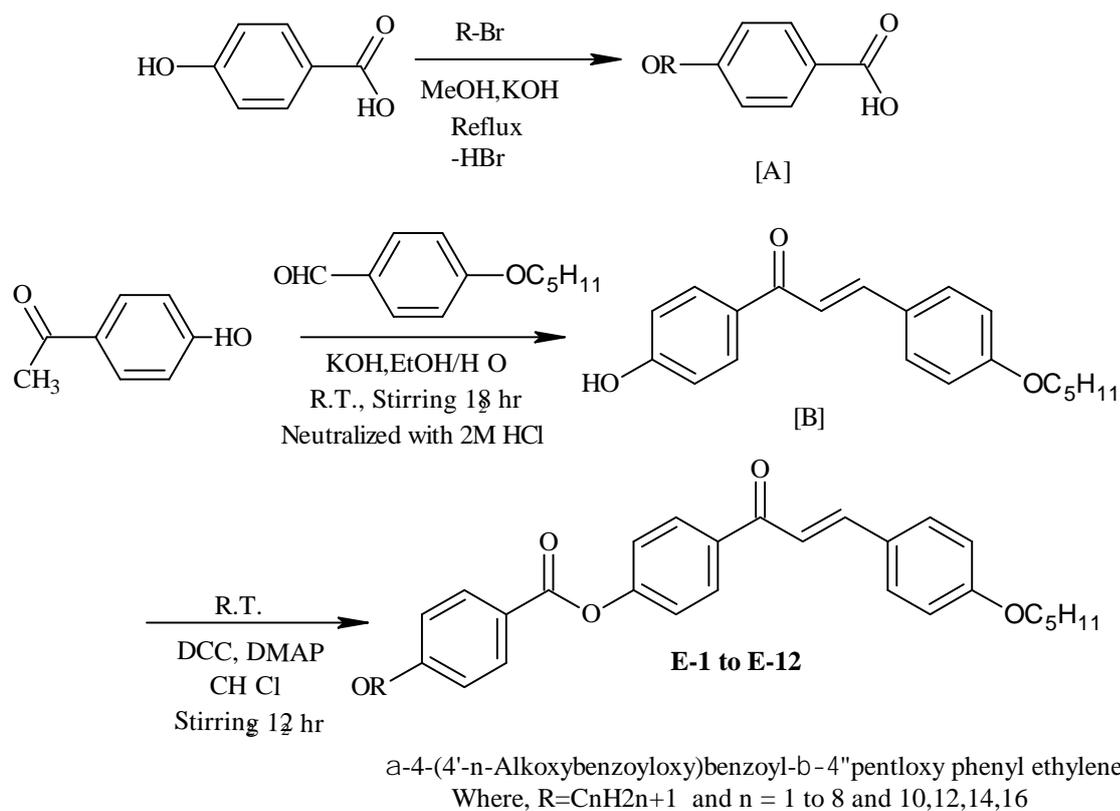
**Final product**

**Scheme-1: Synthetic route to the series-1.**

The chemicals 4- hydroxyl Benzoic acid, alkyl halides, 4- Hydroxy acetophenone, 4-Pentyloxy benzaldehyde, potassium Hydroxide, hydrochloric acid etc. required for synthesis were used as received except solvents which were dried and distilled prior to use.

**Characterization**

Some selected members of the titled novel series were characterized by elemental analysis, $H^1NMR$ spectra and IR spectra, Microanalysis for C,H,N, elements was performed on Perkin Elmer PE 2400 analyzer (Table-1). 1HNMR spectra were obtained on Bruker spectrometer using CDCl3 as solvent. IR spectra were recorded on a Perkin- Elmer spectrum GX. Transition temperatures and liquid crystal properties were investigated using an optical polarizing microscope equipped with a heating stage. Textures of mesophases were characterized by cmiscibility method.

### 3. ANALYTICAL DATA

**Table 1: Elemental analysis for methyloxy, ethyloxy and propyloxy derivatives.**

| Sr. No. | Molecular Formula | Elements % Found | | Elements % Calculated | |
|---|---|---|---|---|---|
| | | C | H | C | H |
| 1. | $C_{28}H_{28}O_5$ | 75.30 | 6.10 | 75.67 | 6.30 |
| 2. | $C_{29}H_{30}O_5$ | 76.09 | 6.41 | 75.98 | 6.55 |

**H$^1$NMR: in ppm.** For Pentyloxy homologue.

Ethylene: (200 MHZ) δ (CDCl$_3$) (ppm) 0.9 (-CH$_3$-CH$_2$ of –C$_5$H$_{11}$), 1.4 (long-CH$_2$- chain), 3.8 -OCH2 of (–OCH$_2$ of –C$_5$H$_{11}$), 4.64 and 4.50 – CH=CH, 7.09 & 6.92,(p-sub. benzene rings) 7.80 & 8.02 (two p-sub. benzene rings).

**H$^1$NMR: in ppm.** For Decyloxy homologue.

Ethylene: (200 MHZ) δ (CDCl$_3$) (ppm) 1.29 – CH3, 3.95 – O CH$_2$, 4.11 – O CH$_2$ of -OCH$_2$- 4.50 and 4.62 – CH=CH- , 7.09, 6.92, 8.02, and 8.10 –p-sub. phenyl, (two p sub benzene), 7.34 and 8.12 – p-sub phenyl two p-sub benzene.

**IR in Cm$^{-1}$,** For Octyloxy homologue

Ethylene's: (vmax/cm-1): 2900, 2850, (-C-H, aliphatic), 1740, 1160 (ester group), 1720 (>C=O group), 1600 (-C=C-, aromatic), 1050.1,1255 (ether group), 850.7 (p- sub. Benzene ring), 1600, 1590, 1450 (Aromatic ring).

For Decyloxy homologue

Ethylene's: (vmax/cm-1): 2930, 2860, 1337.1, (-C-H, aliphatic), 1744, 1164.4 (ester group), 1720 (>C=O group), 1590.3 (-C=C-, aromatic), 1053.4,1150 (ether group), 846.7 (p- sub. Benzene ring), 1610, 1486, 1450 (Aromatic ring).

**Textures by miscibility method**

Threaded nematic.

**Table 2: Transition Temperatures in °C.**

| Comp. No. | n-alkyl (CnH2n+1) group | Smectic | Nematic | Isotropic |
|---|---|---|---|---|
| 1 | C1 | - | - | 148 |
| 2 | C2 | - | - | 162 |
| 3 | C3 | - | - | 170 |
| 4 | C4 | - | - | 163 |
| 5 | C5 | - | - | 165 |
| 6 | C6 | - | 148 | 162 |
| 7 | C8 | - | 172 | 185 |
| 8 | C10 | - | 158 | 184 |
| 9 | C12 | - | 155 | 180 |
| 10 | C14 | - | 140 | 162 |
| 11 | C16 | - | 108 | 138 |

## 4. RESULTS AND DISCUSSION

n-alkoxybenzoic acids and α-4 Hydroxy benzoyl β -4' –n-Pentyl phenylethyleneare nonmesomorphic innature. However, on linking chemically both of them, they combine and gives rise to liquid crystal property from n-hexyl derivative of the homologous Chalcone series First five homologues i.e. methyl to n-pentyl derivatives of the series are nonmesomorphic in character. Transition temperatures of the homologues are plotted versus the number of carbon atoms in n-alkyl chain of left n-alkoxy terminal end groups from table-2. Like points are linked and a phase diagram is obtained, which is shown in figure –I. Nematogenic mesophase start to commence from hexyl derivative and ends to hexadecyl derivative i.e. intermolecular anisotropic force of suitable magnitude are occurred from hexyl to hexadecyl derivatives of the series to cause properly required type of molecular alignment to keep and maintain statically parallel orientations of molecules as a consequence of molecular rigidity and flexibility in floating condition. Careful examination of a phase diagram (figure-1) reveals that, solid-isotropic or solid-mesomorphic transition curve follows zigzag path of rising and falling as series is ascended in usual manner. Nematic-isotropic transition curve initially rises and then adopt descending tendency as series is ascended with overall descending manner following expected trend of behavior. Mesomorphic range varies between 13.0˚C to 30.0˚C at the with 168.5˚C nematogenic thermal stability. Thus, mesomorphic range is short and series is of middle ordered melting type without exhibition of any smectic character, even in the monotropic condition. Odd-even effect doesn'tobserved for nematic-isotropic transition curve. Intermolecular force of attractions due to molecular rigidity and flexibility are not anisotropic and of suitable magnitude of p-n-alkoxy benzoic

acid and α-4 Hydroxy benzoyl β -4' –n-Pentyl phenylethylenebut, on linking them through the enantiotropic nematogenic mesophase is induced for hexyl homologue to hexadecyl homologue with absence of smectogenic character. The titled homologous series induce thermotropic mesomorphism i.e. mesophase appears by application of thermal energy from surrounding [Rest of the universe other than system] to system [crystalline homologue under study]. When a crystalline un layered homologue undergo formation and reaches to crystalline solid state, it releases energy (ΔH) and tend to move towards a state of higher entropy (ΔS) to as far as lower entropy to acquire the most, thermodynamically stable state of existence. Now, heat (ΔH) is supplied to a thermodynamically stable system (homologue) from surrounding to a system, a system under investigation tend to absorb heat energy which acts against the intermolecular end to end and lateral attractive forces, fighting against binding forces of solid homologue. Thus, loosely bonded molecules undergo translational motion to vibrational motion through rotational motion. As a result of this, molecules of a system tend to acquire interstate transition of thermodynamically more stable state to less stable state of high entropy or randomness. As temperature exposed upon system rises, the vibrating molecular system may or may not resist thermal vibrations imposed upon them. The molecular system which resist thermal vibrations resisting disalignment of molecules at an angle less than 900, are able to maintain statically parallel orientational order of molecules in floating condition causing format on of nematic mesophase at temperature $t_1$ at constant pressure as observed for n-hexyl homologue to tetradecyl homologue. Thus, nematic mesophase commence to appear from temperature $t_1$ and continue till the higher temperature $t_2$ for enantiotropic nematic mesophase corresponding to randomness or entropy, $\Delta S = \Delta H/ T$ where $T = t + 273$, Absolute temperature in $^0K$. and t= temperature of transition in ˚C. The range of liquid crystallinity of a homologue or a substance $t_R = t_2 - t_1 = T_2 - T_1$. If a molecular system is unable to resist the thermal vibrations exposed upon it, $t_2 - t_1 = 0$ or $t_2 = t_1 = t$. Thus, molecular system under examination undergo disalignment of molecules in floating condition without formation of mesomorphic state and passes directly into isotropic liquid state from un-layered crystalline solid state. i.e. solid crystalline material directly melts at temperature t˚C without passing through an intermediate state of existence, called liquid crystal state or mesomorphic state or nonamphiphiles state as observed for the, methyl to Pentyl homologues of titled homologous series. The appearance of zigzag path of solid-isotropic or mesomorphic curve and alternation of transition temperatures for allhomologues are attributed to the sequentially and progressively added methylene unit to the left n-alkyl chain of n-alkoxy terminal end group.

**Table 3: Average thermal stability.**

| Series | 1 |
|---|---|
| Nematic-Isotropic Commencement of Nematic phase | 168.5 ˚C (C$_5$ - C$_{16}$) C$_5$ |
| Total upper and lower mesophase length range in 0C Ci to Cj | 13.0 ˚C to 30.0 ˚C C$_8$ C$_{16}$ |

Careful examination of table-3 indicate that, the thermal stability for series is zero. i.e. smectic mesophase is not exhibited by the molecules of series. Chalcone series is long linear rod like with n-pentyl linkage is relatively more molecular length than the homologous. Therefore, from the intermolecular distance point of view, molecules of series is more closely packed. This difference in width may reduce the intermolecular end to end attractions. However molecularpolarizability of seriesdue to widening of a molecule is less. Thus, two opposing effects are operating at a time. Viz; increased length and linearity increases intermolecular attractions in series while, widening of molecule decreases intermolecular attractions due to increase in intermolecular distance and on the other hand it increases molecularpolarizability and hence it increases intermolecular lateral and end to end attractions. Under this situation of two opposing effects operating at a time, the resultant effect will depend on predominating effect. Thus, the effect due to increased polarizability predominates in series. Thus, thermal stability for nematic of series is less. On the homologous series entirely nematic character, without exhibition of any smectic character. The molecules of series involve-CO–CH=CH- group at the central. The, -CO-CH=CH- group is relatively longer than –COO- group by –CH=CH- which causes relatively more noncoplanarity than –COO- due to a twist obtained as the oxygen atoms of the vinyl carboxy group bump into the non-bonded adjacent hydrogen atoms of aromatic phenyl rings. The smectic mesophase does not appear till the hexadecyl derivative of the series.

**CONCLUSION**

A novel homologous series consisted of three phenyl rings and ester and Chalcone central bridges which acts as rigid core and two end groups contributing flexible core of the molecules, induces nematic type of mesomorphism.Series is middle ordered melting type with high thermal stability.

- Suitable magnitudes of combined effect through molecular rigidity and flexibility can induce mesomorphism.

- Mesomorphism is very sensitive and susceptible to molecular structure.
- Present novel Chalcone compounds may be useful in the study of binary systems and agricultural field.
- Presence of vinyl group is predominantly nematogenic.

## ACKNOWLEDGEMENT

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