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Synthesis, characterization, and mesomorphic investigation of vinyl ester-substituted chalcones and effect of lateral $-\text{NO}_2$ and $-\text{OCH}_3$ group

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ABSTRACT

A novel homologous series of α -4-(4'-n-alkoxy cinnamoyloxy) phenyl β -2''-nitro, 3''-4'' di methoxy benzoyl ethylenes, $\text{H}_{2n+1}\text{CnO}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COO}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}=\text{CH}-\text{C}_6\text{H}_2(\text{NO}_2)(\text{OCH}_3)_2$ ($n = 1-8, 10, 12, 14, 16, 18$) has been synthesized. All these compounds have been characterized by suitable spectroscopic techniques. C_1 homologue is nonmesogenic, while C_2 homologue shows enantiotropic nematogenic property and the rest of the homologous (C_3-C_{18}) displayed enantiotropically smectogenic plus nematogenic phase. Phase transition temperatures and textures of the LC phase were determined by an optical polarizing microscopy (POM) equipped with a heating stage. The mesomorphic properties of these compounds were confirmed by differential scanning calorimetry (DSC) analysis.

KEYWORDS

Liquid crystal; mesomorphic; smectic; nematic; enantiotropic

1. Introduction

Liquid crystals are matter in a state that has properties between those of conventional flow like 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. Presently, we have focus on thermotropic liquid crystals in which, phase transition into liquid crystal phase as temperature changed [5–10]. Liquid crystals of the nematic type are most commonly used in the production of liquid crystal displays (LCD) due to their unique physical properties and wide temperature range and stability [11–14]. Liquid crystals are fascinating functional materials and are important in the field of advanced materials such as electro-optical devices, laser addressed devices, passive block filters, and devices based on thermochromism such as fever indicators, gadgets, reflective-type LCDs, field effect transistors, and sensors [15]. They are indispensable in biological systems and are becoming part of high-tech processes [16]. The mesomorphic behavior of an organic compound is basically dependent on its molecular architecture in which a slight change in the molecular geometry brings about considerable change in its mesomorphic properties. Detailed studies on liquid crystals have led to empirical rules which include the effect of chemical constitution in the nematogenic and smectogenic mesophases [17, 18].

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C. V. Yellamagad et al. reported the bent-core unsymmetrical dimers based on cholesteryl ester and chalconyl moiety, which enhances the biaxiality and chirality of the system [19].

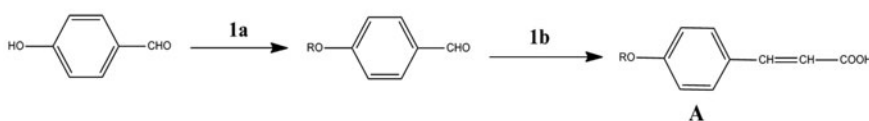
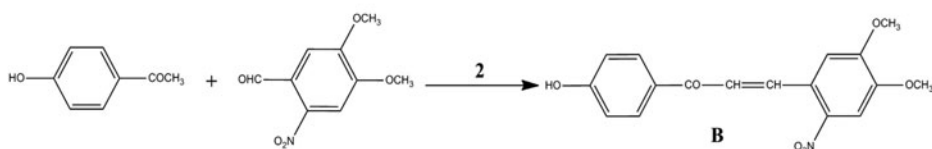
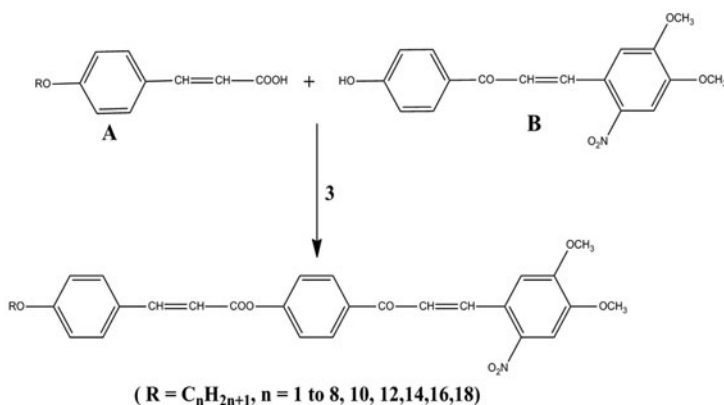
A number of chalcone having reported to exhibit a broad spectrum of antibacterial, antifungal, antiulcer, antimalarial, antitumor, anticancer, anti-inflammatory, and antitubercular. The presence of α , β -unsaturated functional group in chalcone ($-\text{CH}=\text{CH}-\text{CO}-$) is responsible for the anti-microbial activity, which can be altered depending upon the type of substituent present on the aromatic rings [20–24]. Thus, the object of present work is to synthesize and studied the mesomorphism in chalconyl vinyl ester linkage group and also the effect of lateral nitro group and methoxy group on LCs. 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 [25, 26]. R. Gopalakrishnan et al. reported chalcone based single crystals, growth, and comparison of two new enone shifted chalcones and their NLO behaviour [27]. Tandel et al. studied the chain chalconyl polymers compounds to exhibiting threaded type nematic phases [28]. Doshi et al. reported homologous series based on chalconyl-ester and chalconyl-vinylester linkage group [29–31]. Sadashiva et al. 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 [32]. Prajapati et al. studied some homologous series consisted cinnamate linkage group and show its effect on mesomorphic properties of liquid crystalline compounds [33, 34]. Bhoya et al. reported chalconyl vinyl-ester linking group and studied the effect of bromo group at a lateral position on the mesomorphic property [35].

In order to explore further factors which govern the thermal stability and mesophase-length of liquid crystals with vinyl-ester containing chalconyl linking group based on three benzene core rings. Here, in present study, we compare the effect of linkage group on LC behaviour, thermal stability, mesophase length and commencement of mesophase in present synthesized series with structurally similar reported series. Recently, our group reported various isomeric and nonisomeric chalconyl ester linking group based homologous series [36–40].

2. Experimental

2.1. Synthesis

The target chalconyl vinylester compounds were synthesized as outlined in Scheme 1. *Trans* 4-*n*-alkoxy cinnamic acids (**A**) were prepared by the modified method of Dave and Vora et. al. [41]. (3-(4, 5-dimethoxy-2-nitrophenyl)-1-(4-hydroxy phenyl)-prop-2-en-1-one) (**B**) was prepared by the usual established method [42]. In the final step, the coupling of the compound (**A**) and (**B**) is done by Steglich esterification to yield the target product [43]. Thus, chalconyl-ester homologue derivatives were filtered, washed with sodium bicarbonate and dilute sodium hydroxide solution, dried and purified till constant transition temperatures appear, using an optical polarizing microscope equipped with a heating stage. Alkyl halides, 4-hydroxy acetophenone, 4-hydroxy benzaldehyde, 4,5-dimethoxy-2-nitro benzaldehyde, malonic acid, dicyclohexyl carbodimide (DCC), dimethyl amino pyridine (DMAP), dichloro methane, ethanol, pyridine, piperidine, Acetone required for the synthesis was used as received except solvents which was dried and distilled prior to use. The molecular structures of the target products and the intermediates were confirmed by spectroscopic analysis and elemental analysis.

Step-1**Step-2****Step-3**

1a. R-Br, K₂CO₃, Acetone, Reflux; **1b.** Malonic acid, Pyridine, Piperidine, 3 to 4 hours, Reflux; **2.** KOH, Ethanol, Room temperature Stirring; **3.** DCC, DMAP, DCM, 48 hour stirring.

Scheme 1. Synthetic route of target compounds.

2.2. Reaction scheme

2.3. Characterization

Representative homologues series were characterised by elemental analysis, infrared spectroscopy, and ¹H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX, ¹HNMR spectra were recorded on Bruker using CDCl₃ as solvent (400 MHz). Micro-analysis was performed on Perkin-Elmer PE 2400 CHN analyzer shown in Table 1. Texture image of some homologues for the nematic phase was determined by the miscibility method (Table 2). Transition temperature (Table 3) and LC properties (textures image) were

Table 1. Elemental analysis for (1) ethoxy, (2) propyloxy, (3) butyloxy, (4) pentyloxy and (5) hexyloxy derivatives.

S.	No. Molecular formula	Elements % found			Elements % Calculated		
		C	H	N	C	H	N
1	C ₂₈ H ₂₅ O ₈ N	71.23	5.21	2.93	71.33	5.30	2.97
2	C ₂₉ H ₂₈ O ₈ N	71.54	5.68	2.83	71.60	5.76	2.88
3	C ₃₀ H ₃₁ O ₈ N	71.76	6.08	2.74	71.85	6.18	2.79
4	C ₃₁ H ₃₄ O ₈ N	71.98	6.48	2.64	72.09	6.58	2.71
5	C ₃₂ H ₃₇ O ₈ N	72.27	6.87	2.57s	72.31	6.96	2.63

Table 2. Texture of Nematic Phase of C_{10} , C_{12} , C_{14} , C_{16} by miscibility method.

S. No.	Homologue	Texture
1	C_{10}	Rodlike
2	C_{12}	Rodlike
3	C_{14}	Threaded
4	C_{16}	Threaded

determined by using an optical polarising microscopy (POM) equipped with the heating stage. Decomposition temperatures were determined using of Shimadzu DSC 60 differential Scanning Calorimeter with a heating rate of $5-10.0^{\circ}\text{C min}^{-1}$. Thermodynamic quantities enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed. The mesophase length and thermal stability of mesophase were determined by POM study and the enthalpies for all newly chalconyl vinylester-based liquid crystals compound were determined by differential scanning calorimetry (DSC) analysis.

2.4. Analytical data

IR Spectra in cm^{-1} :

Chalcone (B): 3624 ($-\text{OH}$ str.-bonded), 3016 ($-\text{C}-\text{H}$ - str in CH_3), 941 ($-\text{C}-\text{H}$ - def. hydrocarbon), 1076 and 1022 ($-\text{C}-\text{O}-$) str, 1253, ($-\text{C}-\text{H}$ - def. in CH_2), 1175 ($-\text{O}-\text{CH}_3$), 1430 ($-\text{NO}_2$ group), 1512 ($-\text{C}=\text{C}-$)str, 1662 ($-\text{C}=\text{O}$ group), 2812 and 2927 (aromatic $-\text{C}-\text{H}$ str.), 960 (trans, $-\text{CH}=\text{CH}-$) group.

Propyloxy (C_3): 810 Polymethylene group of $(-\text{CH}_2-)_n$ of $-\text{OC}_3\text{H}_7$, 820 ($-\text{C}-\text{H}$ - def. di-substituted), 930 ($-\text{C}-\text{H}$ - def. hydrocarbon), 1022 ($-\text{C}-\text{O}-$) str, 1253 ($-\text{C}-\text{O}$) str in $-(\text{CH}_2)_n$ chain, 1405 ($-\text{C}-\text{H}$ - def. in CH_2), 1440 ($-\text{NO}_2$ group), 1175 ($-\text{O}-\text{CH}_3$), 1540 ($-\text{C}=\text{C}-$)str, 1630 ($-\text{C}=\text{O}$ group), 1720 ($-\text{COO}-$ ester group), 2812 and 2927 (aromatic $-\text{C}-\text{H}$ str. $-\text{OCH}_3$ group), 3140, 3170 ($=\text{C}-\text{H}$ str.), 970 (trans, $-\text{CH}=\text{CH}-$) group.

Pentyloxy (C_5): 780 Polymethylene group of $(-\text{CH}_2-)_n$ of $-\text{OC}_5\text{H}_{11}$, 820 ($-\text{C}-\text{H}$ - def. di-substituted), 931 ($-\text{C}-\text{H}$ - def. hydrocarbon), 1076 ($-\text{C}-\text{O}-$) str, 1225 ($-\text{C}-\text{O}$) str in $-(\text{CH}_2)_n$ chain, 1405 ($-\text{C}-\text{H}$ - def. in CH_2), 1175 ($-\text{O}-\text{CH}_3$), 1440–1446 ($-\text{NO}_2$ group), 1545 ($-\text{C}=\text{C}-$)str, 1640 ($-\text{C}=\text{O}$ group), 1730 ($-\text{COO}-$ ester group), 2830 and 2928 (aromatic $-\text{C}-\text{H}$ str. $-\text{OCH}_3$ group), 3240, 3170 ($=\text{C}-\text{H}$ str.), 970 (trans, $-\text{CH}=\text{CH}-$) group.

Table 3. Transition temperature in $^{\circ}\text{C}$ by POM.

S. no.	R = <i>n</i> -alkyl group	Transition temperatures in ($^{\circ}\text{C}$)					
		Cr	Smectic		Nematic		Isotropic
1	C_1	.	—	—	—	.	185.0
2	C_2	.	—	—	174.0	.	202.0
3	C_3	.	133.0	.	171.0	.	198.0
4	C_4	.	142.0	.	162.0	.	185.0
5	C_5	.	144.0	.	168.0	.	182.0
6	C_6	.	138.0	.	154.0	.	190.0
7	C_7	.	142.0	.	152.0	.	192.0
8	C_8	.	136.0	.	149.0	.	174.0
9	C_{10}	.	128.0	.	146.0	.	188.0
10	C_{12}	.	122.0	.	151.0	.	184.0
11	C_{14}	.	101.0	.	154.0	.	180.0
12	C_{16}	.	96.0	.	142.0	.	166.0
13	C_{18}	.	94.0	.	135.0	.	144.0

Dodecyloxy (C₁₂): 760 Polymethylene group of $(-\text{CH}_2-)_n$ of $-\text{OC}_{12}\text{H}_{25}$, 820 ($-\text{C}-\text{H}$ - def. di-substituted), 932 ($-\text{C}-\text{H}$ - def. hydrocarbon), 1024 ($-\text{C}-\text{O}-$) str, 1245 ($-\text{C}-\text{O}$) str in $-(\text{CH}_2)_n$ chain, 1405 ($-\text{C}-\text{H}$ - def. in CH_2), 1175 ($-\text{O}-\text{CH}_3$), 1446 ($-\text{NO}_2$ group), 1540 ($-\text{C}=\text{C}-$)str, 1660 ($-\text{C}=\text{O}$ group), 1740 ($-\text{COO}-$ ester group), 2840 and 2930 (aromatic $-\text{C}-\text{H}$ str. $-\text{OCH}_3$ group), 3130 ($=\text{C}-\text{H}$ str.), 975(trans, $-\text{CH}=\text{CH}-$) group.

Tetradecyloxy (C₁₄): 741 Polymethylene group of $(-\text{CH}_2-)_n$ of $-\text{OC}_{14}\text{H}_{29}$, 820 ($-\text{C}-\text{H}$ - def. di-substituted), 931 ($-\text{C}-\text{H}$ - def. hydrocarbon), 1076 ($-\text{C}-\text{O}-$) str, 1253 ($-\text{C}-\text{O}$) str in $-(\text{CH}_2)_n$ chain, 1175 ($-\text{O}-\text{CH}_3$), 1405 ($-\text{C}-\text{H}$ - def. in CH_2), 1441 ($-\text{NO}_2$ group), 1540 ($-\text{C}=\text{C}-$)str, 1640 ($-\text{C}=\text{O}$ group), 1730 ($-\text{COO}-$ ester group), 2830 and 2927 (aromatic $-\text{C}-\text{H}$ str. $-\text{OCH}_3$ group), 3130 ($=\text{C}-\text{H}$ str.), 960 (trans, $-\text{CH}=\text{CH}-$) group.

¹H NMR spectra in CDCl₃ in δ ppm:

Chalcone (B): 3.84 (s, 6H, 2 $(-\text{OCH}_3)_2$ group, 7.70 (1H, d, $J = 17\text{Hz}$, $=\text{CH}-\text{Ar}$), 7.50 (1H, d, $J = 17\text{Hz}$, $-\text{CO}-\text{CH} =$), 6.80 (s, 1H, $-\text{OH}$ group), 6.92 (d, 2H, first phenyl ring), 7.44 (d, 2H, first phenyl ring), 8.02 (s, 1H, second phenyl ring), 7.47 (s, 1H, second phenyl ring).

Propyloxy (C₃): 0.90 (t, 3H, $-\text{CH}_3$ of $-\text{OC}_3\text{H}_7$), 1.72 (q, 2H, of $-\text{OC}_3\text{H}_7$), 3.83 (6H, 2 $(-\text{OCH}_3)_2$), 4.06 (t, 2H, $-\text{O}-\text{CH}_2-$ of $-\text{OC}_3\text{H}_7$), 7.05 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 8.54 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 7.44 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.26 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.94 & 7.61 (d, 4H, left side phenyl ring), 7.51 & 8.14 (d, 4H, central phenyl ring), 7.04 & 7.72 (d, 2H, terminal phenyl ring).

Octyloxy (C₈): 0.88–0.90 (t, 3H, $-\text{CH}_3$ of $-\text{OC}_8\text{H}_{17}$), 1.29–1.31 (m, 6H of $-\text{OC}_8\text{H}_{17}$), 1.74 (t, 2H, $-\text{OC}_8\text{H}_{17}$), 3.83 (6H, $(-\text{OCH}_3)_2$), 4.06 (t, 3H, $-\text{O}-\text{CH}_2-$ of $-\text{OC}_8\text{H}_{17}$), 7.06 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 8.56 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 7.44 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.26 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.84 & 7.61 (d, 4H, left side phenyl ring), 7.51 & 8.14 (d, 4H, central phenyl ring), 7.04 & 7.71 (d, 2H, terminal phenyl ring).

Decyloxy (C₁₀): 0.88–0.90 (t, 3H, $-\text{CH}_3$ of $-\text{OC}_{10}\text{H}_{21}$), 1.29–1.31 (m, 6H of $-\text{OC}_{10}\text{H}_{21}$), 1.74 (t, 2H, $-\text{OC}_{10}\text{H}_{21}$), 1.31 (q, 2H, $-\text{OC}_{10}\text{H}_{21}$), 3.83 (6H, $(-\text{OCH}_3)_2$), 4.06 (t, 3H, $-\text{O}-\text{CH}_2-$ of $-\text{OC}_{10}\text{H}_{21}$), 7.06 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 8.56–8.58 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 7.43 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.26 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.84 & 7.61 (d, 4H, left side phenyl ring), 7.52 & 8.16 (d, 4H, central phenyl ring), 7.04 & 7.71 (d, 2H, terminal phenyl ring).

Dodecyloxy (C₁₂): 0.88–0.90 (t, 3H, $-\text{CH}_3$ of $-\text{OC}_{12}\text{H}_{25}$), 1.26–1.29 (m, 14H of $-\text{OC}_{12}\text{H}_{25}$), 1.31 (q, 2H, $-\text{OC}_{12}\text{H}_{25}$), 1.74 (t, 2H, $-\text{OC}_{12}\text{H}_{25}$), 3.83 (6H, $(-\text{OCH}_3)_2$), 4.06 (t, 3H, $-\text{O}-\text{CH}_2-$ of $-\text{OC}_{12}\text{H}_{25}$), 7.06 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 8.56 (d, 1H, $-\text{CO}-\text{CH}=\text{CH}-$), 7.44 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.26 (d, 1H, $-\text{CH}=\text{CH}-\text{COO}-$), 6.82 & 7.64 (d, 4H, left side phenyl ring), 7.51 & 8.14 (d, 4H, central phenyl ring), 7.04 & 7.70 (d, 2H, terminal phenyl ring).

3. Result and discussion

The synthetic route for the preparation of chalcone and trans 4-*n*-alkoxy cinnamic acid and the target compounds α -4-[4'-*n*-alkoxy cinnamoyloxy] benzoyl- β -2''-nitro, 4''-5''-dimethoxy phenyl ethylenes is outlined in Scheme 1. In the present study, we have synthesized total 13 homologous (C₁ to C₈, C₁₀, C₁₂, C₁₄, C₁₆, C₁₈). The mesomorphic properties of synthesized novel compounds were characterized and investigated by DSC and POM.

3.1. DSC analysis

DSC is a valuable method for the detection of phase transitions. It yields quantitative results. In the present study, DSC data of two homologous are mention in Fig. 1, which helps to further confirm the mesophase appeared during POM investigation. C₁₈ homologue reveals two

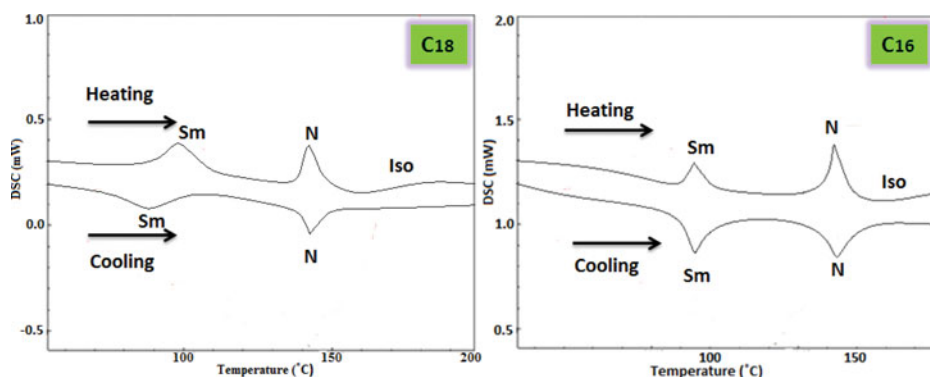


Figure 1. DSC curves of compound C_{18} and C_{16} homologous.

separate endothermic peaks at 98.26°C and 140.8°C on heating condition, which indicates the presence of SmC and nematic mesophase. While on cooling condition, again two peaks were trace at 86.34°C and 141.8°C, respectively. The similar phase behaviour was obtained for C_{16} homologue, first endothermic peak traced at 95.48°C and second endothermic peak observed at 143.7°C, while on the cooling stage again two endothermic peaks appeared at 94.72°C and 141.4°C. which was further confirmed by POM analysis.

3.2. POM investigation

As a preliminary investigation, the mesophases exhibited by present series were examined by using a polarising optical microscope. The samples were sandwich between a glass slide and a cover slip. All the compounds of the series show mesomorphism except C_1 homologue which displayed the nonmesogenic property. In present synthesized series, the nematic mesophase commences from C_2 to C_{18} homologue and the smectic phase commences from C_3 to C_{18} homologous, respectively. Compound C_2 to C_{18} shows enantiotropically LCs property. In addition, compound C_2 shows only nematic phase and compound C_3 to C_{18} displayed smectic as well as nematic phase enantiotropically manner. Transition temperatures (Table 3) determined by optical polarization microscope and the phase diagram was 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).

The phase diagram shows I/Cr–M, Sm–N and N–I transition curve drawn by linking like or related transition points as mention in Fig. 2. The I/Cr–M curve falling up to C_3 homologue and then ascends at C_4 homologue and continued to decreased at C_6 homologue and again reaching maxima at C_7 homologue. The odd–even effect is present in the I/Cr–M transition curve mentioned the in the phase diagram. The Sm–N transition curve initially falls at C_4 homologue and rising to C_5 homologue, this is due to the presence of the odd–even effect and then continued to decrease up to C_{10} homologue. The Sm–N transition curve slightly increases at C_{12} to C_{14} homologue because of the effect of abnormality and decreasing transition curve from C_{16} to C_{18} homologue due to the number of methylene units increase which inducing molecule to more polar and flexible. The N–I phase transition curve descending at C_5 homologue and ascends at C_6 homologue and reaching maxima at C_7 homologue and again descends at C_8 homologue and rising up to C_{10} homologue and then gradually decreased up to last homologues. The odd and even parity of carbon present at C_5 to C_6 and C_7 to C_8 in the N–I transition curve. While increasing number of carbon it behaves due to fairly

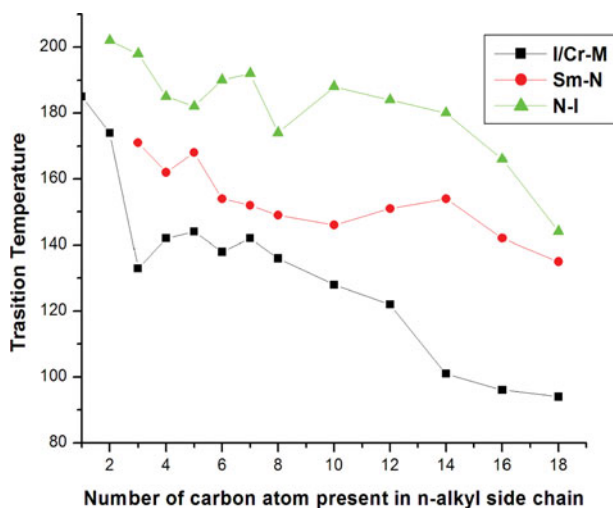


Figure 2. Phase diagram of present series.

abnormality from decyloxy to octadecyloxy derivative. The mesogenic properties are varying from homologue to homologue in same series because of numbers of methylene group $(-\text{CH}_2-)_n$ added in left side of alkoxy terminal side chain group.

On cooling the isotropic mass on a slide, the nematic mesophase observed and on applying further cooling the nematic mesophase is reappeared to the smectic C phase in present series. A Smectic C mesophase with rod-like texture is revealed for compound C_6 in the heating and cooling cycle on the basis of POM mention in Fig. 3(a). Compound C_{14} shows nematic type droplets at 138°C on the cooling condition. Compound C_{16} displayed mosaic type smectic A phase at nearly 96°C in the cooling cycle and further increasing temperature up to 142°C , SmA mesophase transfer into the nematic phase. This is due to the flexibility of the layers leads to more distortions within the molecules to floating on the surface with statistically parallel orientational order within the definite range of temperature to exhibiting nematogenic character. C_8 homologue shows the typical texture image of the smectic C phase at 136°C on the cooling cycle.

Compound C_1 directly transforms from the solid phase to the isotropic phase without showing LCs property and on cooling condition solidification occurs from isotropic mass without display any LC phase. The nonmesomorphic property of C_1 homologue attributed to the presence of short alkyl spacer $(-\text{OCH}_3)$ at left side chain and become less flexible as compared to other homologues in present series. The LC properties of newly synthesized compounds are changing from varying left side chain in the same series as a result of changing its molecular structure from lower homologue to higher homologue and keeping rest of right side laterally substituted $-\text{NO}_2$ and two sides substituted $-\text{OCH}_3$ group.

Nonmesomorphic chalcone linking with Trans 4-*n*-alkoxy cinnamic acid, as a result increases the molecular length, permanent dipole moment across the axis, dispersion forces, dipole-dipole interaction and polarizability of molecule with left side alkyl chain and lateral attractions due to the presence of nitro group and $-\text{OCH}_3$ group which increase the polarity of molecule to induce mesophase. Which disalign the molecules of all the homologues of a series except C_1 at an angle ninety degree or less than ninety degree under the control of exposed thermal vibration as a consequence of molecular rigidity and flexibility [44]. In the previous study, we reported that chalconyl-vinylester based liquid crystalline compounds shows good biologically and fungal activity [23]. It has been studied that $-\text{CO}-\text{CH}=\text{CH}-$ linkage group is

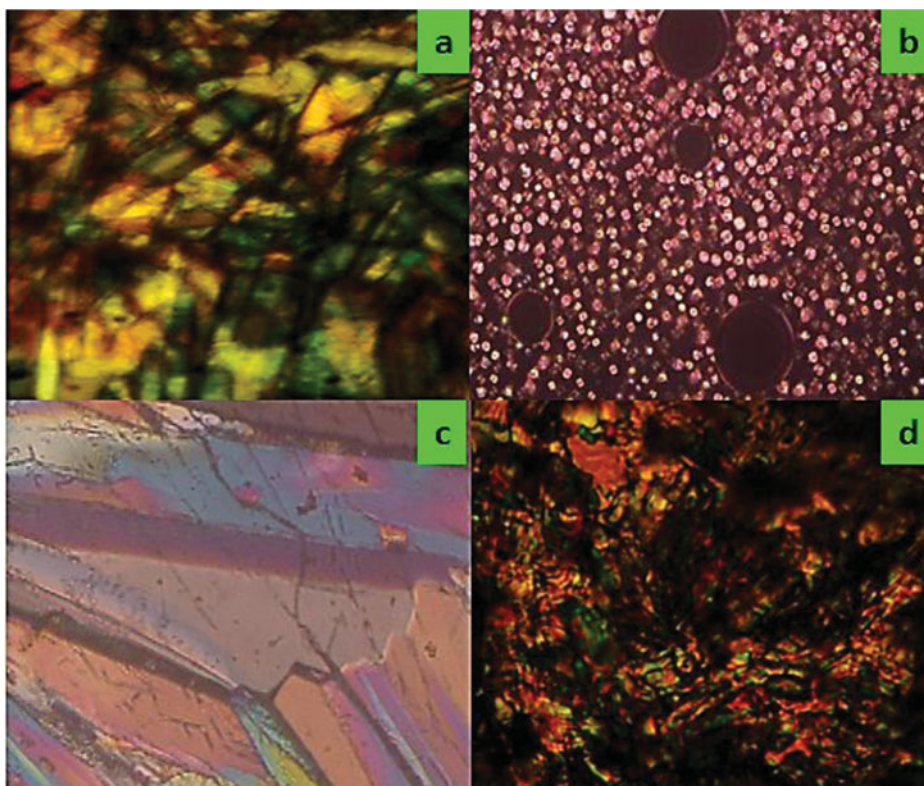


Figure 3. Microphotographs of the compounds (a) rod-like texture image of C_6 at 138°C in the heating cycle; (b) nematic droplets type texture image of C_{14} at 154°C in the cooling cycle; (c) mosaic texture of C_{16} at 96°C in the cooling cycle; (d) typical texture image of C_8 homologue at 136°C in the cooling cycle.

less conducive to induce mesomorphism as compared to benzoate ($-\text{COO}-$) and cinnamate ($-\text{CH}=\text{CH}-\text{COO}-$) group.

The liquid crystal property of newly homologous series-1 is compared with the other structurally similar series-X [45] and series-Y [46] as shown in Fig. 4. Homologous series X and Y chosen for comparison and the novel homologous series 1 is similar in respect of three phenyl rings inbuilt with one central linking groups $-\text{CH}=\text{CH}-\text{CO}-$ and the presence of left n -alkoxy

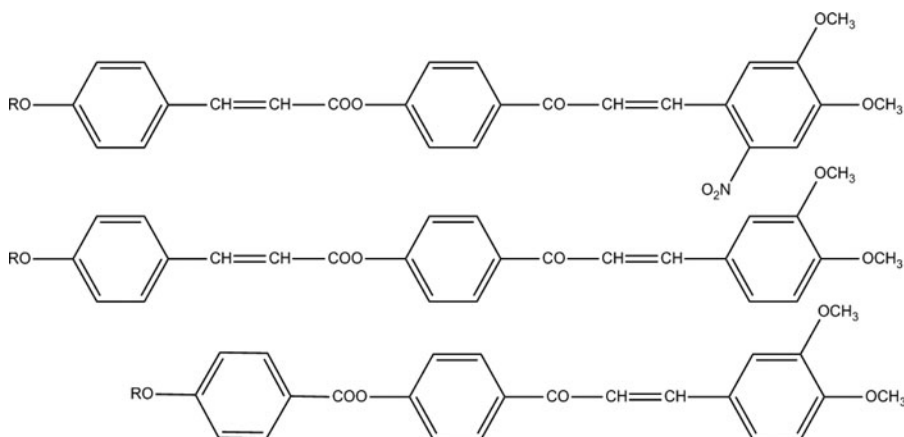


Figure 4. Structurally similar series.

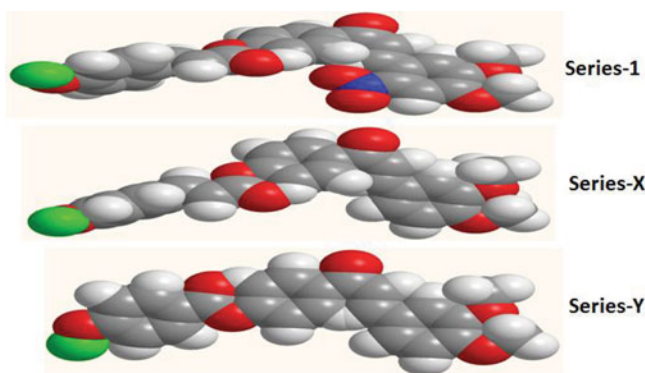


Figure 5. Space filling diagram of structurally similar series.

side chain present in (–OR) left terminal end group. Series-1 and series-X having vinyl-ester linking group as compared to series-Y. They also differ in respect of the lateral groups in the terminal or lateral positions on third phenyl ring. Therefore, the observed variations in their mesomorphic properties and the degree of mesomorphism can be attributed to the differing features of series 1, X and Y. The molecular length to breadth ratio, intermolecular end-to-end and lateral attractions by substituted group and molecular polarizability of compounds is increased by the presence of more polar lateral groups.

The geometrical shapes of molecules are linear rod like with the presence of lateral group in series-1, -X, -Y mention in Fig. 5. The linearity and width of molecules in series-1, -X are more as compared to series-X. The highest width of compounds in series-1 as compared to series-X and series-Y, due to the presence of three lateral groups. In addition, the presence of ethylene (–CH=CH–) unit in (–CH=CH–COO–) group in both series-1, -X, while in series-Y, only carboxy (–COO–) group is present. In series-1, three lateral polar groups are present, while in series-X, -Y only two methoxy groups are present.

Table 4 represents the thermal stability of series-1 with series-X and series-Y. In series-1 and series-Y, smectic and nematic phases are present and the absence of the smectic phase in series-X respectively. In series-X, the smectic phase commences from C₃ to C₁₈ homologous, while in series-Y, it commences from C₆ to C₁₆ homologous. Total mesophase length (smectic + nematic) vary from maximum to minimum between C₅ to C₁₄ in series-1. N–I thermal stability of series-X is higher as compared to series-1 and series-X, because of the linearity of series-X is more than series-Y. Sm–N thermal stability of series-1 is higher as compared to series-Y, for the reason that series 1 contains three highly polar groups –NO₂ & –OCH₃, which increases its polarity and polarizability more as compared to series-X, -Y. However, in series-X and series-Y it contains only one polar group. The presence of the double

Table 4. Average thermal stabilities in °C.

Series	Series-1	Series-X	Series-Y
Sm–N or Sm–I	125.0	—	115.6
Commencement of smectic phase	(C ₃ –C ₁₈)		(C ₆ –C ₁₄)
N–I	154.8	163.1	156.6
Commencement of nematic phase	(C ₂ –C ₁₈)	(C ₅ –C ₁₆)	(C ₂ –C ₁₆)
Total mesophase length in °C from minimum to maximum	38.0 to 79.0	24.0 to 59.0	33.0 to 65.0
	C ₅ C ₁₄	C ₁₆ C ₈	C ₁₆ C ₇

bond in vinyl ester group can cause the isomerism and arrangement of atoms in space may operate and create such an extent of noncoplanarity of molecules that smectic mesophase is observed. Molecular rigidity is also changed from homologue to homologue and series to series due to the presence of two different central bridges and vibrations cause by lateral group. All three homologous series-1, -X, -Y contain common chalconyl ($-\text{CH}=\text{CH}-\text{CO}-$) group. This result suggests that the presence of chalconyl unit can act as stronger activating group due to the presence of α , β -unsaturated ketone.

4. Conclusion

In summary, we have successfully synthesized a new homologous series based on chalconyl ($-\text{CO}-\text{CH}=\text{CH}-$) and vinyl ester ($-\text{CH}=\text{CH}-\text{COO}-$) linkage group. The present synthesized series having left terminal alkoxy side chains ($n = 1-8, 10, 12, 14, 16, 18$) has been . The lower member of the series (C_1) shows the nonmesomorphic property and (C_2) homologue displayed only the nematic mesophase. While other members of the series ($n = 3-8, 10, 12, 14, 16, 18$) shows smectic as well as nematic property. We have also studied the effect of lateral side group on the mesomorphic property and compare against previously reported similar series. Present synthesized series exhibits good thermal stability and mesophase length.

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References

- [1] Reinitzer, F. (1888). *Monatsh. Chem.*, 9, 421.
- [2] Narmura, S. (2001). *Displays*, 22(1), 1.
- [3] Kim, W. S., Elston, S. J., & Ranyes, F. P. (2008). *Display*, 29, 458.
- [4] Glendenning, M. E., Goodby, J. W., Hird, M., Jones, J. C., Toyne, K. J., Slaney, A. J., & Minter, V. (1999). *Mol. Cryst. Liq. Cryst.*, 332, 321.
- [5] Vora, R.A., & Dixit, N. (1980). *Mol. Cryst. Liq. Cryst.*, 59, 63.
- [6] Demus, D. (1988). *Mol. Cryst. Liq. Cryst.*, 165, 45.
- [7] Hird, M. (2005). *Liq. Cryst. Tod.*, 4, 9.
- [8] Imrie, C. T. (1999). *Struct. Bond.*, 95, 149.
- [9] Seed, A. J., Hird, M., Styring, P., Gleeson, H. F., & Mills, J. T. (1997). *Mol. Cryst. Liq. Cryst.*, 299, 19.
- [10] Hird, M., Toyne, K. J., Goodby, J. W., Gray, G. W., Minter, V., Tuffin, R. P., & Mc Donnell, D. G. (2004). *J. Mater. Chem.*, 14, 1731.
- [11] Yelamaggad, C. V., Prabhu, R., Shanker, G., & Bruce, D. W. (2009). *Liq. Cryst.*, 36, 247.
- [12] Klein, C., Baranoff, E., Nazeeruddin, M. K., & Gratzel, M. (2010). *Tetrahedron Lett.*, 51, 6161.
- [13] Prajapati, A. K., & Bonde, N. L. (2009). *Mol. Cryst. Liq. Cryst.*, 501, 72.
- [14] Aldred, N. L., Vlachos, P., & Dong, D. (2005). *Liq. Cryst.*, 32, 951.
- [15] (a) Sago, K. K., & Fujita, A. (2007). *Mol. Cryst. Liq. Cryst.*, 479, 151. (b) Chulson, K., Park, D. J., & Kim, Y. B. (2007). *Mol. Cryst. Liq. Cryst.*, 479, 81.
- [16] (a) Seredyuk, M., Gasper, A. B., & Reiman, S. (2006). *Chem. Mater.*, 18, 2513. (b) Stewart, G. T. (2003). *Liq. Cryst.*, 30, 541. (c) Stewart, G. T. (2004). *Liquid Cryst.*, 31, 443.
- [17] Singh, S. K., Singh, M. K., Singh, H. K., & Singh, B. (2016). *Mol. Cryst. Liq. Cryst.*, 624, 77.
- [18] Singh, H. K., Singh, S. K., Kumar, V., & Singh, B. (2013). *Mol. Cryst. Liq. Cryst.*, 587, 1.
- [19] Yelamaggad, C. V., Bonde, N. L., Ammathnadu, S. A., Doddamani, S. R., Prasad, S.K., & Prajapati, A. K., (2007). *Chem. Mater.*, 19, 2463.

- [20] Sashidhara, K. V., Rao, K. B., Kushwaha, P., Modukuri, R. K., Singh, P., Soni, I., Shukla, P. K., Chopra, S., & Pasupuleti, M. (2015). *ACS Med. Chem. Lett.*, 6, 809.
- [21] Gaikwad, P. P., Desai, M. T. (2013). *Interna. J. Pharma Res. Rev.*, 2(12), 40.
- [22] Jose, N., Leo, D. C., Rodrigues, J., Dominguez, N. G., Gut, J., & Rosenthal, P. J. (2005). *J. Med. Chem.*, 48, 3654.
- [23] Sharma, V. S., & Patel, R. B., (2016). *WSN*, 54, 240.
- [24] Sashidhara, K. V., Kumar, A., Kumar, M., Sarkar, J., & Sinha, S. (2010). *Bio Org. Med. Chem. Lett.*, 20, 7205.
- [25] Nielsen, S. F., Larsen, M., Boesen, T., Schonning, K., & Kromann, H. (2005). *J. Med. Chem.*, 48, 2667.
- [26] Shah, D. R., Lakum, H. P., & Chikhalia, K. H. (2014). *ILCPA*, 17(2), 207.
- [27] Ramkumar, V., Anandhi, S., Kannan, P., & Gopalakrishnan, R. (2013). *Cryst. Eng. Comm.*, 15, 2438.
- [28] Tandel, R. C., Gohil, J., & Patel, N. K. (2012). *Res. J. Rec. Scis.*, 1, 122.
- [29] Patel, R. B., & Doshi, A. V. (2011). *Der Pharma Chemica.*, 3(2), 147.
- [30] Chauhan, H. N., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 570, 92.
- [31] (a) Chaudhari, R. P., Chauhan, M. L., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 575, 88. (b) Patel, R. B., Patel, V. R., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, 552, 3. (c) Chauhan, H. N., Shah, R. R., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 577, 36.
- [32] Sadashiva, B. K., Ksthuraiah, N., Krishnaprasad, S., & Nair, G. C. (1998). *Liq. Cryst.*, 24, 639.
- [33] Prajapati, A. K., Thakkar, V., & Bonde, N. (2003). *Mol. Cryst. Liq. Cryst.*, 393, 41.
- [34] Prajapati, A. K., & Patel, H. N. (2007). *Mol. Cryst. Liq. Cryst.*, 34, 903.
- [35] Maheta, S. A., Bhola, G. N., & Bhoya, U. C. (2015). *ILCPA*, 8(1), 77.
- [36] (a) Sharma, V. S., Solanki, R. B., Patel, P. K., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 625, 137. (b) Solanki, R. B., Sharma, V. S., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 631, 107. (c) Sharma, V. S., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 630, 162.
- [37] (a) Sharma, V. S., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 633, 80. (b) Solanki, R. B., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 634, 24. (c) Solanki, R. B., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 634, 50.
- [38] Sharma, V. S., Jain, B. B., Chauhan, H. N., & Patel, R. B. (2016). *Mol. Cryst. Liq. Cryst.*, 630, 79.
- [39] Sharma, V. S., & Patel, R. B. (2016). *ILCPA Scipress*, 64, 69.
- [40] Sharma, V. S., & Patel, R. B. (2015). *ILCPA Scipress*, 60, 182.
- [41] Dave, J.S., & Vora. R. A. (1970). In: *Liquid crystals and ordered fluids*, Johnson, J. F. & Porter R. S. (Eds.), Plenum Press: New York, 477.
- [42] Furniss, B. S., Hannford, A. J., Smith, P. W. G., & Tatchell, A. R. (Eds.). (1989). *Vogel's Textbook 245 of Practical Organic Chemistry* (4th ed.), 563, Longmann Singapore Publishers Pvt. Ltd.: Singapore.
- [43] Pinol, R., Ros, M. B., Serrano, J. L., & Sierra, T. (2004). *Liq. Cryst.*, 31, 1293
- [44] Bhola, G. N., Bhoya, U. C. (2016). *Mol. Cryst. Liq. Cryst.*, 630, 188.
- [45] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 577, 51.
- [46] Suthar, D. M., Doshi, A. A., & Doshi, A. V. (2013). *Mol. Cryst. Liq. Cryst.*, 582, 79.