Mesomorphic properties of liquid crystalline compounds with central linkage chalconyl ester and laterally substituted bromo group

Priya K. Patel\textsuperscript{a}, R. B. Patel\textsuperscript{b} and R. R. Shah\textsuperscript{c}

Chemistry Department, K. K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India

\textsuperscript{a-c}E-mail address: pp2541991@gmail.com, roshanpatel17@gmail.com, ruteshshah67@gmail.com

ABSTRACT

To investigate the mesomorphic property of the substitution on mesomorphism, the new series of liquid crystals having the following structures have been synthesized. Presently synthesized series contain thirteen homologue (C\textsubscript{1} to C\textsubscript{8}, C\textsubscript{10}, C\textsubscript{12}, C\textsubscript{14}, C\textsubscript{16}, C\textsubscript{18}) in which eleven homologue (C\textsubscript{3} to C\textsubscript{18}) shows both smectic as well as nematic phase during heating and cooling condition in enantiotropic manner, while C\textsubscript{2} homologue shows only nematic phase. All the homologues were characterised by elemental analysis and spectroscopic techniques like \textsuperscript{1}H-NMR and IR analysis. Their liquid crystalline behaviours were measured by polarised optical microscope (POM) and Differential Scanning Calorimetry (DSC).

Keywords: Smectic, Nematic; Liquid crystalline; Mesomorphic; Enantiotropic
Graphical Structure

1. INTRODUCTION

From the last many years, the field of liquid crystal, is becoming very innovative and more useful to mankind. Liquid Crystal is a very delicate, beautiful and unique state in between Liquid and Crystal. Liquid Crystals have different molecular geometry, different phases and phase transition [1-2]. Liquid crystalline property (LC) of a substance is an unique property, which flows on the surface like liquid and possesses optical properties like crystals. Therefore such substances of theromotropic or lyotropic varieties are neither fully crystalline nor fully liquidous [3-8]. A little change in geometry of molecule brings big difference in molecule’s mesomorphic property [9-12]. Now a days liquid crystalline compound are used in many fields. Many compounds of liquid crystal are based on chalcones, are products of simple or substituted aromatic aldehydes with simple or substituted acetophenone in presence of base and alcohol. A number of chalcone having reported to exhibit a broad spectrum of anti-bacterial, antifungal, antiulcer, antimalarial, antitumor, anticancer, anti-inflammatory, antitubercular. The presence of \( \alpha, \beta \)-unsaturated functional group in chalcone (\(-\text{CH}=\text{CH}-\text{CO}-\)) is responsible for anti-microbial activity, which can be altered depending upon the type of substituent present on the aromatic rings [13-17]. Chalcone possess biological activity like antitubercular, antifungal, antiviral, anticancer, antibacterial, etc. [18-20]. In this present article, we have demonstrated the rod like structure of present newly synthesized homologous series makes them more suitable to establish or invent the liquid crystalline characteristics and to establish the effect or relation between chalconyl ester and lateral halogenated (\(-\text{Br}\)) group and three phenyl ring through two central linkage \(-\text{CH}=\text{CH}-\text{COO} -\) and \(-\text{CH}=\text{CH}-\text{CO} -\) which has terminal end groups \(-\text{OR}\) at left side chain. Doshi et al. reported benzoates and cinnamate based linking group in-built with chalconyl linkage group to exhibit LCs property [21-26]. Recently, our research group studied chalconyl ester based linear and nonlinear homologues series and observed the effect of flexibility by increasing alkyl spacer at terminal group and effect of lateral side group on mesomorphism [27-33]. Consequently, an attempt to made liquid crystalline compound that display LCs property with good thermal stability and
commencement of mesophase from lower homologue to higher homologue respectively. Rod like structure of series indicates that rigidity and flexibility of molecule vary from homologue to homologue with changing alkyl group at left alkoxy terminal.

2. EXPERIMENTAL

2.1. Reaction Scheme

**Scheme 1.** Synthetic route of the series
2. 2. Synthesis

4-hydroxy benzaldehyde was alkylated by using suitable alkyl halides (R-X) to convert it into 4-n-alkoxy benzaldehyde which reacts with malonic acid in presence of pyridine and piperidine as catalyst to form trans 4-n-alkoxy Cinnamic acid [A] [34].

4-hydroxy benzaldehyde and o-bromo acetophenone reacts with each other to produce α-1-bromo benzoyl-β-4'-hydroxy phenyl ethylene [B] [35]. Then 4-n-alkoxy cinnamic acid and α-1-bromo benzoyl-β-4'-hydroxy phenyl ethylene were condensed in 1,3-di-cyclohexyl carbodiimide (DCC), 4-dimethyl amino pyridine ( DMAP ) and dichloro methane ( DCM ) to produce α-4-[4'-n-alkoxy cinnamoyloxy]phenyl-β-1”-bromo benzoyl ethylenes [C] [36].

The final product were filtered, washed with water and NaHCO₃ solution then dried and purified till constant transition temperatures obtained using an optical polarising microscope equipped with a heating stage. Alkyl halides, EtOH, KOH, 4-Hydroxy 3-Bromo acetophenone, 4-Hydroxy benzaldehyde 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 as Scheme 1.

2. 3. Characterization

The homologous of present series were characterised by IR and ¹H-NMR. IR analysis were recorded on a Perkin-Elmer spectrum GX and ¹H-NMR were recorded on a Bruker instrument using CDCl₃ as a solvent. Elemental analysis was performed by Perkin Elmer PE 2400 CHN analyser (Table 1). Texture image of some homologues for smectic and nematic mesophases were determined by miscibility method (Table 2). The textures of smectic and nematic mesophase were determined by a miscibility method. The mesomorphic properties and transition temperature (Table 3) were determined by optical polarising microscope.

The compound is sandwiched between glass slide and cover slip and the heating and cooling rate is 2 °C. Decomposition temperatures were determined using of Shimadzu DSC 60 differential Scanning Calorimeter with a heating rate of 5 to 10.0 °C min⁻¹.

2. 4. Analytical data

Table 1. Elemental Analysis for (1) Ethyloxy (2) Pentyloxy (3) Hexyloxy (4) Heptyloxy (5) Octyloxy (6) Decyloxy.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Molecular formula</th>
<th>Elements % found</th>
<th>Elements % Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>1</td>
<td>C₂₉H₂₃O₄Br</td>
<td>64.24</td>
<td>4.00</td>
</tr>
<tr>
<td>2</td>
<td>C₂₉H₂₈O₄Br</td>
<td>64.87</td>
<td>4.74</td>
</tr>
<tr>
<td>3</td>
<td>C₃₀H₃₀O₄Br</td>
<td>65.62</td>
<td>5.21</td>
</tr>
<tr>
<td>4</td>
<td>C₃₁H₃₂O₄Br</td>
<td>65.86</td>
<td>5.34</td>
</tr>
</tbody>
</table>

-205-
Table 2. Texture of Nematic Phase of C₇, C₁₂, C₁₄, C₁₈ by miscibility method.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Homologue</th>
<th>Texture</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₇</td>
<td>Threaded type</td>
</tr>
<tr>
<td>2</td>
<td>C₁₂</td>
<td>Nematic droplets</td>
</tr>
<tr>
<td>3</td>
<td>C₁₄</td>
<td>Schlieren</td>
</tr>
<tr>
<td>4</td>
<td>C₁₈</td>
<td>Rod like broken fan</td>
</tr>
</tbody>
</table>

IR Spectra in cm⁻¹ for propyloxy and tetradecyloxy derivatives:

**Propyloxy derivative** (C₃): 655.80 (-CH-Br stretching), 823.60 (polymethylene (-CH₂)ₙ of –OC₃H₇), 891.11 (-C-H def. of o, p-disubstituted), 977.91 (-C-H def. of hydrocarbon), 1068.56, 1165.00 (-C-O stretching), 1381.03 (-C-O stretching in (-CH₂)ₙ chain), 1508.33 (-C=C- stretching), 1571.99 (-C-H def. in –CH₂), 1645.28 (C=O group), 2856.79, 2929.87 (-CH stretching in –CH₃). IR data confirms the molecular structure.

**Tetradecyloxy derivative**(C₁₄): 648.08 (-CH-Br stretching), 815.89 (polymethylene (-CH₂)ₙ of –OC₁₄H₂₉), 891.11 (-C-H def. of o, p-disubstituted), 979.84 (-C-H def. of hydrocarbon), 1006.84, 1070.49, 1170.79 (-C-O stretching), 1247.94 (-C-O stretching in (-CH₂)ₙ chain), 1508.33 (-C=C- stretching), 1573.91 (-C-H def. in –CH₂), 1625.99 (C=O group), 2850.79, 2920.23 (-CH stretching in –CH₃). IR data confirms the molecular structure.

**¹H-NMR:**

**¹H NMR spectra in CDCl₃ in δ ppm for butyloxy and hexadecyloxy Derivative:**

**Butyloxy** (C₄): 0.83 (t, 6H, -CH₃ of –C₄H₉), 1.0 (-CH₃ of –C₄H₉), 1.2-1.3 (m, n-polyethylene groups of –C₄H₉), 1.32 (q, m, n-polyethylene groups of –C₄H₉), 1.54 (m, n-polyethylene groups of –OC₄H₉), 2.22-2.29 (-CH=CH-), 3-3.4 (s, -O-CH₂-CH₂- of –OC₄H₉), NMR confirms the structure.

**Hexadecyloxy** (C₁₆): 0.82-0.94 (t, 6H, CH₃ of –C₁₆H₃₃), 1.0 (-CH₃ of –C₁₆H₃₃), 1.2-1.3 (m, n-polyethylene groups of –C₁₆H₃₃), 1.56 (m, n-polyethylene groups of –OC₁₆H₃₃), 1.63 (m, n-polyethylene groups of –OC₁₆H₃₃), 2.70-2.78 (-CH=CH-), 3.09 (s, -O-CH₂-CH₂- of –OC₁₆H₃₃), 5.06 (-OCH₂ of –OC₁₆H₃₃), 5.54 (=CH-Ar). NMR confirms the structure. C₄ and C₁₆ are as shown below.
C₄:
$C_{16}$:
Table 3. Transition Temperature in °C.

<table>
<thead>
<tr>
<th>Sr.no</th>
<th>R= n-alkyl group</th>
<th>Transition temperatures in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cr</td>
<td>Smectic</td>
</tr>
<tr>
<td>1</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>C&lt;sub&gt;10&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>C&lt;sub&gt;12&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>C&lt;sub&gt;14&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>C&lt;sub&gt;16&lt;/sub&gt;</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>-</td>
</tr>
</tbody>
</table>

3. RESULT AND DISCUSSION

3.1. POM analysis

α-4-[4'-n-alkoxy cinnamoyloxy] phenyl-β-1-bromo benzoyl ethylenes was produced by condensation of α-1-bromo benzoyl-β-4'-hydroxy phenyl ethylene and trans 4-n-alkoxy cinnamic acid which both possess non mesomorphic properties. Present series contain thirteen homologous (C<sub>1</sub> to C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>) in which C<sub>1</sub> is non-mesomorphs while C<sub>2</sub> to C<sub>18</sub> possess mesomorphic properties in enantiotropic manner. Transition temperature (Table 3) determined by polarizing optical microscope and the phase diagram (Figure 1) is plotted against the transition temperature versus the number of carbon atoms present in n-alkyl chain of the left n-alkoxy terminal end group (-OR). In present series, we have discussed the effect of mesomorphic property by geometrical shape, rigidity and flexibility due to bromo group (-ortho) at right side and varying alkoxy side chain at left side of series. Cr-I/M curves increased and then decreased as series is increased, -CH<sub>2</sub> (methylene group) linked in it. Odd-even effect is present in Cr/M curves Cr-I/M curves ascended at C<sub>7</sub> homologue because of presence of odd-even parity and then abnormally descended at C<sub>8</sub> and then ascended at C<sub>10</sub> to
C_{12} homologue and again descended at C_{14} to C_{18} homologue. The mesomorphic properties are varying from homologue to homologue because of addition of –CH\(_2\) group at left side of n-alkoxy side chain. As we increased the number of methylene group at left n-alkoxy side chain moving of sliding arrangement causes smectic (broken fan type / needle type) from C\(_3\) to C\(_{18}\) homologues. Sm-N transition curve falling from C\(_5\) to C\(_8\) homologue and then rising up to C\(_{10}\) and again falling at C\(_{12}\) upto C\(_{18}\) respectively.

**Figure 1.** Phase diagram of Series-1.
The presence of liquid crystalline property from C₂ to C₁₈ homologue, indicates the presence of lamellar packing in molecule while applying heating. As a result of favourable molecular rigidity and flexibility which facilitated statistically parallel orientational manner of molecules in floating condition on the surface causes nematic phases. N-I/M transition curve descended at C₇ to C₈ and ascended at C₁₀ while again descended at C₁₂ up to C₁₈ homologue respectively due to anisotropic forces of intermolecular attractions due to fittest magnitudes of molecular polarity and polarizability and permanent dipole moment etc.

Absence of LCs property due to short alkyl spacer of molecule causes high crystallising tendency and directly converted to isotropic phase without passing any liquid crystalline mesophase and again on cooling condition its directly converting isotropic to solid crystal.

Some mesomorphic characteristics were obtained from thermotropic analysis of present series-1 which compared with series-X [26] as shown below (Figure 2). In Series-1, three phenyl rings bonded through \(-\text{CH}=(\text{CH})=\text{COO}^{-}\) and \(-\text{CH}=\text{CH}=\text{C}=\text{O}^{-}\) group while in series-X, three phenyl rings were bonded via \(-\text{COO}^{-}\) and \(-\text{CO}-\text{CH}=(\text{CH})\) group. They also differ from each other to right end terminal group. Therefore, degree and characteristics of mesomorphism depends upon changing group from series to series.

![Figure 2. Structurally similar Series.](image)

The variation in mesomorphic property in the both Series-1 and X is due to molecular length, length and breadth ratio, permanent dipole moment, suitable or unsuitable magnitudes of intermolecular anisotropic forces or dispersion forces of cohesion and closeness, molecular flexibility and rigidity etc.

| Table 4. Thermal stabilities in °C. |
|-----------------|-----------------|-----------------|
| Series→         | Series-1         | Series-X         |
| Smectic-Isotropic or smectic- Nematic Commencement of Smectic phase | 141.0            | -               |
| (C₃ – C₁₈)      | (C₃)             |                 |

-211-
Table 4 indicates, Series-1 shows smectic phase in presence of nematic phase while Series-X shows only nematic mesophase. Smectic phase commences from C₃ homologue in Series-1. Nematic mesophase commences from C₂ homologue in Series-1 while from C₆ homologue in series-X. Total mesophase lengths vary from minimum to maximum between C₂ to C₁₄ for all the series under comparison. Difference in mesogenic and physical properties of both series is attributed to changing flexibility due to sequentially added –CH₂ group at n-alkyl chain of left side terminal group. Molecular rigidity is also differing from homologue to homologue and series to series due to different two central bridges. Thermal stability of Series-1 is higher than series-X due to presence of halogenated bromo group which increase the polarity and polarizability of molecule to induce mesophase earlier from lower homologue to higher homologue. While in series-X, the molecule become more flexible due to presence of terminal dodecyloxy group as results mesophase appeared at lower transition temperature.

3.2. DSC analysis

![DSC thermogram of Compound C₁₀](image)
DSC is a valuable method for detecting phase transitions. The thermal behaviour of novel homologous Series-1 was confirmed by using DSC measurement shown in Figure 3 & 4. Thermogram is traces in both heating and cooling condition. For compound C_{10}, first endothermic peak is observed at 106.64 °C on heating condition, this indicates the presence of SmC phase, while second endothermic peak traced at 148.56 °C, which indicates the presence of nematic phase, on cooled condition again two endothermic were traces at 105.92 °C and 149.87 °C. For compound C_{4}, first endothermic peak is observed at 118.15 °C on heating condition, this indicates the presence of SmC phase, while second endothermic peak traced at 142.23 °C, which indicates the presence of nematic phase, on cooled condition again two endothermic were traces at 119.23 °C and 144.10 °C. Smectic mesophase is observed at 110 °C by POM analysis, while in DSC thermogram it traced at 118.15 °C on heating and 119.23 °C on cooling condition.

Figure 4. DSC thermogram of Compound C_{10}

Series-1 consisted three phenyl rings, and presence of –CH=CH-CO- linkage group while in Series-X contain –CO-CH=CH- linkage group. In Series-2, -CO- group is directly linked with phenyl ring causes variation of molecular rigidity and flexibility which affects to the physical properties of a substance to exhibits a nematic mesophase with low thermal stability and late commencement of mesophase. In Series-1, presence of vinyl carboxy (-CH=CH-COO-) group which increases the length of molecule and –CH=CH- linked with second phenyl ring to maintain its linearity. The non-coplanarity of molecule due to twist received on account of the bumping of the oxygen and hydrogen atoms of the adjacent benzene core [37]. The commencement of smectic as well as nematic phase in series-1 early as compared to series-X due to the lateral interaction to terminal attractions maintain the proportionate molecular force [38].
4. CONCLUSION

Present novel linear series having chalconyl-ester central linkage group with three phenyl rings and different terminal end group. C_3 to C_{18} homologue shows smectic mesophase. The observed smectic phase is fan type and needle type. From C_2 to C_{18} homologue shows nematic mesophase and is threaded and schlieren. Tail ended n-alkoxy chain can induce mesomorphic property in chalconyl-ester homologous series. The mesomorphic property was confirmed by POM and DSC. Group efficiency order derived on the basis of (i) thermal stability (ii) early commencement of mesophase and (iii) mesophase length for smectic and nematic are as under.

Acknowledgement

Authors thanks to the K. K. Shah Jarodwala Maninagar Science College to providing facilities. Authors also thank to NFDD Centre, Rajkot for providing analytical and spectral services like ^1H-NMR and IR study.

References


( Received 14 August 2016; accepted 31 August 2016 )