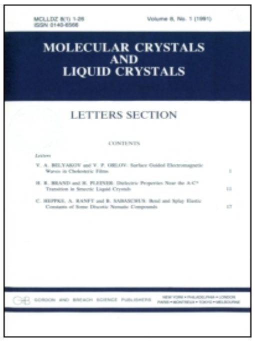
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Tuning the mesomorphic properties of nonisomeric chalconyl-ester bases homologous series: The effect of tail group

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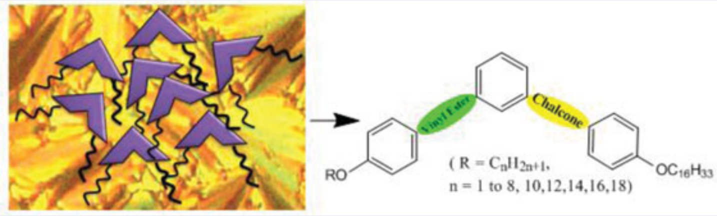
ABSTRACT

The mesomorphic properties of nonlinear chalconyl ester homologous series can be tuned in a predictable fashion with tail groups ($-OC_{16}H_{33}$) substituents on the terminal side. Novel series consisted thirteen members (C_1–C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}). C_1 to C_5 homologues are nonliquid crystal, C_6 to C_{14} homologues shows nematic mesophase enantiotropically, while C_{16}, C_{18} exhibits smectic as well nematic properties. The texture of the nematic mesophase is of fan shaped, schlieren and nematic droplets type. All these compounds were characterized by elemental analyses and spectroscopic techniques such as [FTIR] and ^1H Nuclear magnetic resonance [NMR] spectroscopy. The mesomorphic properties of these compounds were observed by optical polarized light microscopy (POM) and differential scanning calorimetry (DSC).

KEYWORDS
Enantiotropic; liquid crystal; nematic; smectic

GRAPHICAL ABSTRACT



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 oriented 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

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changed [5–7]. 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. 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 [8–10].

A number of chalcone having reported to exhibit a broad spectrum of anti-bacterial, antifungal, antiulcer, antimalarial, antitumor, anticancer, anti-inflammatory, and antitubercular [11–13]. 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 [14,15]. Thus, the object of work to synthesized and studied the effect of chalconyl-ester linkage group and geometrical shape on mesomorphism. Vorlander et al. reported bent-core liquid crystals and reported their mesogenic properties [16]. Matsunaga et al. reported first time on a series of bent-core molecule, as 1,3-phenylene bis[4-(4-n-octyloxyphenyliminomethyl) benzoate] derivatives [17]. In 1996, Niori et al. reported on ferro electricity in a smectic phase formed by bent-shaped Schiff base derivatives in an achiral mesogen [18]. Takezoe and Takanishi et al. reported chiral nonlinear optic effect shown in achiral bent-core molecules is due to interaction between polarity and chirality [19]. Ros et al. studied the banana shaped mesophases synthesization is based on the appropriate combination between rigid bent-core units with terminal side chain [20]. Subala et al. reported the same homologues series with the same core and increasing number of chain length are responsible in the contribution of the phase sequence B_6-B_1-B_2 [21]. 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 [22,23].

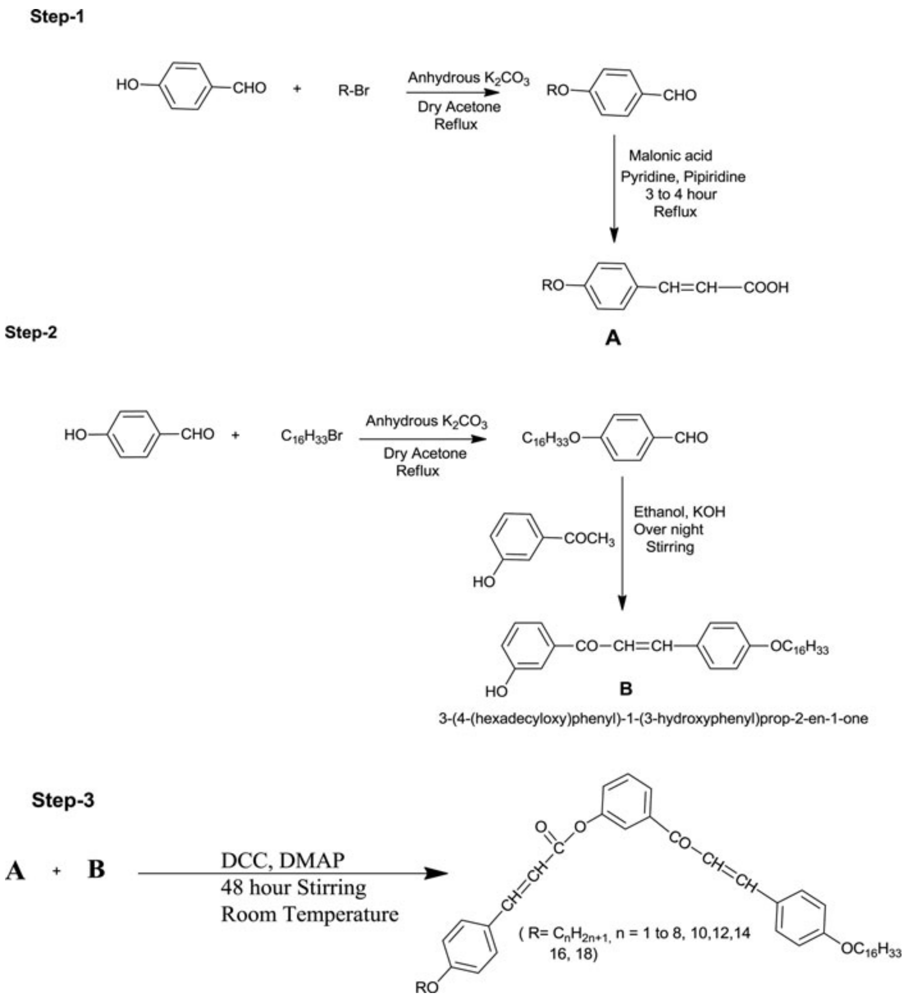
In present article, we are going to present nonlinear homologous series which consisted of three phenyl rings bonded through vinyl ester (-CH=CH-COO-) and chalcone (-CO-CH=CH-) central groups and varying left n-alkoxy terminal end group ($-OC_{16}H_{33}$). Doshi et al. synthesized and studied the molecular structure of LC property of chalconyl ester based homologous series [24, 25]. In previous work, we have demonstrated isomeric and nonisomeric homologues series with chalconyl ester linkage group [26,27]. Group efficiency order and structure relation with mesomorphism will be derived.

Experimental

Synthesis

The target chalconyl-ester compounds and their derivatives were synthesized as outlined in (Scheme-1). Trans 4-n-alkoxy cinnamic acids (**A**) were prepared by modified method of Dave et al. and Vora et al. [28]. 3-(4-(hexadecyloxy) phenyl)-1-(3-hydroxy phenyl prop-2-en-1-one) (**B**) was prepared by usual established method [29]. In the final step, Coupling of compound (**A**) and (**B**) is done by Steglich esterification to yield final product [30]. Thus, Chalconyl - Ester homologue derivatives were filtered, washed with sodium bicarbonate solution, dried and purified till constant transition temperatures using an optical polarizing microscope equipped with a heating stage. Alkyl halides, 3-hydroxy acetophenone, dicyclohexyl carbodimide (DCC), dimethyl amino pyridine (DMAP), dichloro methane, ethanol, acetone required for synthesis were 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.

Reaction scheme



Scheme 1. Synthesis route of series-1.

Characterization

Representative homologues series were characterised by elemental analysis, Infrared spectroscopy, ^{1}H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX, ^{1}HNMR spectra were recorded on Bruker using $CDCl_3$ as solvent. Microanalysis was performed on Perkin-Elmer PE 2400 CHN analyzer (Table 1). Texture image of some homologues for nematic phase were determined by miscibility method (Table 2). Transition temperature (Table 3) and LC properties (Textures) were determined using an optical polarizing microscopy equipped with heating stage. Decomposition temperatures (Table 4) were determined using of Shimadzu DSC 60 differential Scanning Calorimeter with a heating rate of 5 to 10.0 °C min^{-1} in air and it was calibrated with indium (156.6 °C, 28.45 Jg^{-1}) Holland. Thermodynamic quantities enthalpy (ΔH) and entropy (ΔS=ΔH/T) are qualitatively discussed. The mesophase and transition temperatures and enthalpies for all chalconyl-ester bases liquid crystals were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

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

		Elements % found			Elements % Calculated		
Sr. no.	Molecular formula	C	H	O	C	H	O
1	$C_{41}H_{52}O_5$	77.98	8.20	12.03	78.84	8.33	12.82
2	$C_{43}H_{57}O_5$	78.16	8.73	12.18	79.01	8.72	12.25
3	$C_{44}H_{59}O_5$	79.01	8.78	11.76	79.16	8.84	11.99
4	$C_{45}H_{61}O_5$	78.21	8.90	11.62	79.29	8.95	11.74
5	$C_{46}H_{63}O_5$	78.04	8.82	11.40	79.42	9.06	11.51

Table 2. Texture of nematic phase of C_8, C_{10}, C_{12}, $C1_6$ by miscibility method.

Sr. no.	Homologue	Texture
1	C_8	Threaded
2	C_{10}	Schlieren
3	C_{12}	Threaded
4	C_{16}	Schlieren

Analytical data

IR Spectra in cm^{-1} for heptyloxy (C_7), pentyloxy (C_5), decyloxy (C_{10}), hexadecyloxy (C_{16}), and octadecyloxy (C_{18}) derivatives

Heptyloxy (C_7): 721 Polymethylene group of (-CH_2-)n of –OC_7H_{15}, 833(–C-H- def. m di-substituted), 748 Polymethylene group of (-CH_2-) of –$OC_{16}H_{33}$, 941 (–C-H- def. hydrocarbon), 1076 and 1022(-C-O-) str, 1253, 1165 (-C-O) str in –(CH_2)n chain, 1446 and 1465 (-C-H- def. in CH_2), 1512 (-C=C-)str, 1662 (-C=O group), 1724 (-COO- ester group), 2812 and 2927 (aromatic -C-H str.), 3140, 3170 (=C-H str.), 975 (trans, -CH=CH-) group.

Pentyloxy (C_5): 740 Polymethylene group of (-CH_2-)n of –OC_5H_{11}, 648 Polymethylene group of (-CH_2-)n of -$OC_{16}H_{33}$, 810(–C-H- def. m di-substituted), 972 (–C-H- def. hydrocarbon), 1064 (-C-O-) str, 1381 and 1230, 1157 (-C-O str in –(CH_2)n chain, 1381 and 1442 (-C-H- def.

Table 3. Transition temperature in °C by POM.

		Transition temperatures in °C						
Sr. no	R = n-alkyl group	Cr	Smectic		Nematic		Isotropic	
1	C_1	·	—	—	—	—	136.0	·
2	C_2	·	—	—	—	—	134.0	·
3	C_3	·		—	—	—	130.0	·
4	C_4	·	—	—	—	—	121.0	·
5	C_5	·	—	—	—	·	106.0	·
6	C_6	·	—	·	98.0	·	108.0	·
7	C_7	·	—	·	92.0	·	98.0	·
8	C_8	·	—	·	90.0	·	102.0	·
9	C_{10}	·	—	·	82.0	·	94.0	·
10	C_{12}	·	—	·	86.0	·	93.0	·
11	C_{14}	·	—	·	80.0	·	92.0	·
12	C_{16}	·	69.0	·	78.0	·	88.0	·
13	C_{18}	·	52.0	·	69.0	·	80.0	·

Table 4. Thermal stability comparison of Sm-N and N-I in series-1 and series-X.

Series	Series-1	Series-X
Sm-I or Sm-N or N-Sm Commencement of Smectic phase	73.5 (C_{16} - C_{18}) C_{16}	—
N-I or I-N Commencement of Nematic phase	94.37 (C_6- C_{18}) C_6	104.5 (C_6- C_{18}) C_6
Total mesophaselength from t_1°C to $t_{2°}$C	06.0°C to 28.0°C C_7 C_{18}	13.0°C to 37.0°C C_{10} C_6

in CH_2),1504 -C=C-)str, 1604 and 1658 (-C=O group), 1724 (-COO- ester group), 2854 and 2924(-C-H str in CH_3), 972 (trans, -CH=CH-) group.

Decyloxy (C_{10}): 763 Polymethylene group of (-CH_2-)n of –$OC_{10}H_{21}$, 640 Polymethylene group of (-CH2-)n of –$OC_{16}H_{33}$, 833(–C-H- def. m di-substituted), 941 (–C-H- def. hydrocarbon), 1056 (-C-O-) str, 1373 and 1303 and 1249, 1165 (-C-O str in –(CH_2)n chain, 1388 and 1468 (-C-H- def. in CH_2),1512 (-C=C-)str, 1640 and 1660 (-C=O group), 1760 (-COO- ester group), 2854 and 2916 (-C-H str in CH_3), 972 (trans, -CH=CH-) group.

Hexadecyloxy (C_{16}): 643 Polymethylene (-CH_2-)n of –$OC_{16}H_{33}$, 640 Polymethylene group of (-CH2-)n of –$OC_{16}H_{33}$, 833(–C-H- def. m di-substituted), 941 (–C-H- def. hydrocarbon), 1056 (-C-O-) Str, 1373 and 1303 and 1249, 1165 (-C-O str in –(CH_2)n chain, 1388 and 1468 (-C-H- def. in CH_2),1512, 1562 (-C=C-)str, 1608 and 1661 (-C=O group), 1760 (-COO- ester group), 2854 and 2916 (-C-H str in CH_3), 971 (trans, -CH=CH-) group.

Octadecyloxy (C_{18}):621 Polymethylene (-CH_2-)n of –$OC_{18}H_{37}$, 640 Polymethylene group of (-CH_2-)n of –$OC_{16}H_{33}$, 833(–C-H- def. m di-substituted), 941 (–C-H- def. hydrocarbon), 1056 (-C-O-) str, 1373 and 1303 and 1249, 1165 (-C-O str in –(CH_2)n chain, 1380 and 1462 (-C-H- def. in CH_2),1512 (-C=C-) str, 1604 and 1660 (-C=O group), 1735 (-COO- ester group), 2854 and 3024(-C-H str in CH_3), 972 (trans, -CH=CH-) group.

^1H NMR spectra in $CDCl_3$ in δ ppm for methoxy (C_1), heptyloxy (C_7), octyloxy (C_8), decyloxy (C_{10}), and dodecyloxy (C_{12}) derivative

Methoxy (C_1): 0.88 (t, 3H, -CH_3 of –$C_{16}H_{33}$), 1.26 (m, 2H n-poly methylene groups of-$OC_{16}H_{33}$),1.75 (m, 2H, n-poly methylene groups of –$OC_{16}H_{33}$), 1.29 (p, 10 H of –$OC_{16}H_{33}$ group), 3.81 (s,-O-CH_2-CH_3-of –OCH_3), 4.06 (t,3H,-O-CH_2-CH_2-of –$OC_{16}H_{33}$), 6.93-6.95 (d, 1H, J = 15.6 Hz, -CO-CH=CH-), 7.53-7.55 (d, 1H, J = 15.6 Hz, -CO-CH=CH-), 7.28-7.31 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.50 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.92 and 7.62-7.62 (d, 4H, left side phenyl ring), 7.74 and 8.58, 8.41 (3H, central phenyl ring), 7.62-7.62 and 6.94-6.92 (d, 4H, terminal phenyl ring).

Heptyloxy(C_7): 0.88-0.90 (t, 6H, -CH_3 of –OC_7H_{15} and –$OC_{16}H_{33}$), 1.26 (m, n-poly methylene groups of -$OC_{16}H_{33}$), 1.31 (q, 8H, -CH_2 of –OC_7H_{15} and –$OC_{16}H_{33}$), 1.29 (P, 10 H of –OC_7H_{15} and –$OC_{16}H_{33}$ group), 1.75 (m, n-poly methylene groups of –OC_7H_{15}), 3.5-3.6 (s,-OCH_2-CH_2-of-$OC_{16}H_{33}$), 4.06 (t,6H,-O-CH_2-CH_2-of –OC_7H_{15} and -$OC_{16}H_{33}$), 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, 4H, left side phenyl ring), 7.71 and 8.56, 8.41 (3H, central phenyl ring), 7.60-7.61 and 6.95-6.92 (d, 4H, terminal phenyl ring).

Octyloxy (C_8): 0.88 (t, 6H, -CH_3 of –OC_8H_{17} and –$OC_{16}H_{33}$), 1.2-1.3 (m, n-poly methylene groups of –OC_8H_{17} and -$OC_{16}H_{33}$), 1.29 (P, 10 H of –OC_8H_{17} and –$OC_{16}H_{33}$ group), 1.74-1.76 (m, n-poly methylene groups of –OC_8H_{17} and -$OC_{16}H_{33}$), 4.06 (t,6H,-O-CH_2-CH_2-of –OC_8H_{17} and –$OC_{16}H_{33}$), 6.92-6.95 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.52-7.55 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.28-7.31 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.50 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.90 and 7.61-7.62 (d, 4H, left side phenyl ring), 7.74 and 8.58, 8.41 (3H, central phenyl ring), 7.62-7.60 and 6.95-6.92 (d, 4H, terminal phenyl ring).

Decyloxy (C_{10}): 0.88 (t, 6H,-CH_3 of –$OC_{10}H_{21}$ and –$OC_{16}H_{33}$), 1.2-1.5 (m, n-poly methylene groups of –$OC_{10}H_{21}$ and -$OC_{16}H_{33}$), 1.29 (P, 10 H of –$OC_{10}H_{21}$ and –$OC_{16}H_{33}$ group), 1.31 (q, 8H of 1.80 (m, n-poly methylene groups of –$OC_{10}H_{21}$ and –$OC_{16}H_{33}$), 4.06 (t,6H,-O-CH_2-CH_2-of –$OC_{10}H_{21}$ and –$OC_{16}H_{33}$), 6.93-6.95 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.53-7.55 (d, J = 15.6 Hz1H, -CO-CH=CH-), 7.28-7.31 (d, J = 15.2 Hz, -CH=CH-COO-), 6.50 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.92 and 7.62-7.62 (d, 4H, left side phenyl ring), 7.74 and 8.58, 8.40 (3H, central phenyl ring), 7.62-7.61 and 6.94-6.92 (d, 4H, terminal phenyl ring).

Dodecyloxy (C_{12}): 0.88 (t, 6H, -CH_3 of –$OC_{12}H_{25}$ and –$OC_{16}H_{33}$), 1.2-1.5(m, n-poly methylene groups of –$OC_{12}H_{25}$ and -$OC_{16}H_{33}$), 1.81 (m, n-poly methylene groups of –$OC_{12}H_{25}$ and –$OC_{16}H_{33}$), 1.29 (P, 10 H of –$OC_{12}H_{25}$ and –$OC_{16}H_{33}$ group), 1.31 (q, 8H of 1.80 (m, n-poly methylene groups of –$OC_{12}H_{25}$ and –$OC_{16}H_{33}$), 4.06 (t, 6H,-O-CH_2-CH_2-of -$OC_{12}H_{25}$ and –$OC_{16}H_{33}$), 6.93-6.95 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.53-7.55 (d, J = 15.6 Hz, 1H, -CO-CH=CH-), 7.28-7.31 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.50 (d, J = 15.2 Hz, 1H, -CH=CH-COO-), 6.94-6.92 and 7.62-7.62 (d, 4H, left side phenyl ring), 7.74 and 8.58, 8.41 (3H, central phenyl ring), 7.62-7.61 and 6.95-6.92 (d, 4H, terminal phenyl ring).

Result and discussion

POM investigation

Presently, we have synthesized nonlinear homologous series by the condensation of Trans 4-n-alkoxy cinnamic acid and α-3-Hydroxy benzoyl β-4′-n-hexadecyloxy phenyl ethylene (chalcone). Here in present article, we prepared thirteen homologue (C_1 to C_8, C_{12}, C_{14}, C_{16}, C_{18}) in which C_1 to C_5 homologues are non LCs while C_6 to C_{18} shows LCs property at heating and cooling condition. Mesomorphism commences in homologues series from C_6 homologue to last C_{18} homologue as enantiotropically manner respectively. Transition temperatures (Table 2) determined by polarization optical microscope were plotted against 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 Cr-I, Cr-Sm, N-I transition curve drawn by linking like or related transition points as shown in (Fig. 1). In present case, we have studied the effect on liquid crystalline property by geometrical shape and flexibility due to present long chain at terminal side (-$OC_{16}H_{33}$) at right side and varying left alkoxy side chain. Cr-I curve falling as series is increased with number of methylene unit linked in it and ascended at dodecyloxy (C_{12}) homologue attributable to abnormality and continued to descend upto C_{18} homologue. The smectic to nematic transition curve falls in descended manner from C_{16} to C_{18} homologue, because of increasing number of methylene units which induce smectic mesophase. Nematic-isotropic phase transition curve descending at C_7 homologue and falling at C_8 homologue, this is due to odd and even parity of carbon present in alkyl chain and continued decreasing up to last C_{18} homologue respectively. While increasing number of carbon it behaves due to fairly abnormality from dodecyloxy to octadecyloxy derivative.

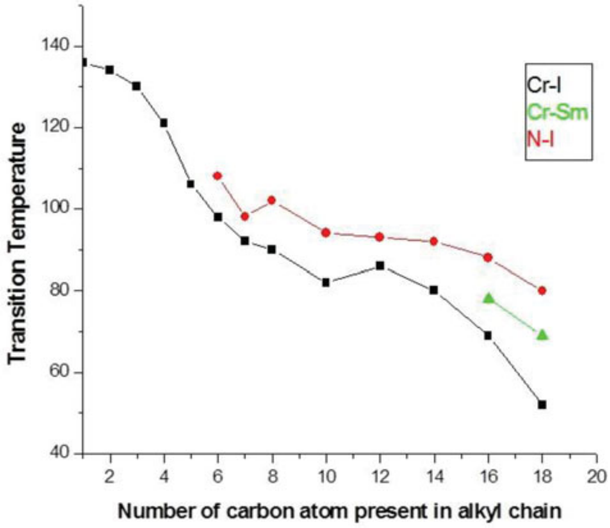


Figure 1. Phase diagram of series by POM.

The mesogenic properties are varying from homologue to homologue in same series because of added methylene group in left side of n-alkoxy terminal side chain. The presence of odd-even effect in (N-I) curve diminishes as series is increase beyond C_{18} homologue.

The absence of mesomorphism in C_1 to C_5 homologue, due to absence of lamellar packing of molecules in their solid crystal lattices at solid from and after applying heating, unsuitable magnitudes of intermolecular anisotropic forces of lateral attractions which hinders to maintain sliding moving layered of molecules on the surface under exposed thermal vibrations at floating condition. As increasing the numbers of carbon in side chain moving of sliding arrangement of molecules causes smectic mesophase (fan and needle) C_{16},C_{18} homologue. The exhibition of nematogenic mesophase for definite range of temperature in C_6 to C_{18} homologue is attributed to the suitable magnitudes of anisotropic forces of intermolecular attractions due to fittest magnitudes of molecular polarity and polarizability, permanent dipole-moment across long molecular axis with increasing chain, dispersion forces, etc. as a consequence of favourable molecular rigidity and flexibility which facilitated statistically parallel orientational order of molecules in floating condition on the surface to cause nematic mesophase (threaded and schlieren type) in the presence of thermal energy.

Texture images of comp.C_{10}, C_{12}, C_{18}, and C_{16} are mention in Fig. 2, for C_{10} homologue, the schlieren type texture image observed at 82 °C, (b) schlieren type texture of C_{12} homologue at 82 °C, (c) fan type texture of smectic phase observed for C_{18} homologue at 52 °C, (d) broken fan texture of smectic phase of C_{16} homologue at 69 °C at heating and cooling conditions, respectively.

Some LC properties evaluated from thermotropic data of presently novel series-1 and compared with structurally similar analogous series X [31] and Y [32] as shown in (Fig. 3). The geometrical shape of both the series are equal. However, the linearity of the both series are different with first linking group so their magnitudes of combined effects of molecular rigidity and flexibility change by –CH=CH- group more in series-1. Therefore magnitudes of molecular rigidity and flexibility of left side chain undergo variations but flexibility at tail group remains unaltered for the same homologue from series-1 and series X, respectively.

Figure 4 represents the space filling diagram of both the series. The trans isomer of chalcone is form by reaction of 3-hydroxy acetophenone with 4-hexadecyloxy benzaldehyde which was

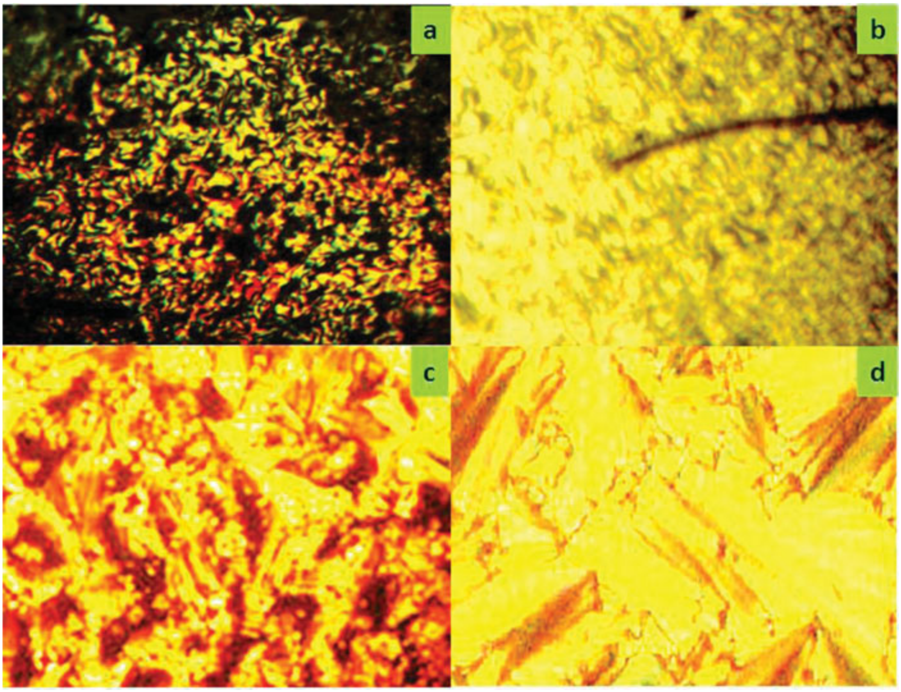


Figure 2. Texture of series-I observed between cross polarizers: (a) nematic phase of C_{10} homologue at 82 °C; (b) nematic phase of C12 homologue at 86 °C; (c) SmC phase of C18 homologue at 52 °C, (d) SmC phase of C16 homologue at 69 °C.

confirmed by IR. Chalcone linkage group is present in both series with unaltered flexibility at terminal side chain group.

Some physical thermometric properties are mentioned in (Table 4) for the analogous series under comparative study. Thermal stability of nematic is 94.37 which is lower than the series X, this is due to present of –COO- central group in place of –CH=CH-COO- central linkage which effectively contribute to molecular rigidity and flexibility due to decreases in length by the absence of –CH=CH- unit and increases suitable magnitudes of intermolecular end to end attractions and closeness. Thus, transition temperature and hence the thermal stability for nematic are higher in series X as compare to series 1. However, the total mesophaselength

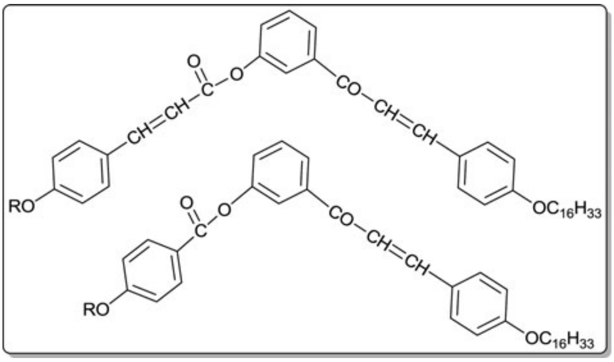


Figure 3. Structurally similar series-1 and series-X.

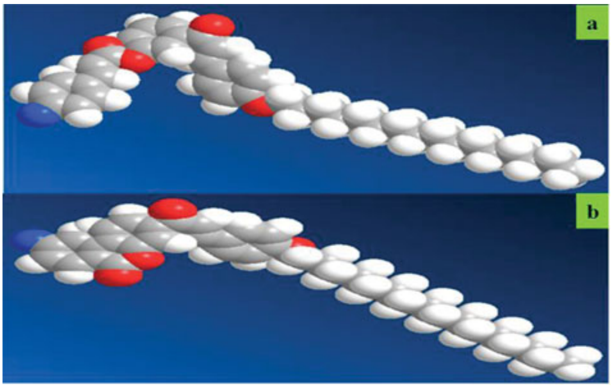


Figure 4. Space filling model of (a) series-1 and (b) series-X.

of series X is higher than series 1. The Sm-N thermal stability of series 1 is 73.5. An exhibition of smectic phase in series 1, due to suitable magnitudes of anisotropic forces in presence of –CH=CH- causes trans isomerism which facilitate to induce intermolecular cohesions and closeness as a consequence of favourable magnitudes of molecular rigidity and flexibility cause by presence of long side hexadecyloxy, octadecyloxy chain at left ending side and unaltered terminal side chain (-$OC_{16}H_{33}$). The early or late commencement of mesomorphism depends upon the extent of molecular noncoplanarity. The late commencement of smectic phase in present synthesized series may be due to deteriorating of the lateral attractions because of the disproportionate length to breadth ratio, rigidity in higher homologues C_{16}, C_{18}. Gray et al. [32] explained that the addition of the double bond to the system increases the length and polarizability of rod like molecules. Therefore, the greater molecular length ratio and polarizability of the molecule resulting from additional –CH=CH- units in the central linkage.

DSC study

DSC is a valuable method for detecting phase transitions. The thermal behaviour of novel homologues series were confirmed by using DSC measurement shown in (Fig. 5). Thermogram is traces in both heating and cooling condition. For C_{18} homologue, heating condition first endothermic peak at 47.24 °C, which indicates the presence of SmC phase shown in texture image. That was observed by POM study. While second endothermic peak observed at 74.21 °C, which indicates the presence of nematic phase, cooled condition again two endothermic were traces at 44.64 °C and 72.12 °C. C_7 homologue, only one significant peak is observed at 92.18 °C, while in cooling stage it trace at 94.67 °C. In C_{12} homologue, endothermic peak observed at 88.78 °C confirmed the presence of nematic phase confirmed by POM study while at cooled condition endothermic peak trace at nearly 90.52 °C. For C_8 homologue, it was observed that no smectic phase is present by POM analysis which was confirmed by DSC measurement. One significant peak is observed at heating and cooling condition, at heating condition endothermic peak observed at 92.18 °C and cooling condition endothermic peak traces at 96.10 °C, respectively. Thus, chalconyl-ester based nonlinear compound displays lower melting type mesomorphism. In addition, presently homologues series shows LCs property at low temperature.

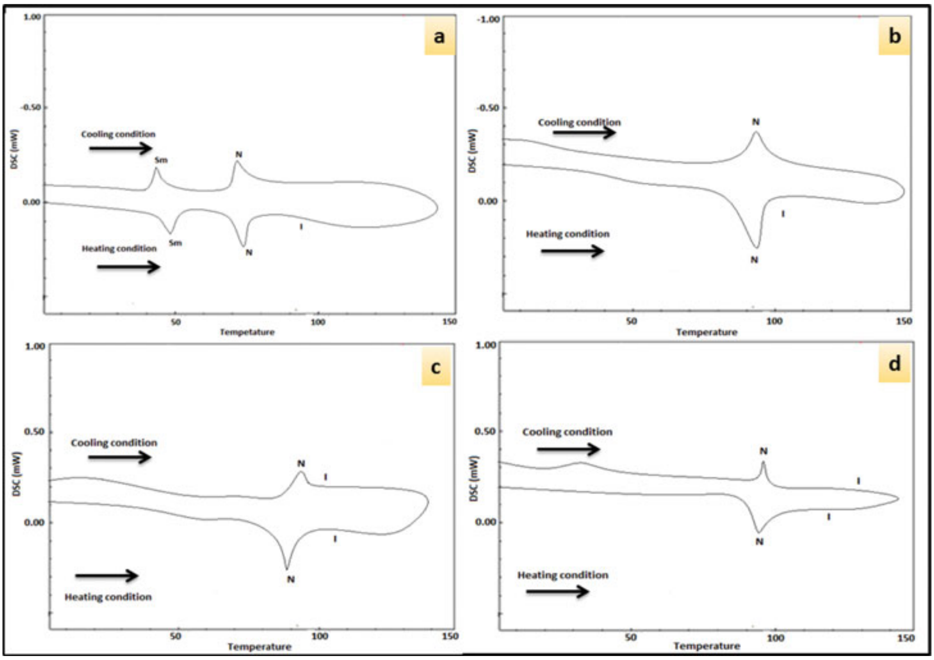


Figure 5. DSC measurement (a) C_{18} homologue (b) C_7 homologue (c) C_{12} homologue (d) C_8 homologue.

Transition temperature obtained by DSC analysis at heating and cooling condition and the value of enthalpy and entropy is mention in (Table 5). Molecules of every homologue 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 mesophase obtained enantiotropically manner in present series is smectogenic and nematogenic, respectively.

The proposed molecular packing of the smectic C phase is given in (Fig. 6). The arrangement of molecule is nonisomeric bent type shape. This is due to the molecular packing of the

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

Homologues or Comp.	Transition	Heating scan (°C)	Cooling scan (°C)	ΔH (-Jg^{-1})	ΔH (Jg^{-1})	ΔS(J $g^{-1}k^{-1}$)	ΔS(J $g^{-1}k^{-1}$)
C_{18}	Cr-SmC	47.24	44.64	2.17	4.26	0.0067	0.0134
	SmC-N	74.21	72.12	30.24	23.67	0.0870	0.0685
	N-I	>79.86	—	20.12	—	0.0563	—
C_7	Cr-N	92.18	94.67	38.92	30.90	0.1065	0.0840
	N-I	>98.21	—	10.21	—	0.0275	—
C_{12}	Cr-N	88.78	90.52	43.26	42.54	0.1195	0.1203
	N-I	>93.20	—	14.25	—	0.0393	—
C_8	Cr-N	92.18	96.10	41.23	39.69	0.1129	0.1075
	N-I	>101.01	—	23.62	—	0.0631	—

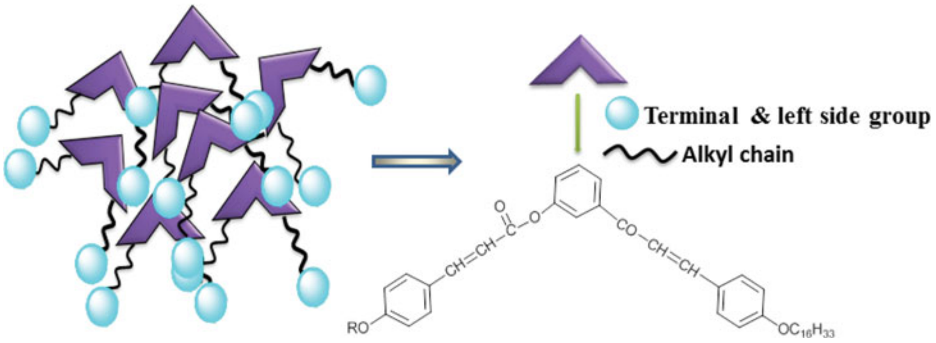


Figure 6. Proposed molecular packing of the Sm C phase in present series.

alkyl chains with linking groups oriented tilted way directions in smectic layers structure and effect of flexibility to induce smectic mesophase.

Conclusions

In this article we have presented the synthesis and characterization of novel nonlinear homologous series having chalconyl-ester central group with benzene core. C_1 to C_5 do not exhibit LC behaviour due to high crystallising tendency, while rest of homologues shows lower melting type mesomorphism. The group efficiency order derived on the basis of thermal stability, early commencement of mesophase, upper and lower mesophaselength. Tail ended n-alkoxy group can induce mesomorphism in chalconyl-ester homologous series. The mesomorphism was confirmed by POM, DSC. Present study supported and raised the credibility to the conclusions drawn earlier.

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