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The effect of position of octadecyloxy tail on the formation of liquid crystal with chalconyl-ester and chalconyl-vinyl ester series: Comparison with corresponding linkage group

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ABSTRACT

Two series of chalconyl-based liquid crystals which differ from each other in the position of the first linking group have been synthesized and characterized by elemental analyses and spectroscopic techniques such as Fourier transform infrared and proton magnetic resonance magnetic resonance [¹H NMR] spectroscopy. The mesomorphic properties of these compounds were observed by optical polarized light microscopy (POM) and differential scanning calorimetry (DSC). We have synthesized two homologous series viz. 3-(3-(4-(Octadecyloxy) phenyl) acrylonyl) phenyl 3-(4-n-alkoxyphenyl) acrylate (series-1) and 3-(3-(4-(Octadecyloxy) phenyl) acryloyl) phenyl acryloyl) phenyl acryloyl phenyl acryloyl series central linkage group while in series-2 chalconyl-vinyl ester group is present and tail octadecyloxy side chain is common in both homologous series. All the homologous in present series display LC property in enantiotropical manner except first three homologous in both series.

KEYWORDS

Liquid crystal; chalcone; smectic; nematic; enantiotropy



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1. Introduction

Liquid crystals 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 [1-4]. 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 have focus on thermotropic liquid crystals in which, phase transition into liquid crystal phase as temperature changed [5-10]. Liquid crystals in the nematic group are most commonly used in the production of liquid crystal displays (LCD) due to their unique physical properties and wide temperature range [10-14]. 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 [15-18]. Yelamaggad et al. reported the bent-core unsymmetrical dimers in which cholesteryl ester and chalconyl moiety are present, which enhances the biaxiality and chirality of the system [19].

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 α , β -unsaturated functional group in chalcone (-CH=CH-CO-) is responsible for anti-microbial activity, which can be altered depending upon the type of substituent present on the aromatic rings [20-24]. Thus, the objective of the work is to synthesize and study the effect of chalconyl-ester linkage group and geometrical shape on mesomorphism. Vorlander and Dtsch reported bent-core liquid crystals and reported their mesogenic properties [25]. Matsunaga and Miyamoto reported first time on a series of bent-core molecule, as 1,3-phenylene bis[4-(4-n-octyloxyphenyliminomethyl) benzoate] derivatives [26]. In 1996, Niori et al. reported on ferro electricity in a smectic phase formed by bent-shaped Schiff base derivatives in an achiral mesogens [27]. Gorecka et al. reported that chiral nonlinear optic effect shown in achiral bent-core molecules is due to interaction between polarity and chirality [28]. Ros et al. studied that the banana-shaped mesophase synthesization is based on the appropriate combination between rigid bent-core units with terminal side chain [29]. Subala et al. reported that the same homologous series with the same core and increasing number of chain length is responsible in the contribution of the phase sequence $B_6-B_1-B_2$ [30]. Many series of liquid crystalline compounds containing heterocyclic groups have been synthesized due to their usefulness in wide application electrical, optical, biological, and medical field [31,32]. Gopalakrishnan et al. reported chalcone-based single crystals, growth, and comparison of two new enone shifted chalcones and their NLO behavior [33]. Tandel et al. studied the chain chalconyl polymers compound to exhibiting threaded-type nematic phases [34]. Vinyl esters linkage group have been well known for last decades of years, Vora et al. [35] reported that binary mixtures of cinnamate esters exhibit a wide range of smectic and nematic mesophase. Doshi et al. reported homologous series based on chalconyl vinyl ester linkage group [36-40]. Sadashiva et al. [41] reported the synthesis and mesomorphic properties of some ester of *trans*-4-n-alkoxy cinnamic acid and trans-4-n-alkoxy- α -methyl cinnamic acid with branched chain alkyl tails exhibiting ferroelectric and anti-ferroelectric phases. Prajapati et al. studied [42,43] some homologous series consisted of cinnamate linkage group and show its effect on mesomorphic properties of liquid crystalline compounds. The ethylene unit is connecting one part of rigid core with another in calamatic mesogenic molecules.

In this present article, an attempt has been made to synthesize two nonlinear homologous series-1 and series-2. Series-1 has -CH=CH-COO and -CO-CH=CH- linkage group and series-2 has -COO- and -CO-CH=CH- linkage group. However, the terminal (-OC₁₈H₃₇)

group is same in both the present homologous series. Here, in the present study, we compare the effect of linkage group on LC behavior, thermal stability, mesophase length, and commencement of mesophase in present article. Recently, our group reported isomeric and nonisomeric chalconyl ester linking group-based homologous series [44–46]. Group efficiency order and structure relation with mesomorphism will be derived.

2. Experimental

2.1. General

For the synthesis of target chalconyl-ester homologous series, the following materials were used: 4-hydroxy benzoic acid, 4-hydroxy benzaldehyde, Alkyl halides (Lancaster, England), Anhydrous K₂CO₃, 3-hydroxy acetophenone was purchased from (SRL, India), DCC (Dicyclohexyl carbodimide) was purchased from Fluka Chemie (Switzerland), Dimethyl amino pyridine DMAP (4,4'-dimethylamino pyridine) was obtained from Finar chemicals (India), Dichloro methane, Ethanol, Acetone required for synthesis were used as received except solvents that were dried and distilled prior to use. The molecular structures of the target products and the intermediates were confirmed by spectroscopic analysis and elemental analysis. Representative homologous series were characterized by elemental analysis, Infrared spectroscopy, ¹H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX, ¹HNMR spectra were recorded on Bruker using CDCl₃ as solvent. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer. Texture image of some homologous for nematic phase was determined by miscibility method. Transition temperature and LC properties (Textures) were determined using an optical polarizing microscopy equipped with heating stage and digital camera. Decomposition temperatures were determined by using Shimadzu (DSC) differential Scanning Calorimeter with a heating rate of 5°C to 10.0°C min⁻¹. Thermodynamic quantities enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed. The mesophase and transition temperatures and enthalpies for all chalconyl-ester-based liquid crystals were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

2.2. Synthesis of series-1 and series-2 compounds

2.2.1. Synthesis of 4-n-alkoxy benzoic acid (C) and 4-n-alkoxy cinnamic acid (A)

4-n-alkoxy benzoic acid and 4-n-alkoxy cinnamic acid were prepared by method reported by Dave and Vora [47].

2.2.2. Synthesis of 4-n-alkoxy benzaldehyde

4-n-Alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with corresponding n-alkyl bromides (1 equiv.) in the presence of Anhydrous K_2CO_3 (1 equiv.) and dry acetone as a solvent [48].

2.2.3. Synthesis of 1-(3-hydroxyphenyl)-3-(4-(octadecyloxy)phenyl)prop-2-en-1-one (B)

Chalcone (B) was prepared by usual established method [49]. (Yield: 72%, m.p. 86°C, IR (KBr): v_{max} / cm⁻¹ 3390 (-OH str.-bonded), 3079–3120 (-CH str. aliphatic alkyl group), 1660 (-C=O, group), 1580–1620 (-C=C-) aromatic, 1205–1280 (-OCH₂- ether linkage), 960 (Trans alkene), 750–780 (-meta substituted phenyl ring).

2.3.4. General procedure for the synthesis of α -3-(4'-n-alkoxy-cinnamoyloxy) benzoyl- β -4"-octadecyloxy phenyl ethylene (series-1)

The chalconyl ester based compound which had been prepared by the esterification of the appropriate 4-n-alkoxy cinnamic acid (A) (2.02 mmol) and chalcone (C) (0.246 g, 2.02 mmol), dicyclohexyl carbodiimide (DCC) (0.457 g, 2.22 mmol), and dimethylaminopyridine (DMAP) in catalytic amount (0.002 g, 0.2 mmol) in dry CH_2Cl_2 (DCM) (30 mL) was stirred at room temperature for 48 hr. The white precipitate of DCU was obtained, which was isolated by filtration and discarded, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with dichloromethane, recrystallization from methanol: chloroform as eluent (2:3) until constant transition temperatures were observed [50].

C₅ (Series-1): IR (KBr): v_{max}/cm^{-1} 740 Polymethylene group of (-CH₂-)n of -OC₅H₁₁, 648 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 810(-C-H- def. m di-substituted), 972 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in -(CH₂)n chain, 1381 and 1442 (-C-H- def. in CH₂), 1504 (-C=C-)str, 1658 (-C=O group), 1724 (-COO- ester group), 2854 and 2924(-C-H str in CH₃), 972 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88–0.90 (t, J = 7.2 Hz, 6H, -CH₃ of $-OC_5H_{11}$ and $-OC_{18}H_{37}$), 1.26 (m, n-poly methylene groups of $-OC_{18}H_{37}$), 1.31 (q, 8H, $-CH_2$ of $-OC_5H_{11}$ and $-OC_{18}H_{37}$), 1.29 (P, J = 8.1 Hz, 10 H of $-OC_5H_{11}$ and $-OC_{18}H_{37}$ group), 1.75 (m, npoly methylene groups of $-OC_5H_{11}$), 3.5–3.6 (s, $-OCH_2-CH_2-of-OC_{18}H_{37}$), 4.06 (t, J = 6.1 Hz, 6H, $-O-CH_2-CH_2$ - of $-OC_5H_{11}$ and $-OC_{18}H_{37}$), 7.54–7.56 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 8.30-8.32 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.62-7.64 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.30 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.91 and 7.60–7.62 (d, J = 8.2 Hz, 4H, left side phenyl ring), 7.71 and 8.56, 8.41 (d, J = 7.8 Hz, 4H, central phenyl ring), 7.61 and 6.95–6.92 (d, J = 8.4 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C47H62O5: C, 79.88; H, 8.78; O, 11.33; found: 79.82; H, 8.70; O, 11.24%.

C₇ (Series-1): IR (KBr): v_{max}/cm^{-1} 740 Polymethylene group of (-CH₂-)n of -OC₇H₁₅, 648 Polymethylene group of (-CH2-)n of -OC18H37, 810(-C-H- def. m di-substituted), 972 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in -(CH₂)n chain, 1381 and 1442 (-C-H- def. in CH₂),1504 (-C=C-)str, 1658 (-C=O group), 1724 (-COO- ester group), 2854 and 2924(-C-H str in CH₃), 972 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88–0.90 (t, J = 7.2 Hz, 6H, -CH₃ of -OC₇H₁₅ and -OC₁₈H₃₇), 1.26 (m, n-poly methylene groups of $-OC_{18}H_{37}$), 1.31 (q, 8H, $-CH_2$ of $-OC_7H_{15}$ and -OC₁₈H₃₇), 1.29 (P, J = 8.1 Hz, 10 H of -OC₇H₁₅ and -OC₁₈H₃₇ group), 1.75 (m, npoly methylene groups of $-OC_7H_{15}$), 3.5–3.6 (s, $-OCH_2-CH_2$ - of $-OC_{18}H_{37}$), 4.06 (t, J =7.6 Hz, 6H, $-O-CH_2-CH_2$ of $-OC_7H_{15}$ and $-OC_{18}H_{37}$), 7.54–7.56 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 8.30-8.32 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.62-7.64 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.30 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.91 and 7.60-7.62 (d, J = 8.2 Hz, 4H, left side phenyl ring), 7.71 and 8.56, 8.42 (d, J = 7.6 Hz, 4H, central phenyl ring), 7.60–7.61 and 6.95–6.92 (d, J = 8.4 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C44H58O5: C, 79.89; H, 9.23; O, 10.86; found: 79.12; H, 9.10; O, 10.80%.

C₁ (Series-1): IR (KBr): ν_{max}/cm^{-1} 740 Polymethylene group of (-CH₂-)n of -OCH₃, 648 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 810(-C-H- def. m di-substituted), 972 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in -(CH₂)n chain, 1381 and 1442 (-C-H- def. in CH₂), 1504–1560 (-C=C-)str, 1658 (-C=O group),

1730 (-COO- ester group), 2854 and 2990 (-C-H str in CH₃), 932 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88–0.90 (t, J = 7.2 Hz, 6H, -CH₃ of -OCH₃ and -OC₁₈H₃₇), 1.26 (m, n-poly methylene groups of -OC₁₈H₃₇), 1.31 (q, 8H, -CH₂ of -OC₅H₁₁ and -OC₁₈H₃₇), 1.29 (P, J = 8.1 Hz, 10 H of -OCH₃ and -OC₁₈H₃₇ group), 1.75 (m, n-poly methylene groups of -OCH₃), 3.5–3.6 (s, -OCH₂-CH₂- of -OC₁₈H₃₇), 4.06 (t, J = 7.6 Hz, 6H, -O-CH₂-CH₂- of -OCH₃ and -OC₁₈H₃₇), 7.54–7.56 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 8.30–8.32 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.62–7.64 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.30 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94–6.91 and 7.60–7.62 (d, J = 8.2 Hz, 4H, left side phenyl ring), 7.71 and 8.56, 8.41 (d, J = 7.6 Hz, 4H, central phenyl ring), 7.61 and 6.95–6.92 (d, J = 8.4 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₄₃H₅₆O₅: C, 79.14; H, 8.58; O, 12.26; found: 79.04; H, 8.51; O, 12.20%.

C₂ (Series-1): IR (KBr): v_{max}/cm^{-1} 740 Polymethylene group of (-CH₂-)n of -OC₂H₅, 648 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 810(-C-H- def. m di-substituted), 972 (-C-H- def. hydrocarbon), 1044 (-C-O-) str, 1381 and 1234, 1158 (-C-O str in -(CH₂)n chain, 1381 and 1450 (-C-H- def. in CH₂), 1510 (-C=C-)str, 1658 (-C=O group), 1740 (-COO- ester group), 2854 and 2991(-C-H str in CH₃), 962 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88-0.90 (t, *J* = 7.1 Hz, 6H, -CH₃ of -OC₂H₅ and -OC₁₈H₃₇), 1.26 (m, n-poly methylene groups of -OC₁₈H₃₇), 1.31 (q, 8H, -CH₂ of -OC₂H₅ and -OC₁₈H₃₇), 1.29 (P, *J* = 8.1 Hz, 10 H of -OC₂H₅ and -OC₁₈H₃₇), 4.06 (t, *J* = 7.6 Hz, 6H, -O-CH₂-CH₂-of -OC₂H₅ and -OC₁₈H₃₇), 7.54-7.56 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 8.30-8.32 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 7.62-7.64 (d, *J* = 15.2 Hz, 1H, -CH=CH-COO-), 6.30 (d, *J* = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.90 and 7.60-7.62 (d, *J* = 8.2 Hz, 4H, left side phenyl ring), 7.71 and 8.56, 8.42 (d, *J* = 7.6 Hz, 4H, central phenyl ring), 7.61 and 6.95-6.92 (d, *J* = 8.4 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₄₄H₅₈O₅: C, 79.27; H, 8.70; O, 12.01; found: 79.21; H, 8.62; O, 11.90%.

C₁₂ (**Series-1**): IR (KBr): v_{max}/cm^{-1} 740 Polymethylene group of (-CH₂-)n of -OC₁₂H₂₅, 648 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 810(-C-H- def. m di-substituted), 972 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in -(CH₂)n chain, 1381 and 1442 (-C-H- def. in CH₂), 1504 (-C=C-)str, 1658 (-C=O group), 1724 (-COO- ester group), 2854 and 2924 (-C-H str in CH₃), 972 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88-0.90 (t, *J* = 6.2 Hz, 6H, -CH₃ of -OC₁₂H₂₅ and -OC₁₈H₃₇), 1.26 (m, n-poly methylene groups of -OC₁₈H₃₇), 1.31 (q, 8H, -CH₂ of -OC₁₂H₂₅ and -OC₁₈H₃₇), 1.29 (P, *J* = 8.1 Hz, 10 H of -OC₁₂H₂₅ and -OC₁₈H₃₇ group), 1.75 (m, n-poly methylene groups of -OC₁₂H₂₅ of -OC₁₂H₂₅), 3.5-3.6 (s, -OCH₂-CH₂- of -OC₁₈H₃₇), 4.06 (t, *J* = 7.6 Hz, 6H, -O-CH₂-CH₂- of -OC₅H₁₁ and -OC₁₈H₃₇), 7.54-7.56 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 8.30-8.31 (d, *J* = 15.4 Hz, 1H, -CO-CH=CH-), 7.62-7.64 (d, *J* = 15.2 Hz, 1H, -CH=CH-COO-), 6.30 (d, *J* = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.91 and 7.60-7.62 (d, *J* = 8.2 Hz, 4H, left side phenyl ring), 7.71 and 8.56, 8.41 (d, *J* = 7.6 Hz, 4H, central phenyl ring), 7.61 and 6.95-6.92 (d, *J* = 8.4 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₅₄H₇₈O₅: C, 80.39; H, 9.67; O, 9.67; found: 80.30; H, 9.58; O, 9.62%.

C₁₄ (Series-1): IR (KBr): v_{max}/cm^{-1} 740 Polymethylene group of (-CH₂-)n of -OC₁₄H₂₉, 648 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 812 (-C-H- def. m di-substituted), 972 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1281 and 1230, 1159 (-C-O str in -(CH₂)n chain, 1381 and 1440 (-C-H- def. in CH₂), 1534 (-C=C-)str, 1650 (-C=O group), 1734 (-COO- ester group), 2854 and 2921 (-C-H str in CH₃), 962 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88-0.90 (t, *J* = 7.2 Hz, 6H, -CH₃ of -OC₅H₁₁ and -OC₁₈H₃₇), 1.26 (m, n-poly methylene groups of -OC₁₈H₃₇), 1.31 (q, 8H, -CH₂ of -OC₅H₁₁ and -OC₁₈H₃₃),

1.29 (P, J = 8.1 Hz, 10 H of $-OC_{14}H_{11}$ and $-OC_{18}H_{37}$ group), 1.75 (m, n-poly methylene groups of $-OC_5H_{11}$), 3.5–3.6 (s, $-OCH_2-CH_2$ - of $-OC_{16}H_{33}$), 4.06 (t, J = 7.6 Hz, 6H, $-O-CH_2-CH_2$ - of $-OC_{14}H_{29}$ and $-OC_{18}H_{37}$), 7.54–7.56 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 8.30–8.32 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.62–7.64 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.32 (d, J = 15.1 Hz, 1H, -CH=CH-COO-), 6.94–6.91 and 7.60–7.62 (d, J = 8.2 Hz, 4H, left side phenyl ring), 7.71 and 8.56, 8.41 (d, J = 7.4 Hz, 4H, central phenyl ring), 7.60–7.61 and 6.95–6.92 (d, J = 8.4 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for $C_{56}H_{82}O_5$: C, 80.57; H, 9.83; O, 9.59; found: 80.12; H, 9.78; O, 9.50%.

2.3.5. General procedure for the synthesis of α -3-(4'-n-alkoxy benzoyloxy) benzoyl- β -4"-octadecyloxy phenyl ethylene (series-2)

The chalconyl ester based compound which had been prepared by the esterification of the appropriate 4-n-alkoxy benzoic acid (A) (2.02 mmol) and chalcone (C) (0.246 g, 2.02 mmol), dicyclohexylcarbodiimide (DCC) (0.457 g, 2.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.002 g, 0.2 mmol) in dry CH_2Cl_2 (DCM) (30 mL) was stirred at room temperature for 48 hr. The white precipitate of DCU is obtained, which was isolated by filtration and discarded, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with dichloromethane, recrystallization from methanol: chloroform (2:3) until constant transition temperatures were observed [50].

C₅ (Series-2): IR (KBr): v_{max}/cm^{-1} 731 Polymethylene group of (-CH₂-)n of -OC₅H₁₁, 648 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 810(-C-H- def. m di-substituted), 970 (-C-H- def. hydrocarbon), 1064 (-C-O) str, 1381 and 1230, 1157 (-C-O str in -(CH₂-)n chain, 1381 and 1442 (-C-H- def. in CH₂), 1504-1510 (-C=C-)str, 1650 (-C=O group), 1730 (-COO- ester group), 2854 and 2924 (-C-H str in CH₃), 940 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88-0.90 (t, *J* = 7.8 Hz, 6H, -CH₃ of -OC₅H₁₁ and -OC₁₈H₃₇), 1.26-1.29 (m, 28H, -CH₂ of -OC₅H₁₁ and -OC₁₈H₃₇), 1.76 (m, n-poly methylene groups of -OC₅H₁₁ and -OC₁₈H₃₇), 1.43 (t, *J* = 7.1 Hz, 3H, -OC₁₈H₃₇), 1.31 (q, *J* = 7.6 Hz, 4H, -OC₅H₁₁ and -OC₁₈H₃₇), 4.06 (t, *J* = 7.6 Hz, 6H, -O-CH₂-CH₂- of -OC₅H₁₁ and -OC₁₈H₃₇), 7.54-7.56 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 8.30-8.32 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 7.14-8.12 (d, *J* = 8.4 Hz, 4H, left side phenyl ring), 7.67-7.82, 8.01 (d, *J* = 8.2 Hz, 4H, central phenyl ring), 6.95-7.64 (d, *J* = 7.8 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₄₅H₆₂O₅: C, 79.17; H, 9.99; O, 11.73; found: C, 79.12; H, 8.90; O, 11.72%.

C₈ (Series-2): IR (KBr): v_{max}/cm^{-1} 728 Polymethylene group of (-CH₂-)n of -OC₈H₁₇, 647 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 812 (-C-H- def. m di-substituted), 971 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in -(CH₂-)n chain, 1381 and 1442 (-C-H- def. in CH₂), 1508–1510 (-C=C-)str, 1650 (-C=O group), 1730 (-COO- ester group), 2850 and 2990 (-C-H str in CH₃), 960 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88–0.90 (t, *J* = 7.8 Hz, 6H, -CH₃ of -OC₈H₁₇ and -OC₁₈H₃₇), 1.26–1.29 (m, 32H, -CH₂ of -OC₈H₁₇ and -OC₁₈H₃₇), 1.76 (m, 4H, n-poly methylene groups of -OC₈H₁₇ and -OC₁₈H₃₇), 1.43 (t, *J* = 7.1 Hz, 3H, -OC₁₈H₃₇), 4.06 (t, *J* = 7.6 Hz, 6H, -O-CH₂-CH₂- of -OC₈H₁₇ and -OC₁₈H₃₇), 7.54–7.56 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 8.30–8.32 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 7.14–8.12 (d, *J* = 8.4 Hz, 4H, left side phenyl ring), 7.67–7.82, 8.01 (d, *J* = 8.2 Hz, 4H, central phenyl ring), 6.94–7.64 (d, *J* = 7.8 Hz, 4H, terminal phenyl ring), elemental anal-ysis: calculated for C₄₈H₆₈O₅: C, 79.55; H, 9.39; O, 11.04; found: C, 79.48; H, 9.34; O, 10.94%.

C₁₀ (Series-2): IR (KBr): $v_{\text{max}}/\text{cm}^{-1}$ 718 Polymethylene group of (−CH₂-)n of −OC₁₀H₂₁, 646 Polymethylene group of (−CH₂-)n of −OC₁₈H₃₇, 810(−C−H− def. m di-substituted), 971 (−C−H− def. hydrocarbon), 1064 (−C−O−) str, 1381 and 1230, 1157 (−C−O str in −(CH₂-)n chain, 1381 and 1442 (−C−H− def. in CH₂), 1510 (−C=C−)str, 1630 (−C=O group), 1730 (−COO− of ester group), 2834 and 2984 (−C−H str in CH₃), 960 (trans, −CH=CH−) group, ¹H NMR (CDCl₃): 0.88−0.90 (t, *J* = 7.8 Hz, 6H, −CH₃ of −OC₁₀H₂₁ and −OC₁₈H₃₇), 1.26−1.29 (m, 36H, −CH₂ of −OC₁₀H₂₁ and −OC₁₈H₃₇), 1.76 (m, 4H, n-poly methylene groups of −OC₁₀H₂₁ and −OC₁₈H₃₇), 1.43 (t, *J* = 7.2 Hz, 6H, −OC₁₈H₃₇), 4.06−4.10 (t, *J* = 7.6 Hz, 6H, −O−CH₂−CH₂− of −OC₁₀H₂₁ and −OC₁₈H₃₇), 7.54−7.56 (d, *J* = 15.6 Hz, 1H, −CO−CH=CH−), 8.30−8.32 (d, *J* = 15.6 Hz, 1H, −CO−CH=CH−), 7.14−8.12 (d, *J* = 8.4 Hz, 4H, left side phenyl ring), 7.66−7.82, 8.01 (d, *J* = 8.2 Hz, 4H, central phenyl ring), 6.95−7.64 (d, *J* = 7.8 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₅₀H₇₂O₅: C, 79.78; H, 9.57; O, 10.25; found: C, 79.72; H, 9.48; O, 10.18%.

C₁₂ (Series-2): IR (KBr): v_{max}/cm^{-1} 722 Polymethylene group of (−CH₂-)n of −OC₁₂H₂₅, 648 Polymethylene group of (−CH₂-)n of −OC₁₈H₃₇, 812 (−C−H− def. m di-substituted), 970 (−C−H− def. hydrocarbon), 1064 (−C−O−) str, 1381 and 1281, 1157 (−C−O str in −(CH₂-)n chain, 1381 and 1442 (−C−H− def. in CH₂), 1504−1510 (−C=C−)str, 1630 (−C=O group), 1740 (−COO−, of ester group), 2854 and 2924 (−C−H str in CH₃), 940 (trans, −CH=CH−) group, ¹H NMR (CDCl₃): 0.88−0.90 (t, *J* = 7.8 Hz, 6H, −CH₃ of −OC₁₂H₂₅ and −OC₁₈H₃₇), 1.26−1.29 (m, 40H, −CH₂ of −OC₁₂H₂₅ and −OC₁₈H₃₇), 1.76 (m, 4H, n-poly methylene groups of −OC₁₂H₂₅ and −OC₁₈H₃₇), 1.42 (t, *J* = 7.2 Hz, 6H, −OC₁₂H₂₅ and −OC₁₈H₃₇), 1.31 (q, *J* = 7.6 Hz, 4H, −OC₁₂H₂₅ and −OC₁₈H₃₇), 4.06−4.10 (t, *J* = 7.6 Hz, 6H, −O−CH₂−CH₂−of −OC₅H₁₁ and −OC₁₈H₃₇), 7.54−7.56 (d, *J* = 15.6 Hz, 1H, −CO−CH=CH−), 8.30−8.32 (d, *J* = 15.6 Hz, 1H, −CO−CH=CH−), 7.14−8.12 (d, *J* = 8.4 Hz, 4H, left side phenyl ring), 7.67−7.82, 8.02 (d, *J* = 8.2 Hz, 4H, central phenyl ring), 6.96−7.64 (d, *J* = 7.8 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₅₂H₇₆O₅: C, 80.00; H, 9.75; O, 10.25; found: C, 79.92; H, 9.60; O, 10.14%.

C₁₈ (Series-2): IR (KBr): v_{max}/cm^{-1} 648–680 Polymethylene group of (-CH₂-)n of -OC₁₈H₃₇, 812 (-C-H- def. m di-substituted), 960 (-C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in -(CH₂-)n chain, 1381 and 1442 (-C-H- def. in CH₂), 1504–1560 (-C=C-)str, 1630 (-C=O group), 1760 (-COO- ester group), 2854 and 2990 (-C-H str in CH₃), 930 (trans, -CH=CH-) group, ¹H NMR (CDCl₃): 0.88–0.90 (t, *J* = 7.8 Hz, 6H, -CH₃ of -OC₁₈H₃₇), 1.26–1.29 (m, 52H, -CH₂ of -OC₁₈H₃₇), 1.76 (m, 4H, n-poly methylene groups of -OC₁₈H₃₇), 1.43 (t, *J* = 7.1 Hz, 6H, -OC₁₈H₃₇), 1.31 (q, *J* = 7.6 Hz, 4H, -OC₁₈H₃₇), 4.06–4.10 (t, *J* = 7.8 Hz, 6H, -O-CH₂-CH₂- of -OC₁₈H₃₇), 7.54–7.56 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 8.30–8.31 (d, *J* = 15.6 Hz, 1H, -CO-CH=CH-), 7.14–8.12 (d, *J* = 8.4 Hz, 4H, left side phenyl ring), 7.67–7.82, 8.02 (d, *J* = 8.2 Hz, 4H, central phenyl ring), 6.96–7.64 (d, *J* = 7.8 Hz, 4H, terminal phenyl ring), elemental analysis: calculated for C₅₈H₈₈O₅: C, 80.55; H, 10.18; O, 9.25; found: C, 79.92; H, 10.12; O, 9.14%.

3. Result and discussion

3.1. POM investigation

In order to investigate the influence of the central linkage and terminal substituted octadecyloxy $(-OC_{18}H_{37})$ tail group on the mesophase behavior of liquid crystalline compounds, we

		Transition temperatures in °C							
Sr. no	R = n-alkyl group	Cr	Smectic		Nematic		lsotropic		
1	C1		-	_	_	_	134.0		
2	C,		_	_	_	_	130.0		
3	C ₃	•	—	—	—	—	126.0		
4	C_{4}^{3}			_	84.0	_	109.0		
5	C_5	•	—	—	86.0	•	106.0		
6	C ₆			•	80.0		100.0		
7	C ₇			•	96.0		102.0		
8	C ₈	•	—	•	90.0	•	104.0		
9	C ₁₀	•	68.0	•	88.0	•	101.0		
10	C ₁₂		69.0	•	81.0		98.0		
11	C ₁₄		78.0	•	82.0		96.0		
12	C ₁₆		77.0	•	84.0		94.0		
13	C ₁₈	•	65.0	•	80.0	•	92.0	•	

Table 1. Transition temperature in °C by POM (series-1).

have synthesized and studied the effect of linking group as well as the effect of alkyl aliphatic chain length with rigid core such as benzene ring present in two homologous series. In the present article, we have prepared 13 homologous (C_1 to C_8 , C_{12} , C_{14} , C_{16} , C_{18}) in both series. In series-1, compounds C_4 to C_8 show only an enantiotropic nematic mesophase, while in higher homologous C_{10} , C_{12} , C_{14} , C_{16} , C_{18} show smectic as well as nematic mesophase enantiotropical manner. Odd–even effect has been observed in Sm-N, N-I transition temperature at C_6 to C_7 homolog in series-1. In series-2, mesophase commences from C_4 to C_{18} in which C_4 to C_{18} show nematic phase while C_5 to C_{10} exhibit enantiotropic smectic as well as nematic mesophase. The transition temperatures of series-1, -2 are shown in Tables 1 and 2.

 C_1 to C_3 homologous in both series-1 and series-2 does not show LC phase due to the high crystallinity of compounds. The nonmesomorphicity of C_1 , C_2 , C_3 homolog is attributed to the low magnitudes of intermolecular dispersion forces and low magnitudes of dipole–dipole interactions leading to high crystallizing tendency, which causes abrupt breaking of crystal lattices due to unsuitable and unfavorable magnitudes of anisotropic forces of intermolecular attractions. Thus, irregular breaking of crystal lattices suddenly takes place at relatively higher temperature. Thus, crystalline solid state is directly converted into isotropic phase without showing any LC properties.

				es in °C				
Sr. no	R = n-alkyl group	Cr	Sme	ctic	Nem	atic	lsotrop	oic
1	C ₁		_	_	_	_	130.0	
2	C,		_	_	_	_	126.0	
3	C_3					_	114.0	
4	C_{A}				89.0	_	108.0	
5	C_{5}		66.0	—	80.0		96.0	
6	C ₆		57.0		77.0		92.0	
7	C_7		69.0	-	84.0	•	98.0	
8	C ₈		68.0	-	80.0	•	93.0	
9	C ₁₀		62.0		74.0		89.0	
10	C ₁₂				81.0		90.0	
11	C ¹²				79.0		94.0	
12	C ₁₆				78.0		100.0	
13	C ₁₈	•		•	84.0	•	98.0	

Table 2. Transition temperature in °C by POM (series-2).



Figure 1. Phase diagram of series-1.

Transition curves Cr-I/M, Sm-N, and N-I are plotted against the number of carbon atoms present in n-alkyl chain versus transition temperatures by linking like or related transition points; as depicted in a phase diagrams shown in Figures 1 and 2. In Figure 1, Cr-I/M transition curve initially falls up to C_4 and rises at C_5 and falling to C_6 and then rises to C_7 homolog and then continued to falling at C_{10} and rising at C_{14} and continued to descend up to C_{18} homolog with overall descending tendency. In Cr-I/M curve, odd–even effect is present at C_5 and C_7 homolog. Sm-N transition curve starts falling and rises at C_7 homolog due to odd–even effect and then gradually decreasing with increasing alkyl chain in alkoxy group.

In Figure 2, Cr-I/M transition curve initially falls at C₆ homolog then gradually increases due to exhibition of odd–even effect at C₇ and then continued to falling up to last C₁₈ homolog. Sm-N transition curves descend initially up to C₆ homolog and rise at C₇ homolog because



Figure 2. Phase diagram of series-2.



Figure 3. Textures of compounds of series-1 observed between cross polarizers: (a) Sm C phase of C_{10} at 68°C; (b) Sm C phase of C_{14} at 78°C; (c) nematic phase of C_{16} at 84°C; (d) Blue phase of C_{18} at 80°C.

of exhibition of odd–even parity and falling at C_{10} homolog then continued to rising up to C_{12} homolog with slight decrease in magnitudes and reaching maxima at C_{18} homolog due to its abnormality. N-I transition curves descend at C_6 homolog and then ascend to C_7 homolog and continued decreasing at C_{10} homolog and increase up to C_{18} homolog.

The exhibition of smectic mesophase in C_5 homolog indicates the presence of lamellar packing of molecules in the crystal lattices of rigid crystals, which maintains sliding layered molecular arrangement in floating condition under the influence of exposed thermal vibrations, which causes the formation of smectogenic mesophase in enantiotropic manner.

The crystalline compounds sandwiched between the glass slide and coverslip were heated to the isotropic state, and heating and cooling rate ($2^{\circ}C \min^{-1}$), respectively, and observing mesophase texture images are shown in Figures 3 and 4. Textures of the compounds of series-1 are shown in Figure 3. Compound C₁₀ formed the SmC phase observed at 68°C on heating condition, which was further confirmed by DSC analysis. Compound C₁₄ exhibited a texture of SmC mesophase at 78°C upon cooling condition. Compound C₁₆ displayed nematic mesophase image at 84°C on heating condition. Compound C₁₈ formed a blue phase texture image at 80°C during heating and cooling conditions and it was confirmed by DSC measurement upon heating and cooling trace.

Textures of the compounds of series-2 are shown in Figure 4. Compound C_5 formed the SmC phase observed at 66°C on heating condition and cooling temperature, and by rising the temperature up to 80°C nematic phase is appeared, which was further confirmed by



Figure 4. Textures of compounds of Series-2 observed between cross polarizers: (a) Sm C phase of C_5 at 66°C; (b) Sm C phase of C_6 at 57°C; (c) Sm C phase of C_{10} at 62°C; (d) schlieren texture of C_{16} at 78°C.

DSC analysis. Compound C_6 exhibited a broken fan type texture of SmC mesophase at 57°C upon heating condition. Compound C_{10} formed texture image of SmC mesophase at 62°C on heating condition. Compound C_{16} exhibited schlieren type texture image at 80°C during heating and cooling conditions and it was confirmed by DSC measurement. In addition, we conclude that the mesophase appeared in series-1 and series-2 during heating and cooling condition, respectively.

Table 3 shows the comparison of the Sm-N and N-I thermal stabilities and mesophase length of series-1, -2. Commencement of smectic phase in series-2 is from C_5 homolog while it late commences in C_{10} homolog in series-1. The smectic mesophase range of compounds in series-2 is 5°C lower than the compounds in series-1. While the nematic mesophase range of compounds in series-1 is 3°C lower than the compounds in series-2. Gray explained that increase in the breadth of the molecules reduces both the nematic and smectic thermal stabilities [51]. Series-1 and series-2 were synthesized by various route shown in Schemes 1 and 2, structure-wise both the series differ at first linking group and second linking group while terminal hexadecyloxy chain is same in both series. We have studied comprehensively

· ·		
Series	Series-1	Series-2
Sm-I or Sm-N or N-Sm commencement of smectic phase	83.0 (C ₁₀ - C ₁₈) C ₁₂	79.0 (C ₅ — C ₈ /C ₁₀) C ₅
N-I or I-N commencement of nematic	100.1 (C ₄ — C ₁₈) C ₄	104.5 (C ₄ - C ₁₈) C ₄
Total mesophase length	04.0°C to 20.0°C C ₁₄ C ₁₀	9.0°C to 35.0°C C $_{12}$ C $_{6}$

Table 3. Thermal stability comparison of Sm-N and N-I in series-1, -2.





Scheme 1. Synthetic route of A, B, and C intermediate.

the effect of linking group as well as alkyl aliphatic chain present in left alkoxy side chain and flexibility due to terminal side chain to form mesogens. It has been proven that length altering of the alkyl chain affects LC property. Hence, we have observed the presence of vinyl carboxy (-CH=CH-COO-) linkage group in series-1. Thus, the resultant non-coplanarity, due to twist received on account of the bumping of the oxygen and hydrogen atoms into the nonbonded hydrogen atoms of the adjacent benzene rings. While in absence of -COO- group in series-2 in place of -CH=CH-COO- central bridge effectively contributes to molecular rigidity and flexibility due to decrease in length by the absence of -CH=CH- group and increases suitable magnitudes of intermolecular end to end attractions and closeness. Thus, the thermal stability of nematic phase is highest as compared to series-1. The late commencement of smectic phase in series-1 may be due to weakening of the lateral attractions because of the disproportionate length to breadth ratio. Comparatively, the commencements of smectic phase early in series-2 either lateral to terminal attractions maintain the propionate molecular force or the lateral attractions predominate over the terminal attractions. Thermal stability of smectic phase in series-1 is little higher than series-2, due to involving conjugated double bond (-Ch=CH-), which increases molecular rigidity more than -COO- central bridge. Therefore,

Step-1





Scheme 2. Synthetic route of target compounds of series-1 and series-2.

the stabilization of the smectic phase for series-1 is little more than series-2, due to molecular length, and long chain can obviously be attributed to extent of molecular non-coplanarity maintained favorably to facilitate and weakening of the terminal intermolecular interactions.



Figure 5. DSC curve of the compound. (a) C_{10} homolog (Series-1), (b) C_7 homolog (series-1), (c) C_{12} homolog (series-2), and (d) C_6 homolog (series-2).

Homologous or Comp.	Transition	Heating scan (°C)	Cooling scan (°C)	ΔH (-Jg ⁻¹)	ΔH (J g ⁻¹)	$\Delta S \ (J g^{-1} k^{-1})$	$\Delta S \over (J g^{-1} k^{-1})$
C ₁₀	Cr-SmC SmC-N N-I	60.01 79.28	62.92 87.21	3.10 37.91 12 18	4.82 23.67	0.0093 0.1076 0.0339	0.0143 0.0657
C ₇	Cr-N N-I	95.78 >105.12	100.01	40.32	34.01	0.1064 0.0333	0.0911
C4	Cr-N N-I	81.56 >88.28	84.28	52.26 8.81	40.54	0.1473 0.0243	0.1134
C ₁₈	Cr-SmC SmC-N N-I	50.28 78.30 >89.40	49.82 79.20 —	5.34 30.62 15.42	6.42 24.82 —	0.0165 0.0871 0.0425	0.0198 0.0704 —

Table 4. Transition temperature (°C) and enthalpy (J g^{-1}) and entropy change (J $g^{-1} k^{-1}$) by DSC measurement (series-1).

3.2. DSC study

DSC is a valuable method for detecting phase transitions. The thermal behavior of novel homologous series-1, -2 was confirmed by using DSC measurement shown in Figure 5. Thermogram is traces in both heating and cooling condition. The first endothermic peak of compound C₁₀ (series-1), at heating condition is observed at 60.01°C, this indicates the presence of SmC phase. DSC analysis confirmed the phase observed by POM study. While second endothermic peak observed at 79.28°C, which indicates the presence of nematic phase, on cooled condition again two endothermic peaks were traced at 62.92°C and 87.21°C. For compound C_7 (series-1), only one significant peak is observed at 95.78°C, while on cooling stage it was traced at 100.01°C. For compound C₁₂ (series-2), one endothermic peak which is observed at 82.15°C confirmed the presence of nematic phase, which was confirmed by POM study, while on cooled condition endothermic peak was traced at nearly 85.01°C. For compound C₆ (series-2), it was observed that Sm C phase and blue phase are present by POM analysis, which was further confirmed by DSC measurement. On heating condition, first endothermic peak is observed at 50.67°C and second endothermic peak is observed at 73.92°C and further cooling condition first endothermic peak traces at 53.98°C and second endothermic peak observed at 75.38°C, respectively. Furthermore, compound C₄ (series-1) in Figure S₁ (ESI) exhibited one endothermic peak at 81.56°C on heating condition, and one endothermic peak at 84.28°C on cooling condition. Compound C_{18} (series-1) in Figure S_1 (ESI) exhibited two endothermic peaks at 50.28°C and 78.30°C on heating condition, and two endothermic peaks at 49.82°C and 79.20°C on cooling condition. For compound C_{18}

Homologous or Comp.	Transition	Heating scan (°C)	Cooling scan (°C)	ΔH (-J g ⁻¹)	Δ <i>H</i> (J g ⁻¹)	$\Delta S \over (J g^{-1} k^{-1})$	$\Delta S \ (J g^{-1} k^{-1})$
С ₆	Cr-SmC SmC-N	50.67 73.92	53.98 75.38	1.12 28.24	3.21 21.60	0.0034 0.0814	0.0098 0.0620
C ₁₂	N-I Cr-N N-I	>89.92 82.15 >90.01	85.01	12.12 28.92 5.81	20.83	0.0333 0.0814 0.0160	0.0581
C ₁₄	Cr-N N-I	78.92 >93.20	79.82	32.15 7.22	25.82	0.0913 0.0197	0.0731
C ₁₈	Cr-N N-I	82.38 >96.24	89.92 —	20.65 9.12	19.98 	0.0581 0.0246	0.0550

Table 5. Transition temperature (°C) and enthalpy (J g^{-1}) and entropy change (J $g^{-1} k^{-1}$) by DSC measurement (series-2).



Figure 6. Space filling diagram of series-1 and -2.

(Series-2) in Figure S₁ (ESI), endothermic peak is observed at 82.38° C on heating condition, and again endothermic peak traces at 89.92° C on cooling condition.

Thus, chalconyl-ester-based nonlinear compound displays lower melting type mesomorphism. In addition, present homologous series-1, -2 show mesomorphic behavior at lower temperature. Transition temperature obtained by DSC analysis at heating and cooling condition and the value of enthalpy and entropy are mentioned in Tables 4 and 5. Molecules of every homolog are randomly oriented in all possible directions with high order of disorder or entropy ($\Delta S = \Delta H/T$) beyond isotropic temperature and the enthalpy value (ΔH). But, at cooled condition, the same from and below isotropic temperature, the mesophase is persisted to appear reversibly at the high temperature at observed during heating condition. The mesophases obtained in enantiotropical manner in present series-1, -2 are smectogenic and nematogenic, respectively.

The geometrical shapes of series-1, -2 are nonlinear bent type without any lateral group substitution which is shown in Figure 6. Both the series-1, -2 are differing with each other due to linearity and aromaticity, the presence of ethylene (-CH=CH-) linkage group in series-1 increases the linearity of molecules.



Figure 7. Proposed molecular packing of the Sm C phase in present both series.

The proposed molecular packing of the SmC phase is given in Figure 7. The arrangement of molecule is non-isomeric bent type shape. This is due to the molecular packing of the alkyl chains with linking groups oriented in tilted way directions in smectic layers structure and effect of flexibility to induce smectic mesomorphism.

4. Conclusions

In this article, we have described the synthesis and thermotropic properties of two novel nonlinear homologous series having chalconyl-ester and chalconyl-vinyl ester as central linking group with terminal octadecyloxy tail group. C_1 to C_3 do not exhibit LC behavior due to high crystallizing tendency, while rest of homologs show lower melting type mesomorphism. In addition, the length of alkoxy tail has been varied from homolog to homolog in the same series-1, -2 to induce mesomorphism. In series-1, compounds C_4 - C_8 show only an enantiotropic nematic mesophase, while in higher homologs C_{10} , C_{12} , C_{14} , C_{16} , C_{18} show smectic as well as nematic mesophase in enantiotropical manner. In series-2, mesophase commences from C_4 to C_{18} in which C_4 to C_{18} show nematic phase while C_5 to C_{10} exhibit enantiotropic smectic as well as nematic mesophase. The group efficiency order derived on the basis of thermal stability, early commencement of mesophase, and upper and lower mesophase length. The mesomorphism was confirmed by POM, DSC.

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232 🛞 R. B. SOLANKI ET AL.

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