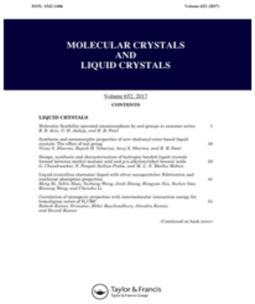

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Synthesis and mesomorphic properties of new chalconyl-ester based liquid crystals: The effect of tail group

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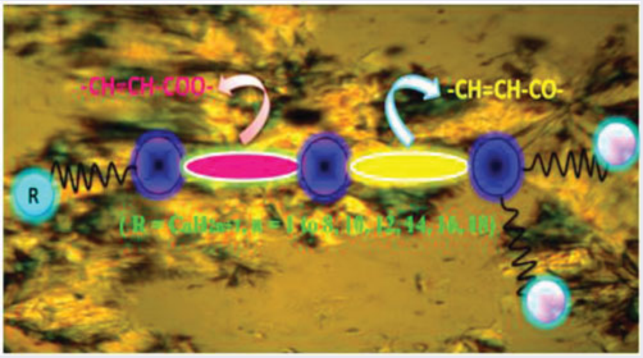
ABSTRACT
A new homologous series viz. 4-(3-(3, 4-dioctadecyloxy) phenyl)-3-oxoprop-1-en-1-yl) phenyl-3-(4-n-alkoxy phenyl) cinnamate) based on two linking groups have been synthesized and characterized. The mesomorphic properties of these compounds were observed by optical polarized light microscopy (POM) and confirmed by differential scanning calorimetry (DSC). All synthesized compounds exhibited LC behaviour except compound C_1. Thermal stability of smectic and nematic phase of present series are 79.0°C and 120.0°C whose temperature range is vary from 14 to 20°C and 24 to 56°C respectively. The mesomorphic properties of present series were compared with other structurally related mesogenic homologous series to evaluate the effects of tail group on mesomorphism.

KEYWORDS
Liquid crystal; nematogenic; smectogenic; thermotropic

GRAPHICAL ABSTRACT



1. Introduction

Study of liquid crystalline state (LC) is a multidisciplinary subject useful to the mankind and industrial applications through scientist, technologists and technocrats [1–4] due to its unique property to flow as liquid and optical properties as crystals. Study on LC state is planned with a view to understand and establish the effect of molecular structure on LC properties as a consequence of molecular rigidity and flexibility [5–10].

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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 [11–13]. Presently, we have focus on thermotropic liquid crystals in which, phase transition into liquid crystal phase as temperature changed [14–18]. Liquid crystals in the nematic group are most commonly used in production of liquid crystal displays (LCD) due to their unique physical properties and wide temperature range [19–20]. 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 [21–27].

A number of chalcone having reported to exhibit a broad spectrum of anti-bacterial, antifungal, antiulcer, antimalarial, antitumor, anticancer, anti-inflammatory and antitubercular activity [28–30]. It is believe that 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 [31–32]. To the best of our knowledge, liquid crystalline materials based on chalconyl central linking group are rarely reported in literature. It has been observed that –CO–CH=CH– linkage is less conducive to mesomorphism as compared to –CH=N–, –COO–, –N=N–, –CH=CH–COO– linkages group because of the presence of non-linearity and angle strain arising from the presence of keto (–C=O) group [33]. Surprisingly, when –CO–CH=CH– linkage is linked with another linking group it becomes conductive to exhibits mesophase. In the literature studies, there are several reports of mesogenic compounds having chalcone linkage.

Previously, Yellamaggad 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 [34]. R.Gopalakrishnan et al. reported chalcone based single crystals, growth, and comparison of two new enone shifted chalcones and their NLO behaviour [35]. Tandel et al. studied the chain chalconyl polymers compounds to exhibiting threaded type nematic phases [36]. Vinyl esters linkage group have been well known for last decades of years, Vora et al. reported binary mixtures of cinnamate esters exhibit a wide range of smectic and nematic mesophase [37]. Doshi et al. reported various homologous series based on chalconyl and vinyl ester linkage group and studied the effect on mesomorphism [38–40]. 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 [41]. Prajapati et al. studied some homologous series consisted cinnamate linkage group and show its effect on mesomorphic properties of liquid crystalline compounds [42–43]. Recently, Bhoya et al. reported a calamatic rod type homologous series containing vinyl ester and azomethine linkage groups [44–45]. Shah et al. studied a nonlinear homologous series based on ester and chalcone linkage group [46]. Patel et al. reported rod type homologous series having chalconyl ester central linkage group and hexyloxy tail group [47]. Gallardo and his coworkers reported a polycatenar liquid crystals series based on bent shaped chalcone and cyanopyridine molecules [48]. Yahya et al. reported a series of azo-ester mesogens containing liquid crystalline acrylate having different terminal groups. They reported –OCH_3, –OC_2H_5 and –OCH_3 substituted compounds exhibited greater mesophase stability as compare to halogen (–F, –Cl, –Br) [49].

Recently, our research team reported different chalconyl ester based linear and nonlinear homologues series and observed the effect of increasing alkyl spacer at terminal group on mesomorphism [50–52]. Present work is planned to investigate a new chalconyl-ester based homologous series and study the effect of disubstituted octyloxy (-$OC_{18}H_{37}$) tail group on LC behaviour.

2. Experimental

2.1. Materials

For present synthesized homologous series required materials: 4-hydroxy benzaldehyde, alkyl bromide (R-Br) were purchased from Lancaster (England) and SRL (Mumbai), 3,4-dihydroxy acetophenone was purchased from (Sigma Aldrich), Malonic acid was purchased from (Sigma Aldrich), Anhydrous K_2CO_3 (Finar Chemicals, India), N,N-dimethyl amino pyridine (DMAP) and Dicyclohexylcarbodiimide (DCC) were purchased from Fluka Chemie (Switzerland). The solvents were dried and purified by standard method prior to use.

2.2. Measurements

Melting points were taken on Opti-Melt (Automated melting point system). The FT-IR spectra were recorded as KBr pellet on Shimadzu in the range of 3800–600 cm^{-1}. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyser. The texture images were studied on a trinocular optical polarising microscope (POM) equipped with a heating plate and digital camera. ^1H NMR spectra was recorded on a 500 MHz ^{1}NMR Bruker Advance- 400 in the range of 0.5 ppm-16 ppm using $CDCl_3$ solvent. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10°C min^{-1}. Texture image of nematic phase were determined by miscibility method, thermodynamic quantities enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed. For the POM study, novel synthesized compound is sandwiched between glass slide and cover slip and heating and cooling rate is (2°C /min) respectively.

2.3. Synthesis

Trans 4-n-alkoxy cinnamic acids **(B)** prepared by reported method [53]. 3,4-dioctadecyloxy acetophenone **(C)** was prepared by usual established method [54]. Chalcone was prepared by reported method [55]. Esters **(D)** were synthesized by a method reported in literature [56]. Thus, the chalconyl-ester homologue derivatives were filtered, washed with sodium bicarbonate solution, dried and purified till constant transition temperatures is obtain, using an optical polarizing microscope equipped with a heating stage. The synthetic route to a series is mentioned in scheme-1.

2.3.1. Synthesis of 4-n-alkoxy benzaldehyde (1a)

4-n-Alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with corresponding n-alkyl bromides (1 equiv.) in the presence of K_2CO_3 (1 equiv.) and dry acetone as a solvent [54].

2.3.2. Synthesis of trans 4-n-alkoxy cinnamic acid (1b)

The resulting 4-n-alkoxybenzaldehydes (1a) were reacted with Malonic acid (1.2 equiv.) in the presence of 1–2 drops piperidine as catalyst and pyridine (20 mL) as solvent, refluxing the reaction mixture 3 to 4 hours to yield corresponding *trans* 4-n-alkoxy cinnamic acids (1b), which was confirmed by IR study [53].

2.3.3. Synthesis of 3, 4-dioctyloxy acetophenone (1c)

3,4-dioctyloxy acetophenone was synthesized by refluxing 3,4 dihydroxy acetophenone (1 equiv.) with corresponding n-octadecyloxy bromides ($C_{18}H_{37}Br$) (2 equiv.) in the presence of Anhy.K_2CO_3 (1.2 equiv.) in dry acetone as a solvent [54].

2.3.4. Synthesis of chalcone (1d)

Chalcone (1d) was prepared by usual established method reported in literature [55]. (light yellow, Yield: 62%), IR (KBr): ν_{max}/cm^{-1} 3440 (–OH str.–bonded), 3079–3020 (–C–H str. aliphatic alkyl group), 1667 (–C=O, group), 1580–1610 (–C=C–) aromatic, 1280 (–O–CH_2– ether linkage), 962 (*trans*, (–CH=CH–) alkene). ^{1}HNMR: 0.88–0.90 (q, 6H, –CH_3 of polymethylene disubstituted –$OC_{18}H_{37}$), 1.26–1.43 (m, 58H, disubstituted –$OC_{18}H_{37}$), 4.08 (t, 4H, –OCH_2–CH_2– of di substituted –$OC_{18}H_{37}$), 5.28 (s, 1H, –OH group), 7.12 (d, 1H, –CH=CH–CO–), 7.56 (d, 1H, –CH=CH–CO–), 6.63–7.52 (4H, first phenyl ring), 7.67–7.16 (2H, second phenyl ring), 7.30 (s, 1H, second phenyl ring). Elemental analysis: calculated for $C_{51}H_{84}O_4$: C, 80.52; H, 11.05; O, 8.42%; found: C, 80.48; H, 10.98; O, 8.37%.

2.3.5. Synthesis of ester derivatives (C)

The compound has been prepared by esterification of the appropriate 4-n-alkoxy cinnamic acid (1b) (2.02 mmol) and chalcone (1d) (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 24 h. The slightly observed white precipitate of DCU is obtained which was isolated by filtration and removed, while the filtrate was evaporated to dryness. The resultant crude residue was purified by column chromatography on silica gel eluting with Ethyl acetate: Hexane (3:2) [56].

Comp.C_4: IR (KBr): v_{max}/cm^{-1} 3051 (C–H str. of alkane), 612 polymethylene–(CH_2)–$_n$ group of –OC_4H_9, 1640 (C=O str. of carbonyl carbon of chalconyl group), 1608 (C=C str. of alkene in chalcone), 1730 (ester, –COO– group), 1510, 1540 (–C=C str. of aromatic ring), 1171 (C–O str. of ether linkage), 1244 (C–O str. of carbonyl (>CO) group, 971 (*trans*, –CH=CH–) group, 770 polymethylene (–CH_2–) of side alkyl chain. ^{1}HNMR: 0.88–0.90 (t, 9H, –CH_3 of disubstituted –$OC_{18}H_{37}$ and monosubstituted –OC_4H_9), 1.26–1.43 (m, 58H, disubstituted –$OC_{18}H_{37}$), 1.76 (m, 6H, disubstituted –$OC_{18}H_{37}$ and monosubstituted –OC_4H_9), 4.06 (t, 6H, disubstituted –$OC_{18}H_{37}$ and monosubstituted –OC_4H_9), 7.62 & 6.30 (d, 2H, –CH=CH–COO–), 8.01 (d, 1H, –CH=CH–CO–), 7.42 (d, 1H, –CH=CH–CO–), 6.81 & 6.62 (4H, first phenyl ring), 7.21 & 7.70 (4H, second phenyl ring), 7.67 & 7.12 (3H, third phenyl ring), 7.32 (s, 1H, third phenyl ring). Elemental analysis: calculated for $C_{64}H_{98}O_6$: C, 79.83; H, 5.94; O, 7.48%; found: C, 79.73; H, 5.92; O, 7.39%.

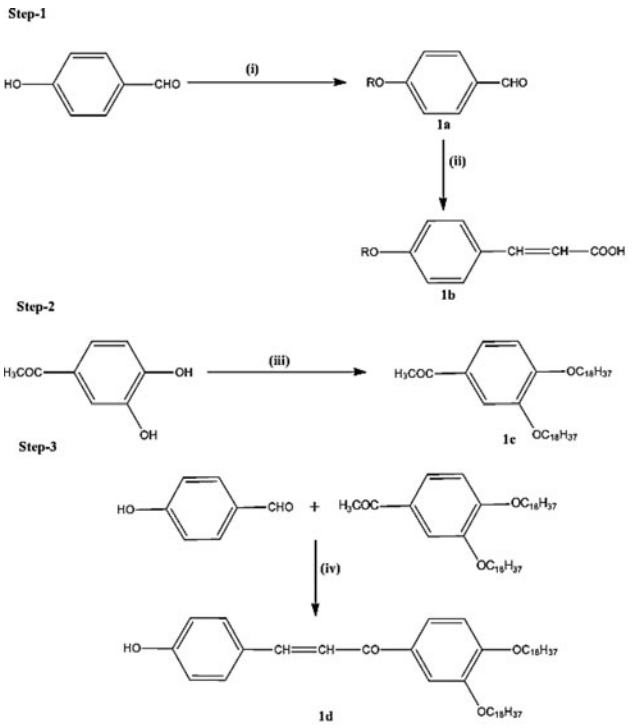
Comp.C_6: IR (KBr): v_{max}/cm^{-1} 2951 (C–H str. of alkane), 632 polymethylene group –$(CH_2$–$)_n$ of –OC_6H_{13}, 1640 (C=O str. of carbonyl carbon of chalconyl group), 1604 (C=C str. of alkene in chalcone), 1740 (ester, –COO– group), 1510 (C=C str. of aromatic ring), 991 (C–H bending of alkene), 1172 (C–O str. of ether linkage), 1284 (C–O str. of carbonyl (>CO) group, 971 (*trans*, –CH=CH–) group, 770 polymethylene (–CH_2–) of –$OC_{12}H_{25}$. ^{1}HNMR: 0.88–0.90 (t, 9H, –CH_3 of disubstituted –$OC_{18}H_{37}$ and monosubstituted –OC_6H_{13}), 1.26–1.43 (m, 60H, disubstituted –$OC_{18}H_{37}$), 1.76 (m, 6H, disubstituted –$OC_{18}H_{37}$ and monosubstituted –OC_6H_{13}), 4.06 (t, 6H, disubstituted –$OC_{18}H_{37}$ and monosubstituted –OC_6H_{13}), 7.61 & 6.30 (d, 2H, –CH=CH–COO–), 8.01 (d, 1H, –CH=CH–CO–), 7.42 (d, 1H, –CH=CH–CO–), 6.80 & 6.62 (4H, first phenyl ring), 7.21 & 7.69 (4H, second phenyl ring), 7.64 & 7.12 (3H, third phenyl ring), 7.32 (s, 1H, third phenyl ring). Elemental analysis: calculated for $C_{66}H_{102}O_6$: C, 80.0; H, 10.30; O, 9.69%; found: C, 79.95; H, 10.21; O, 9.64%.

Comp.C_{10}: IR (KBr): v_{max}/cm^{-1} 2954 (C–H str. of alkane), 643 polymethylene group –$(CH_2$–$)_n$ of –$OC_{10}H_{21}$ alkyl chain, 1640 (C=O str. of carbonyl carbon of chalconyl group), 1604 (C=C str. of alkene in chalcone), 1730 (–COO– group), 1510, 1543 (C=C str. of aromatic ring), 996 (C–H bending of alkene), 1178 (C–O str. of ether linkage), 1288, 1246 (C–O str. of carbonyl (>CO) group, 972 (*trans*, –CH=CH–) group, 770 polymethylene (–CH_2–) of

$-OC_{18}H_{37}$. ^{1}HNMR: 0.88–0.90 (t, 9H, $-CH_3$ of disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_{10}H_{21}$), 1.26–1.43 (m, 68H, disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_{10}H_{21}$), 1.76 (m, 6H, disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_{10}H_{21}$), 4.06 (t, 6H, disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_{10}H_{21}$), 7.61 & 6.30 (d, 2H, −CH=CH−COO−), 8.04 (d, 1H, −CH=CH−CO−), 7.42 (d, 1H, −CH=CH−CO−), 6.81 & 6.62 (4H, first phenyl ring), 7.20 & 7.70 (4H, second phenyl ring), 7.67 & 7.12 (3H, third phenyl ring), 7.32 (s, 1H, third phenyl ring). Elemental analysis: calculated for $C_{70}H_{110}O_6$: C, 80.30; H, 10.51; O, 9.17%; found: C, 80.24; H, 10.48; O, 9.07%.

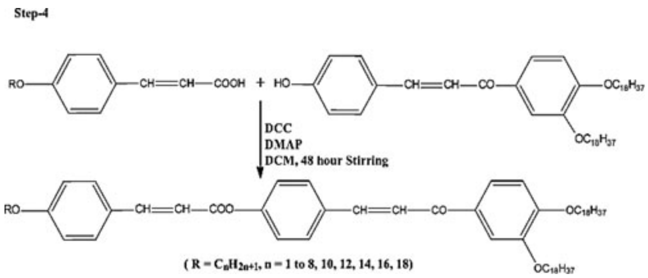
Comp.C_{18}: IR (KBr): v_{max}/cm^{-1} 2954 (C–H str. of alkane), 770 polymethylene $-(CH_2-)n$ group of $-OC_{18}H_{37}$ alkyl chain, 1610 (C=O str. of carbonyl carbon of chalconyl group), 1604 (C=C str. of alkene in chalcone), 1760 (–COO– group), 1510, 1543 (C=C str. of aromatic ring), 996 (C–H bending of alkene), 1171 (C–O str. of ether linkage), 1246 (C–O str. of carbonyl (>CO) group, 972 (*trans*, −CH=CH−) group. ^{1}HNMR: 0.88–0.90 (t, 9H, $-CH_3$ of disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_4H_9$), 1.26–1.43 (m, 78H, disubstituted $-OC_{18}H_{37}$), 1.76 (m, 6H, disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_{18}H_{37}$), 4.06 (t, 6H, disubstituted $-OC_{18}H_{37}$ and monosubstituted $-OC_{18}H_{37}$), 7.62 & 6.30 (d, 2H, −CH=CH−COO−), 8.01 (d, 1H, −CH=CH−CO−), 7.41 (d, 1H, −CH=CH−CO−), 6.81 & 6.62 (4H, first phenyl ring), 7.21 & 7.70 (4H, second phenyl ring), 7.67 & 7.12 (3H, third phenyl ring), 7.32 (s, 1H, third phenyl ring). Elemental analysis: calculated for $C_{78}H_{126}O_6$: C, 80.82; H, 10.88; O, 8.29%; found: C, 80.79; H, 10.82; O, 8.25%.

2.4 Reaction scheme



(i) R-Br, Anby.K_2CO_3, Dry Acetone, Reflux; (ii) Malonic acid, Pyridine, Piperidine, 3 to 4 hours stirring; (iii) $C_{18}H_{37}Br$, Anby.K_2CO_3, Dry Acetone, 6 to 7 hour reflux; (iv) KOH, EtOH, over night stiiring at room temperature.

Scheme 1. Synthetic route for derivatives of series-1.



Scheme 2. Synthetic route of series-1.

3. Result and discussion

Here in, we have synthesized newly chalconyl-ester based homologous series contain di substituted octadecyloxy ($-OC_{18}H_{37}$) side chain at tail group while left terminal part is varying. In the present investigation, we study the effect of linkage group and varying flexibility on mesomorphic behaviour of liquid crystalline compounds. The phase behaviour of all new synthesised compounds has been investigated by polarising optical microscope (POM) and confirm by using differential scanning calorimetry (DSC) analysis.

3.1. DSC analysis

DSC is a valuable method for the detection of phase transitions. The thermal behaviour of newly synthesized compounds was confirmed by using DSC measurement shown in Figure 1. The transition temperatures associated with enthalpy changes and entropy are mention below in Table 1. In present study, DSC thermogram is traces in heating condition. It can be seen that, two endothermic peaks are observed in present series at heating condition.

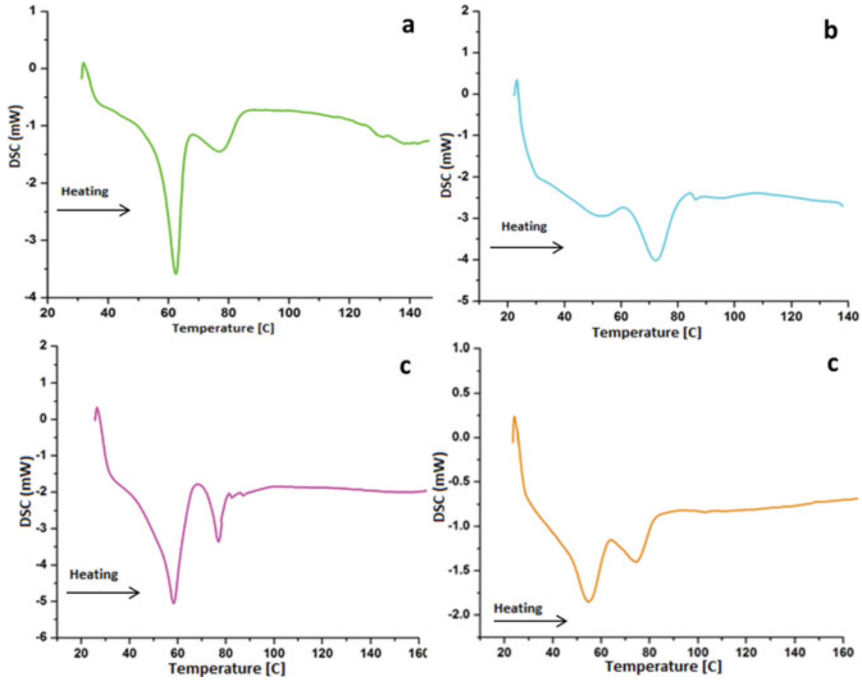


Figure 1. DSC thermogram of (a) comp.C_4; (b) comp.C_8; (c) comp.C_{10}; (d) comp.C_{12} on heating condition.

Table 1. Phase transition temperature (ºC) and enthalpy (J g^{-1}) and entropy change (J g^{-1}k^{-1}) by DSC measurement.

Comp.	Transition	Heating Peak temperature (ºC)	ΔH (−Jg^{-1})	ΔS (J g^{-1}k^{-1})
C_4	Cr-SmC	62.23	40.59	0.1210
	SmC-N	76.83	12.27	0.0350
	N-I	>130	—	—
C_8	Cr-SmC	52.80	52.81	0.1620
	SmC-N	72.23	72.23	0.2092
	N-I	>124	—	—
C_{10}	Cr-SmC	58.32	58.32	0.1760
	SmC-N	77.32	76.71	0.2189
	N-I	>116	—	—
C_{12}	Cr-SmC	54.73	16.10	0.0491
	SmC-N	74.45	11.10	0.0319
	N-I	>112	—	—

Compound C_4 shows first endothermic peak at 62.23°C, which indicates the presence of Cr-SmC mesophase and second endothermic peak observed at 76.83°C, which indicates the presence of SmC-N mesophase. By applying further heating, it is isotropic at >130°C. Compound C_8 shows two endothermic peaks at 52.8°C and 72.23°C on heating condition, which is nearly to the transition temperature observed by POM study. Compound C_{10} shows two endothermic peaks at 58.32°C and 77.32°C on heating condition to confirm the presence of SmC and N phase which was further confirmed by POM analysis. For compound C_{12}, the first endothermic peak trace at 54.73°C which shows the presence of SmC phase and on continue heating second endothermic peak trace at 74.45°C which specifies the presence of nematic mesophase in heating condition and transferred into isotropic at >112°C, which was further study by POM study. Transition temperature obtained by DSC analysis at heating condition and the value of enthalpy and entropy is shown in Table 1.

We measured the phase sequence of C_4 homologue which was confirmed by DSC analysis with presence of two endothermic peaks further confirmed by POM study. The observed textural image is the type of SmC and nematic phase which is mention in below Figure 2.

3.2. POM investigation

Transition temperatures (Table 2) obtained by optical polarising microscope (POM) equipped with a heating stage. The phase diagram plotted against transition temperatures versus the

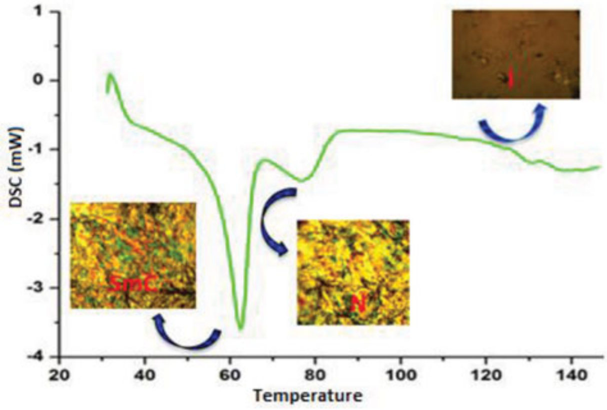


Figure 2. Phase sequence of comp. C_4 on heating condition.

Table 2. Transition Temperature in °C by POM.

		Transition temperatures in ^{0}C						
Sr.no	R = n-alkyl group	Cr		Smectic		Nematic		Isotropic
1	C_1	·	—	—	—	.	143.0	·
2	C_2	·	78.0	—	92.0	.	141.0	·
3	C_3	·	74.0	.	88.0	.	139.0	·
4	C_4	·	63.0	.	81.0	.	136.0	·
5	C_5	·	62.0	.	79.0	·	134.0	·
6	C_6	·	61.0	·	77.0	·	132.0	·
7	C_7	·	59.0	·	76.0	·	130.0	·
8	C_8	·	54.0	·	74.0	·	126.0	·
9	C_{10}	·	52.0	·	73.0	·	118.0	·
10	C_{12}	·	51.0	·	71.0	·	116.0	·
11	C_{14}	·	—	·	68.0	·	98.0	·
12	C_{16}	·	—	·	64.0	·	88.0	·
13	C_{18}	·	—	·	58.0	·	82.0	·

number of carbon atoms present in n-alkyl chain 'R' of left alkyl chain (-OR) group shown in Figure 3. Transition curve of Cr-I starts decreasing from lower homologue (C_1) to higher homologue (C_{18}). In present series, smectic and nematic mesophase commences from C_2 homologue. Sm-N transition curve shows decreasing tendency from C_2 homologue to C_{12} homologue respectively. Mesomorphic properties of present homologues series were varied by increasing left alkyl chain and keeping left unchanged terminal and lateral octyloxy ($-OC_{18}H_{37}$) group. The geometrical shape of molecule keeping unchanged throughout the series except changing of methylene carbon units in left side of alkoxy group (-OR). N-I transition curve starts decreasing from C_2 homologue and continued decreasing upto last C_{18} homologue. It can be noted that, transition temperature decrease when number of methylene $(-CH_2-)_n$ unit increase in alkoxy side chain. The higher homologues (C_{14} to C_{18}) displays nematic phase without exhibition of any smectic phase, this is due to the presence of more flexibility and linearity from both the end side alkoxy groups.

The molecular rigidity due to three phenyl rings and two central linking bridges are constant throughout the series, but the changing molecular length from homologue to homologue

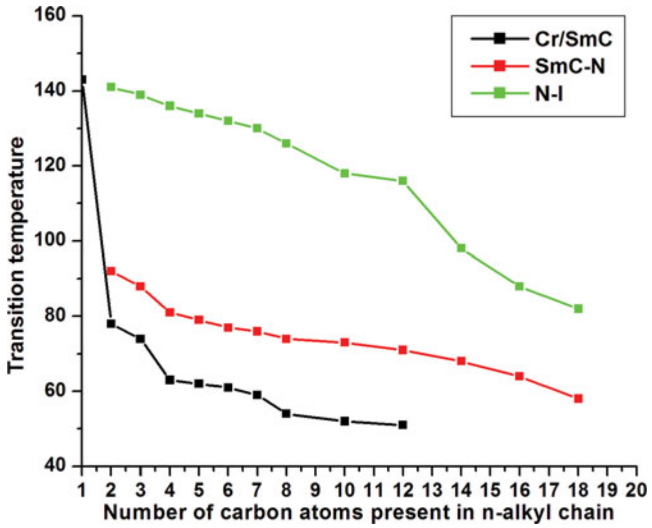


Figure 3. Phase diagram of series-1.

Table 3. Texture of Nematic Phase of C_6, C_{14}, C_7, C_{16} by miscibility method.

Sr. No.	Homologue	Texture
1	C_{10}	Threaded
2	C_{12}	Rod like
3	C_{14}	Threaded
4	C_{16}, C_{18}	Threaded

in the same series due to changing number of $(-CH_2-)_n$ units in alkoxy side chain induces different magnitudes of flexibility contribution to total flexibility including flexibility of common disubstituted octadecyloxy group present at the tail end. Thus, effective molecular flexibility occurred due to difference of polarities between two end groups plays the role for nematic mesophase formation. On the basis of these observations, we can say that moderate alkoxy side chain on tails groups may be anticipated as most appropriate to gain good mesophase stability.

In present article, we have synthesized total thirteen compounds, out of thirteen compounds, compound C_1 shows nonliquid crystal (NLC) behaviour and directly transform solid to isotropic liquid without exhibiting LC property, this is due to the presence of short alkyl spacer methoxy $(-OCH_3)$ group at left side part and low magnitudes of dispersion forces and lower magnitudes of dipole-dipole interaction and electronic vibrations cause high crystalline tendency to directly transform into isotropic mass by breaking of crystal lattices.

3.2.1. Nematic mesophase by miscibility method

The nematic mesophase were also confirmed by using miscibility method which was mention in below Table 3. Comp.C_{10} shows threaded type nematic phase whereas in comp.C_{12}, rod type textural pattern was seen. Comp. C_{14} homologue shows threaded type textural pattern of nematic phase. Comp.C_{16} to C_{18} shows threaded type textural pattern of nematic mesophase.

3.2.2. Textural study

The crystalline compounds placed on clear glass slide sheltered by coverslip were heated to the isotropic state and heating and cooling rate (2°C/min) respectively and observing mesophase texture image shown in Figure 4. POM observations reveal that comp.C_4 exhibited typical textural pattern of nematic phase at 81°C on heating condition. Comp. C_{10} display broken fan type textural pattern of SmC phase at 52°C on heating condition. Compound C_7 shows marble type textural pattern of SmC phase at 54°C on cooling condition. Compound C_{12} display grass like textural pattern of SmC phase at 51°C on heating condition. In cooling cycle, POM reveals the same textural pattern observed in between isotropic to solid crystal. From POM analysis, it is clear that the two peaks observed in DSC heating scan are due to crystal transformation into smectic phase and second peak correspondence to smectic to nematic phase.

We have measure the phase sequence of C_4 homologue on cooling condition as shown in Figure 5. (a) Isotropic mass at 136°C, (b) nematic mesophase start at 82°C, (c) nematic mesophase at 81°C, (d) cooling nematic mesophase upto 71°C, (e) nematic phase transform into SmC phase at 63°C, (f) solid crystals are appeared at room temperature. Observed phase sequence is repeated again during cooled condition and also confirmed by DSC analysis.

The absence of lamellar packing of molecules in their crystal lattice causes absence of smectogenic property in C_{14} to C_{18} homologues. The exhibition of nematic property (C_2 to C_{18}) by appropriate magnitudes of anisotropic forces end to end attractive cohesion and closeness of molecules in stastically parallel in floating conditions that directly associated to its rigidity as well as flexibility exposed thermal vibrations.

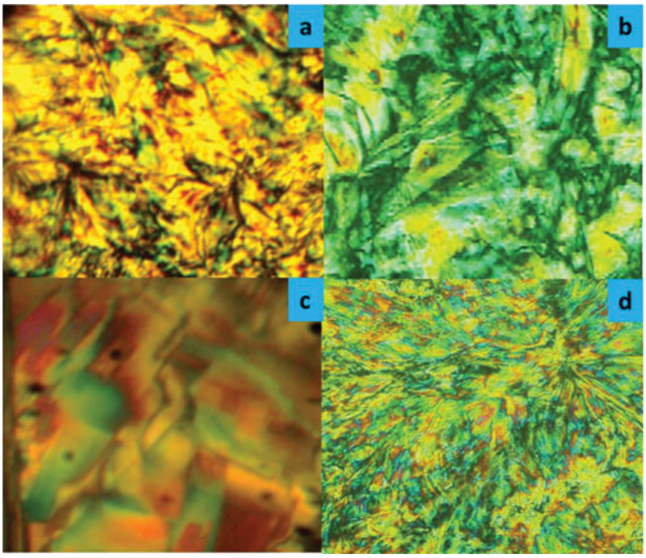


Figure 4. Mesomorphic textures of compounds obtained by POM (a) Nematic phase of C_4 homologue on heating. (b) SmC phase of C_{10} homologue on heating, (c) Sm C phase of C_7 homologue on cooling, (d) Sm C phase of C_{12} homologue on heating.

3.2.3. *Comparative study and thermal stability*

Here, we have compared the mesomorphic property of presently investigated series-1 with structurally similar series-A and series-B which was reported by our research group [59] shown in Figure 6.

Homologous series-1 and series-X, -Y are identical with respect to three phenyl rings and two central linkage group which joining the three phenyl rings. But, they differ with respect to each other at substitution on third phenyl ring. Therefore they differ with respect to combined effects of molecular rigidity and flexibility including intermolecular distance and molecular polarizability which operates LC behaviours of series. In series-1, one

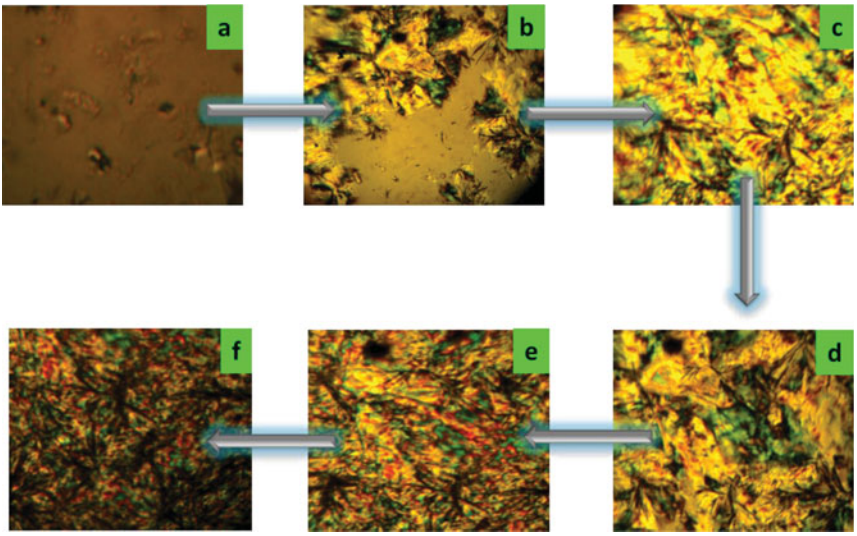


Figure 5. Phase sequence of C_4 homologue on cooling condition by POM.

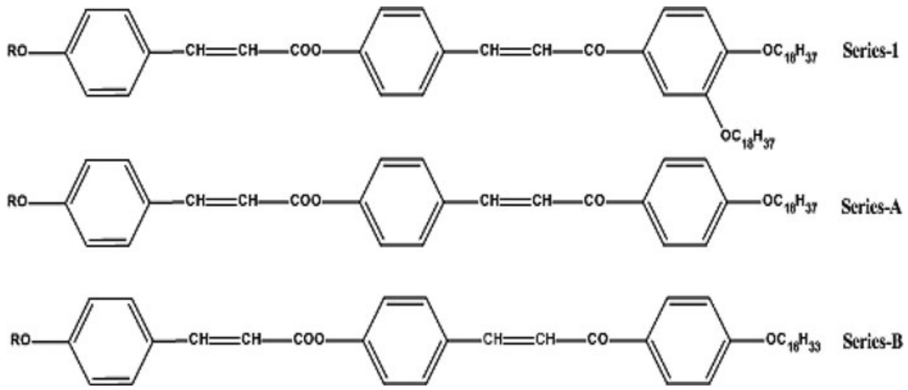


Figure 6. Structurally similar analogous series.

octadecyloxy ($-OC_{18}H_{37}$) side chain presence at lateral side as compare to series-A and series-B, which create more flexibility and vibration. Series-A and Series-B displayed nematogenic property without exhibition of smectogenic character. However, series-1 exhibited smectogenic as well as nematogenic property. In series-1, two octyloxy side chain are present at the tail group while in series-A and series-B, monosubstituted octadecyloxy ($-OC_{18}H_{37}$) and hexadecyloxy ($-OC_{16}H_{33}$) group are present on third phenyl ring.

Thus, variations in mesomorphic (LC) properties are ascribed to the magnitudes of differing features of (shapes and terminal end groups) each series for the same homologue and from lower homologue to higher homologue in the same series. Table 4 shows that smectic and nematic mesophase length as well as thermal stabilities of series-1, series-A and series-B.

Thermal stability of smectic phase is 79.0°C for series-1. Thermal stability of nematic phase of series-A is lower as compare to series-1 and series-B, while nematic mesophase commences early in series-1 as compare to series-A and series-B. Total degree of mesomorphism of series-1 is higher than series-A and series-B. The early or late commencement of mesophase depends upon the extent of molecular noncoplanarity caused by central linkage group and their magnitudes of polarity as well as polarizability.

The space-filling diagram indicate the energy minimize in series-1, series-A and series-B respectively (Figure 7). The geometrical shape of series-1 is nonlinear as compare to series-A and series-B, while the presence of more octyloxy side chain ($-OC_{18}H_{37}$) on third phenyl ring increases its polarity and flexibility. Therefore, it proves that they differ with respect to combined effects of molecular rigidity and flexibility, including intermolecular distance and molecular polarizability which operates LC behaviours of series. The addition of double bond ($-CH{=}CH-$) in the system increases the polarizability and molecular length of the molecule [60].

Table 4. Average thermal stability in °C.

Series	Series-1	Series-A	Series-B
Sm-N	79.0	—	—
Commencement of Smectic phase	(C_2-C_{12}) C_2		
N-I	120.0	113.14	121.88
Commencement of Nematic phase	(C_2- C_{18}) C_2	(C_6- C_{18}) C_6	(C_5- C_{18}) C_5
Degree of mesomorphism in °C from minimum to maximum	24.0 to 70.0 C_{18} C_4	10.0 to 26.0 C_8 C_{10}	04.0 to 34.0 C_{10} C_{16}

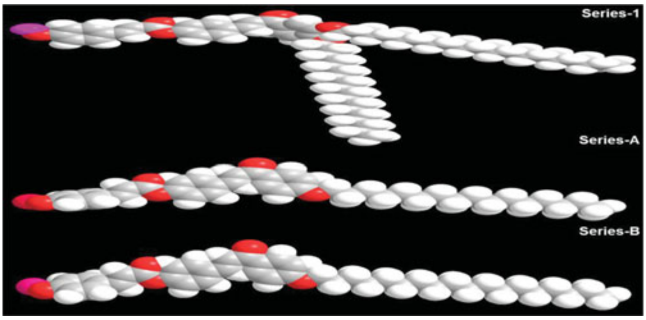


Figure 7. Space filling diagram of series-1 compared with series-X, -Y.

Conclusions

In summary, we have synthesised successfully a novel chalconyl vinyl ester based homologues series. We have found that the following synthesized homologous series shows smectic as well as nematic property. We have confirmed the mesogenic property for compounds by DSC and POM. For more progressive applications of LC phases, it is necessary to recognize more deeply the structure property relation as well as molecular origin of mesophases behaviour.

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