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# Synthesis and mesomorphic properties of new chalconyl-linkage-based liquid crystal compounds: The effect of flexibility

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#### ABSTRACT

A new series of liquid crystals involving chalconyl-based mesogenic units interlinked between two benzene cores were designed and synthesized. The target chalconyl compounds were obtained by the reaction of 4-*n*-alkoxy benzaldehyde with 4-*n*-hexadecyloxy ( $-OC_{16}H_{33}$ ) acetophenone in presence of base. The liquid crystalline properties of synthesized compounds were observed by polarizing optical microscope study. The molecular structures of the compounds were confirmed by Fourier transform infrared, <sup>1</sup>H, and <sup>13</sup>C nuclear magnetic resonance spectra. The compounds of the series C<sub>3</sub> to C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, and C<sub>18</sub> exhibited mesophase in enantiotropically manner. The transition temperature reduced as alkyl spacer of left side group increased. The observed texture images are droplets, broken fan, and threaded like. Thermal stability of current homologous series for (N-I/I-N) is 69.8°C and for smectic phase (Sm + N) is 58.0°C.

#### **KEYWORDS**

Chalconyl LCs; nematic; odd-even; smectic



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## Introduction

Liquid crystals (LCs) are matter in a state that has properties between those of conventional liquid and solid crystals. For instance, a liquid crystal may flow like a liquid, but its molecules may orient in a crystal-like way [1, 2]. Liquid crystals can be divided into thermotropic, lyotropic, and metallotropic phases. Thermotropic and lyotropic liquid crystals consist mostly of organic molecules although few minerals are also known. Presently, we emphasis on thermotropic liquid crystals in which, phase transition into liquid crystal phase as temperature changed [3–8]. Liquid crystals of nematic type are most commonly used in production of liquid crystal displays due to their unique physical properties and wide temperature range. In the nematic phase, liquid crystal molecules are oriented on average along a particular direction. By applying an electric or magnetic field the orientation of the molecules can be derived in a probable approach [9, 10].

A number of chalcone having reported to exhibit a broad spectrum of antibacterial, antifungal, antiulcer, antimalarial, antitumor, anticancer, anti-inflammatory, and antitubercular [11–14]. The presence of  $\alpha$ ,  $\beta$ -unsaturated functional group in chalcone (–CH=CH-CO–) is responsible for antimicrobial activity, which can be altered depending upon the type of substituent present on the aromatic rings [15]. Thus, the purpose of the work to synthesized and studied the effect of chalconyl linkage group and effect of varying alkyl spacer on mesomorphism.

Doshi et al. synthesized and studied the molecular structure of LC property of chalconyl ester-based homologous series [16–18]. In our previous work, we reported the isomeric and nonisomeric homologues series with chalconyl ester linkage group [19–22]. Recently, we reported newly homologues series based on two phenyl ring and one central chalcone linkage group [23–24]. Chalcone (Ar–CH=CH–CO–Ar)-based compounds are important intermediates in the synthesis of many pharmaceuticals. Some of the chalcone derivatives take a vital role in numerous fields such as crystallography and nonlinear optical properties [25–31], liquid crystalline polymers, and dye industries and in solar cells [32–35]. Presence of  $\Pi$ -bond conjugation in chalconyl group ( $\alpha$ ,  $\beta$ -unsaturated ketone), which leads to a good charge transfer axis and the aromatic rings, act as a tool for a donor and an acceptor [36].

### Experimental

#### Synthesis and method

Alkylation of 4-hydroxy benzaldehyde to give 4-*n*-alkoxy benzaldehyde is carried out by reported method [37]. 4-*n*-hexadecyloxy acetophenone is obtained by alkylation of 4-hydroxy acetophenone by reported method [38]. Thus, the (E)-chalconyl homologue derivatives (C) were prepared by usual established method [39]. Final products were collected and filtered, washed with ethanol solution dried and purified till constant transition temperatures obtained using an polarizing optical microscope (POM) equipped with a heating stage. Alkyl halides, acetone, EtOH, KOH, 4-hydroxy acetophenone, 4-hydroxy benzaldehyde required for synthesis were used as received, except solvents which were dried and distilled prior to use. The synthetic route of the series is mentioned in Scheme 1.

#### Characterization

Representative homologues of a series were characterized by elemental analysis, infrared spectroscopy, <sup>1</sup>H NMR spectra. IR spectra were recorded on Perkin-Elmer spectrum GX, <sup>1</sup>H, and <sup>13</sup>C NMR spectra were recorded on Bruker using CDCl<sub>3</sub> as solvent. Microanalysis



Scheme 1. Synthetic route to the series-1.

was performed on Perkin-Elmer PE 2400 CHN analyzer. Texture images of nematic phase were determined by miscibility method (Table 1). Transition temperature (Table 2) and LC properties (textures) were determined using an optical polarizing microscopy equipped with heating stage. The compound is sandwiched between glass slide and cover slip and the heating and cooling rate is 2°C.

#### Analytical data

C<sub>7</sub> (**Heptyloxy**): IR (KBr):  $v_{max}/cm^{-1}$  2914 (C–H str. of alkane), 2842 (C–H str. of  $-(CH_2-)n$  group of  $-OC_{16}H_{33}$  alkyl chain, 1640 (C=O str. of carbonyl carbon of chalconyl group), 1604 (C=C str. of alkene in chalcone), 999 (C–H bending of alkene), 1178 (C-O str. of ether linkage in side chain), 936 (trans, -CH=CH-) group, 770 polymethylene ( $-CH_2-$ ) of  $-OC_7H_{15}$ , 675 polymethylene ( $-CH_2-$ )*n* of  $-OC_{16}H_{33}$ , IR data confirms the molecular structure of compound C<sub>7</sub>, <sup>1</sup>HNMR: 0.88–0.90 (t, *J* = 8.0 Hz, 6H,  $-CH_3$  of polymethylene  $-C_7H_{15}$  and  $-C_{16}H_{33}$ ), 1.76 (*J* = 7.1 Hz, 4H,  $-OC_7H_{15}$ , and  $-OC_{16}H_{33}$ ), 1.26–1.31 (m, *J* = 7.2 Hz, 34H,  $-CH_2-CH_2-CH_2-$  of  $-OC_7H_{15}$  and  $-OC_{16}H_{33}$ ), 1.76 (*J* = 15.1 Hz, 2H, 34H,  $-OC_7H_{15}$  and  $-OC_{16}H_{33}$ ), 7.59–8.06 (d, *J* = 15.1 Hz, 2H, 2H, 2H).

Sr. No.	Homologue	Texture
1	C <sub>4</sub>	Threaded
2	C <sub>5</sub>	Droplets
3	C <sub>7</sub>	Droplets
4	C <sub>10</sub>	Threaded
5	C <sub>18</sub>	Droplets

Table 1. Texture of nematic phase of  $C_4$ ,  $C_5$ ,  $C_7$ ,  $C_{10}$ , and  $C_{18}$  by miscibility method.

		Transition temperatures in °C						
Sr. No.	R = n-alkyl group	Cr	Smectic		Nematic		lsotropic	
1	C <sub>1</sub>		_	_	_	_	108.0	
2	C'		_	_	_		105.0	
3	C <sub>3</sub>		_	_	_		98.0	
4	$C_{A}^{J}$		_	_	88.0		96.0	
5	$C_5$		62.0	_	78.0		86.0	
6	$C_6$		58.0		74.0		82.0	
7	C <sub>7</sub>		56.0		62.0		68.0	
8	C <sub>8</sub>		54.0		57.0		64.0	
9	C <sub>10</sub>		41.0		49.0		58.0	
10	C <sub>12</sub>		38.0		48.0		52.0	
11	C <sub>14</sub>		48.0		56.0		60.0	
12	C <sub>16</sub>		42.0		54.0		68.0	
13	C <sub>18</sub>	•	36.0	•	44.0	•	62.0	•

Table 2. Transition temperature by POM in °C.

-CH=CH-), 7.24, 8.10-8.14 (4H, J = 8.1 Hz, second para-substituted phenyl ring), 6.94-7.61 (4H, J = 8.0 Hz, first phenyl ring with alkoxy chain). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 164.3, 130.2, 129.2, 129.6, 158.8, 114.9, (Ar-C), 14.1 (-CH<sub>3</sub>), 183.3 (-C=O group), (31.9, 66.2, 31.7, 25.9, 29.6, 29.3, 22.7 (-CH<sub>2</sub>), 145.3, 121.2 (-CH of -olefin). Elemental analysis: calculated for C<sub>38</sub>H<sub>58</sub>O<sub>3</sub>: C, 81.11%; H, 10.32%; O, 8.54%; found: C, 80.98%; H, 10.28%; O, 8.47%.

**C**<sub>10</sub> (**Decyloxy**): IR (KBr):  $v_{max}/cm^{-1}$  2920 (C–H str. of alkane), 2848 (C–H str. of  $-(CH_2-)n$  group of  $-OC_{16}H_{33}$  alkyl chain, 1630 (C=O str. of carbonyl carbon of chalconyl group), 1604 (C=C str. of alkene in chalcone), 1510, 1543 (C=C str. of aromatic ring), 996 (C–H bending of alkene), 1178 (C-O str. of ether linkage), 1286, 1240 (C-O str. of carbonyl (>CO) group), 972 (trans, -CH=CH-) group, 761 polymethylene ( $-CH_2-$ ) of  $-OC_{10}H_{21}$ , 782 polymethylene ( $-CH_2-$ )*n* of  $-OC_{16}H_{33}$ , IR data confirms the molecular structure of compound C<sub>10</sub>, <sup>1</sup>HNMR: 0.89–0.90 (t, *J* = 8.0 Hz, 6H,  $-CH_3$  of polymethylene  $-C_{10}H_{21}$  and  $-C_{16}H_{33}$ ), 1.76 (p, 4H, *J* = 7.1 Hz, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-of  $-OC_{10}H_{21}$  and  $-OC_{16}H_{33}$ ), 1.78 (m, *J* = 7.1 Hz, 38H,  $-CH_2-CH_2-CH_2-CH_2-of <math>-OC_{10}H_{21}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, *J* = 7.1 Hz, 38H,  $-CH_2-CH_3$  of  $-OC_{10}H_{21}$  and  $-OC_{16}H_{33}$ ), 4.06 (t, *J* = 7.1 Hz, 4H,  $-OCH_2-CH_2$ - of  $-OC_{10}H_{21}$ ,  $-OC_$ 

**C**<sub>12</sub> (**Dodecyloxy**): IR (KBr):  $v_{max}/cm^{-1}$  2914 (C−H str. of alkane), 2842 (C−H str. of  $-(CH_2-)n$  group of  $-OC_{16}H_{33}$  alkyl chain, 1620 (C=O str. of carbonyl carbon of chalconyl group), 1608 (C=C str. of alkene in chalcone), 1543 (C=C str. of aromatic ring), 991 (C−H bending of alkene), 1178 (C−O str. of ether linkage), 1288, 1246 (C−O str. of carbonyl (>CO) group), 936 (trans, -CH=CH-) group, 761 polymethylene ( $-CH_2-$ ) of  $-OC_{12}H_{25}$ , 791 polymethylene ( $-CH_2-$ )*n* of  $-OC_{16}H_{33}$ , IR data confirms the molecular structure of compound C<sub>12</sub>, <sup>1</sup>HNMR (CDCl<sub>3</sub>): 0.89 to 0.90 (t, *J* = 8.0 Hz, 6H,  $-CH_3$  of polymethylene  $-C_{12}H_{25}$  and  $-C_{16}H_{33}$ ), 1.80 (*J* = 7.0 Hz, 4H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-GH<sub>2</sub> of  $-OC_{12}H_{21}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_{16}H_{33}$ ), 1.28–1.31 (m, 42H,  $-CH_2-CH_2-CH_3$  of  $-OC_{16}H_{33}$ ), 7.59–8.06 (d, *J* = 15.1 Hz, 2H, -CH=CH-), 7.20, 8.10–8.14 (4H, *J* = 8.1 Hz, parasubstituted second phenyl ring), 6.92–7.63 (4H, *J* = 8.0 Hz, first phenyl ring with alkoxy chain), <sup>13</sup>C NMR (CDCl<sub>3</sub>): 165.3, 158.6, 130.4, 129.8, 129.4, 114.9, 114.1, (Ar-C), 14.1 ( $-CH_3$ ), 31.9, 68.7, 68.4, 29.6, 25.9, 29.6, 29.3, 22.7 ( $-CH_2$ ), 189.3 (-C=O), 145.1, 121.3

(-CH of -olefin). Elemental analysis: calculated for C<sub>43</sub>H<sub>68</sub>O<sub>3</sub>: C, 81.64%; H, 10.75%; O, 7.59%; found: C, 81.56%; H, 10.71%; O, 7.52%.

**C**<sub>14</sub> (**Tetradecyloxy**): IR (KBr):  $v_{max}/cm^{-1}$  2991 (C−H str. of alkane), 2870 (C−H str. of  $-(CH_2-)n$  group of  $-OC_{16}H_{33}$  alkyl chain, 1630 (C=O str. of carbonyl group), 1608 (C=C str. of alkene in chalcone), 1510 (C=C str. of aromatic ring), 991 (C−H bending of alkene), 1178 (C-O str. of ether linkage), 936 (trans, -CH=CH-) group, 791 polymethylene ( $-CH_2-$ ) of  $-OC_{14}H_{29}$ , 804 polymethylene ( $-CH_2-$ )*n* of  $-OC_{16}H_{33}$ , IR data confirms the molecular structure of compound C<sub>14</sub>, <sup>1</sup>HNMR: 0.88–0.90 (t, 6H,  $-CH_3$  of polymethylene  $-C_{14}H_{29}$  and  $-C_{16}H_{33}$ ), 1.79 (p, 4H, CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-of  $-OC_{14}H_{29}$  and  $-OC_{16}H_{33}$ ), 1.29–1.31 (m, 46H,  $-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-G_1-OC_{16}H_{33}$ ), 4.06 (t, 4H,  $-OCH_2-CH_2-G_1-OC_{14}H_{29}$  and  $-OC_{16}H_{33}$ ), 7.59–8.02 (d, *J* = 15.1 Hz, 2H, -CH=CH-), 7.16, 8.10–8.14 (4H, *J* = 8.1 Hz, para-substituted second phenyl ring), 6.94–7.62 (4H, *J* = 8.1 Hz, first phenyl ring with alkoxy chain), <sup>13</sup>C NMR (CDCl<sub>3</sub>): 165.6, 158.6, 130.2, 129.3, 126.8, 120.2, 114.6, 114.3, (Ar-C), 14.1 ( $-CH_3$ ), 31.9, 68.2, 29.6, 25.9, 29.6, 29.3, 22.7 ( $-CH_2$ ), 189.3 (-C=O group), 145.1, 121.4 (-CH of -olefin). Elemental analysis: calculated for C<sub>45</sub>H<sub>72</sub>O<sub>3</sub>: C, 81.81%; H, 10.90%; O, 7.27%; found: C, 80.72%; H, 10.83%; O, 7.22%.

**C**<sub>16</sub> (Hexadecyloxy): IR (KBr):  $v_{max}/cm^{-1}$  2990 (C−H str. of alkane), 2891 (C−H str. of  $-(CH_2-)n$  group of  $-OC_{16}H_{33}$  alkyl chain, 1640 (C=O str. of carbonyl carbon of chalconyl group), 1608 (C=C str. of alkene in chalcone), 1543 (C=C str. of aromatic ring), 981 (C−H bending of alkene), 1178 (C-O str. of ether linkage), 1242 (C-O str. of carbonyl (>C=O) group), 932 (trans, -CH=CH-) group, 712–7.20 (polymethylene ( $-CH_2-$ )*n* of  $-OC_{16}H_{33}$ ), IR data confirms the molecular structure of compound  $C_{16}$ , <sup>1</sup>HNMR: 0.88–0.90 (t, 6H,  $-CH_3$  of polymethylene  $-C_{16}H_{33}$ ), 1.79 (p, 4H, CH<sub>3</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>-of  $-OC_{16}H_{33}$ ), 1.29–1.31 (m, 48H,  $-CH_2-CH_2-CH_2-CH_3$  of  $-OC_{16}H_{33}$ ), 4.06 (t, 4H,  $-OCH_2-CH_2-$  of  $-OC_{16}H_{33}$ ), 7.58–8.02 (d, *J* = 15.1 Hz, 2H, -CH=CH-), 7.16, 8.10–8.14 (4H, *J* = 8.1 Hz, para-substituted second phenyl ring), 6.94–7.61 (4H, *J* = 8.1 Hz, first phenyl ring with alkoxy chain), <sup>13</sup>C NMR (CDCl<sub>3</sub>): 164.7, 158.9, 130.2, 129.3, 126.8, 120.2, 114.6, 114.3, (Ar-C), 14.1 ( $-CH_3$ ), 31.9, 68.2, 29.6, 25.9, 29.6, 29.3, 22.7 ( $-CH_2$ ), 189.3 (189.2 -C=O group), 145.1, 121.5 (-CH of -olefin). Elemental analysis: calculated for  $C_{47}H_{76}O_3$ : C, 81.97%; H, 11.04%; O, 6.97%; found: C, 81.11%; H, 10.97%; O, 6.68%.

**C**<sub>18</sub> (**Octadecyloxy**): IR (KBr):  $v_{max}/cm^{-1}$  2990 (C–H str. of alkane), 2886 (C–H str. of  $-(CH_2-)n$  group of  $-OC_{16}H_{33}$  alkyl chain, 1630 (>C=O str. of carbonyl carbon of chalconyl group), 1610 (C=C str. of alkene in chalcone), 1516 (C=C str. of aromatic ring), 990 (C–H bending of alkene), 1178 (C-O str. of ether linkage), 936 (trans, -CH=CH-) group, 706–761 polymethylene ( $-CH_2-$ ) of  $-OC_{18}H_{37}$  and  $-OC_{16}H_{33}$ , IR data confirms the molecular structure of compound  $C_{18}$ , <sup>1</sup>HNMR: 0.88 (t, 6H,  $-CH_3$  of polymethylene  $-C_{12}H_{25}$  and  $-C_4H_9$ ), 1.79 (p, 10H,  $CH_3-CH_2-CH_2-CH_2-CH_2-G_3$  of  $-OC_{12}H_{25}$  and  $-OC_4H_9$ ), 1.28 (m, 8H  $-CH_2-CH_2-CH_2-of -OC_{12}H_{25}$ ), 1.29–1.31 (q, 8H,  $-CH_2-CH_3$  of  $-OC_{12}H_{25}$  and  $-OC_4H_9$ ), 4.06 (t, 4H,  $-OCH_2-CH_2-$ ), 7.59 (d, *J* = 15.2 Hz, 2H, -CH=CH-), 7.43, 7.28 and 7.83 (4H, *J* = 8.0 Hz, para-substituted second phenyl ring), 7.62 and 6.94, 6.45 (4H, *J* = 8.1 Hz, first phenyl ring with alkoxy chain), <sup>13</sup>C NMR (CDCl<sub>3</sub>): 165.6, 158.7, 130.2, 129.8, 129.2, 130.6, 114.6, 114.3, (Ar-C), 14.1 ( $-CH_3$ ), 31.9, 68.2, 29.6, 25.9, 29.6, 29.3, 22.7 ( $-CH_2$ ), 189.2 (-C=O group), 145.1, 121.3 (-CH of -olefin). Elemental analysis: calculated for  $C_{49}H_{80}O_3$ : C, 82.12%; H, 11.17%; O, 6.70%; found: C, 82.08%; H, 10.98%; O, 6.60%.

#### **Result and discussion**

Here in present article, we have synthesized newly liquid crystalline homologous series based on single chalconyl linking group and hexadecyloxy side chain at tail group with varying left



Figure 1. Phase diagram of series-1.

side alkoxy side chain (-OR) group. In the present investigation, we study the effect of chalconyl linkage group and varying flexibility at left side part on mesomorphism in thirteen newly synthesized compounds. The phase behavior of all new synthesized compounds has been investigated by POM.

*n*-Alkoxybenzaldehyde condensation with 4-hexadecyloxy acetophenone to give  $\alpha$ -4-*n*alkoxy phenyl- $\beta$ -4'-n-hexadecyloxy benzoyl ethylenes. Entire novel homologous series except first three members (C<sub>1</sub> to C<sub>3</sub>) of a series are liquid crystalline (C<sub>4</sub> to C<sub>18</sub>). C<sub>5</sub> to C<sub>18</sub> compounds displayed enantiotropic nematic as well as smectic phase, while in C<sub>4</sub> homologue, it exhibited only monotropically nematic phase. C1 to C3 homologues do not shows liquid crystalline property and directly passes into isotropic mass from solid crystal phase without display LCs property; this is due to presence of short alkyl spacer and short chain length of molecule. The phase diagram of present homologous series were plotted against the transition temperature versus the number of carbon atoms present in *n*-alkyl chain "*R*" of left -OR group. The Cr-N/I, N-I or I-N, and Sm-N transition curves are obtained as shown in Fig. 1, respectively. N-I/I-N transition curve gradually descended up to  $C_{12}$  then increased at C<sub>16</sub> homologue due to the effect of abnormality and then continued descends almost linearly prolonged up to  $C_{18}$  homologue with overall descending tendency. The Cr-M/I transition curve initially falling up to C<sub>12</sub> homologue and then rising at C<sub>14</sub> homologue and then continued to decrease up to last homologue C18. The Sm-N transition curve descends up to C12 homologue and then passing through maxima at  $C_{14}$  homologue and then decreasing at  $C_{18}$ homologue. Odd-even effect is absent in phase behavior of present series. The variations of mesogenic properties from homologue to homologue in the same series are observed with changing the number of carbon atoms presence in left *n*-alkyl chain "*R*" in -OR group and keeping rest of the molecular part unaltered throughout the series.

The condensation of nonmesomorphs *n*-alkoxybenzaldehydes with 4-*n*-hexadecyloxy acetophenone molecule to extends its molecular lengths, polarity and polarizability, rigidity and flexibility, permanent dipole moment across a long molecular axis, intermolecular and lateral attractions, suitable magnitude of dispersion forces, and dipole-dipole interaction. These induce resistivity and misalignment of molecules at a 90° or/and less than 90° angle with a plane of floating surface under the influence of exposed thermal vibrations to maintain floating with statistically parallel orientational order and/or with sliding layered molecular arrangement for different range or ranges of temperatures to facilitate only nematic or smectic plus nematic mesophase formation for  $C_4$  to  $C_{18}$  homologues. However, the missing of any sort of mesophase formation in case of  $C_1$  and  $C_3$  homologues is attributed to their high crystallizing tendencies, which arise from low magnitudes of dispersion forces and also low magnitudes of dipole-dipole interaction. Thus, abrupt breaking of crystal lattices on heating the sample substance takes place and sharply transform into isotropic liquid without passing through liquid crystalline state. However, on cooling condition the same, none of the non-mesomorphic homologues  $C_1$  and  $C_3$  exhibited monotropic mesophase in irreversible manner but the homologues from  $C_4$  to  $C_{18}$  on similar cooling from isotropic state exhibit and reappear to nematic and smectic phases.

Lowering of molecular rigidity by only two benzene cores bonded through single chalconyl bridge group which lowers the numbers of inter-atomic bonds and bond energy, which leads to reflect the magnitudes of ( $\Delta H$ ) enthalpy change of a molecule, and consequently lowers the molecular thermal resistivity toward exposed thermal vibrations. Therefore, the lowering of transition temperatures, thermal stabilities for smectic and nematic as well as mesophase lengths are observed. The terminal intermolecular interactions alternate as the series is ascended. However, if longer *n*-alkyl chains bend and come into line with the molecular long axis, the contribution of each new carbon-carbon bond in alkyl chain to change the polarizability of the molecule in the direction of the long axis is the same, irrespective of whether the carbon number is odd or even. Changing of the terminal substitution by increasing the chain length as result alternation of terminal intermolecular attraction and the N-I temperature should therefore again diminish.

From the texture study of mesophase under the optical polarizing microscope, a typical nematic phase was observed upon heating and cooling condition of compound C<sub>6</sub>. Optical texture was observed for compound C<sub>6</sub> at 74°C given in Fig. 2(a). A needle type texture of SmC phase was observed for compounds C<sub>8</sub>. The texture observed at 54°C mentioned in Fig. 2(b). A droplets type image of nematic mesophase was observed for compound C<sub>12</sub> at 48°C shown in Fig. 2(c). A typical texture image of SmC phase was observed for compound C<sub>16</sub> at 42°C mentioned in Fig. 2(d). No other mesophase transition, except crystallization, was realized on further cooling of compound up to room temperature. All the transition temperatures displayed LCs property at lower temperature. The newly synthesized compound is sandwiched between glass slide and cover slip and the heating and cooling rate is (2°C/min), respectively.

The molecular length of 4-*n*-alkoxy benzaldehyde increases by linking with 4-*n*-hexadecyloxy acetophenone, which upgrades the molecular rigidity and flexibility to suitable and favorable magnitudes of intermolecular cohesion and closeness to induce nematic and smectic mesophase in enantiotropically manner. The mesophase appear enenatiotropically manner in present synthesized compounds. Compound  $C_{18}$  shows smectic as well as nematic mesophase on heating and cooling condition, respectively. Figure 3 signifies the presence needle type of SmC mesophase in  $C_{18}$  homologue at 36°C or room temperature observed in cooling condition

The absence of mesogenic character in  $C_1$  to  $C_3$  homologue is due to the low magnitudes of dispersion forces and dipole-dipole interactions. The changing trend in mesogenic properties from homologue to homologue due to increasing the flexibility of molecule causes by altering *n*-alkyl chain "*R*" of -O*R* group and unexpected status of *n*-alkyl chain or end groups of a molecule. The reverse deviating effect from normal sequence of appearing enantiotropy phase is attributed to the unexpected status of *n*-alkyl chains which affected



**Figure 2.** Optical micrographs of (a) rod-type texture image in nematic phase at 74°C of compound C<sub>6</sub>, (b) SmC phase at 54°C of compound C<sub>8</sub>, (c) nematic droplets observed at 48°C of compound C<sub>12</sub>, and (d) SmC phase at 42°C of compound C<sub>16</sub>.

molecular lengths from homologue to homologue in the same series which alters molecular polarity and polarizability. Some thermometric properties and degree of mesomorphism of presently investigated homologous series-1 compared with structurally similar homologous series-A [40] as mentioned in Fig. 4. In series-1 and series-A, chalconyl central linkage group is common part and disubstituted phenyl ring is present in both series.



**Figure 3.** SmC phase at  $36^{\circ}$ C in C<sub>18</sub> homologue.



Figure 4. Structurally similar series.

Following Table 3 represents the thermometric properties in comparative manner as given under. Thermal stability of Sm-N phase in series-1 is more as compare to series-X and commencement of smecticphase in series-1 at  $C_5$  homologue while in series-A, it's started from  $C_7$  homologue. Thermal stability of N-I phase of series-A is higher than series-1. In series-1,  $C_4$  to  $C_{18}$  homologous displayed nematic mesophase enantiotropically while in series-A,  $C_2$  to  $C_{18}$  homologous shows nematic property in which  $C_2$  to  $C_6$  shows nematic mesophase enantiotropically manner while  $C_7$  to  $C_{18}$  homologous exhibited monotropynematic phase. The total mesophase length of (Sm + N) phase of series-1 is slightly higher than series-A, this is due to the higher chain length and linearity of series-1 as compare to nonlinear series-A.

The exhibition of smectogenic and nematogenic properties from the synthesized chalconyl series-1 is attributed to the optimum magnitudes of dispersion forces and dipole-dipole interactions controlling the suitable magnitudes of anisotropic forces of intermolecular cohesion and closeness to induce smectic plus nematic phase in either reversible or irreversible manner.

Series	Series-1 (–OC <sub>16</sub> H <sub>33</sub> ) (-para)	Series-A (–OC <sub>16</sub> H <sub>33</sub> ) (-meta)
Sm-N or N-Sm or Sm-I	58.0°C	54.2°C
Commencement of smectic phase	(C <sub>5</sub> -C <sub>18</sub> ) C <sub>5</sub>	(C <sub>7</sub> -C <sub>18</sub> ) C <sub>7</sub>
N-I or I-N	69.6	72.6
Commencement of nematic phase	(C <sub>4</sub> -C <sub>18</sub> ) C <sub>4</sub>	(C <sub>2</sub> -C <sub>6</sub> ) C <sub>2</sub>
Mesophase length (Sm $+$ N) in °C	10.0–26.0°C	05.0–21.0°C
	C <sub>8</sub> -C <sub>18</sub>	C <sub>18</sub> -C <sub>4</sub>

Table 3. Thermal stability in °C.



Figure 5. Geometrical shape of series-1 and series-A.

The early or late commencement of smectic and nematic phase is depended upon the extent of noncoplanarity of a molecule.

The early or late commencement of mesophase formation is related with the extent of molecular noncoplanirity with the plane of a floating surface. The para-substituted  $-OC_{16}H_{33}$  (*n*), meta-substituted  $-OC_{16}H_{33}$  (*n*) tail ended *n*-alkoxy groups are almost equally noncoplanar. Therefore, smectic and/or nematicmesophase commences by the difference of one to three homologue. The observed difference can be attributed to the positional difference of tailed *n*-alkoxy-ended groups, which causes difference in molecular polarizability. The observed difference in thermal stabilities for nematic by one or six units is attributed to linear or nonlinear geometrical shape, which is related with the positional status and induced degree of polarizability of *n*-alkoxy tail-ended group for the same homologue whose magnitudes of energy stored ( $\Delta H$ ) in a molecule vary from increasing series. Therefore, the resistivity toward exposed thermal vibrations and their corresponding intensity required different suitable magnitudes of mesophase at different lengths with left increasing side chain (-OR).

Geometrical shape of sereis-1 and series-X are different with respect to right side flexible part of molecule. Series-X is nonlinear as compared to series-1, because of substitution of hexadecyloxy side chain  $(-OC_{16}H_{33})$  on -meta position in series-A, while in series-1 the substitution of hexadecyloxy chain at para position. The geometrical shape of series-1 and series-A mentioned in Fig. 5.

#### Conclusions

Newly synthesized homologous series based on single chalconyl (-CH=CH-CO-) central bridge as linking group with side chain is smectogenic and nematogenic in nature, whose thermal stabilities and the mesophase lengths are lower. Chalconyl group is generally nematogenic and bioactive which is useful for devices to be operated at low temperature or room

temperature, as well as its bioactivity importance. Here, in present article, we have successfully synthesized the homologous series which shows LC properties as lower temperature as present demand. The group efficiency order derived on the basis of (i) thermal stabilities, (ii) commencement of mesophase, and (iii) upper and lower mesophase lengths for smectic and nematic are as under.

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