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# Synthesis, mesomorphic properties and biological evolution of calamitic-shaped chalcone-based LCs: effect of lateral and terminal group

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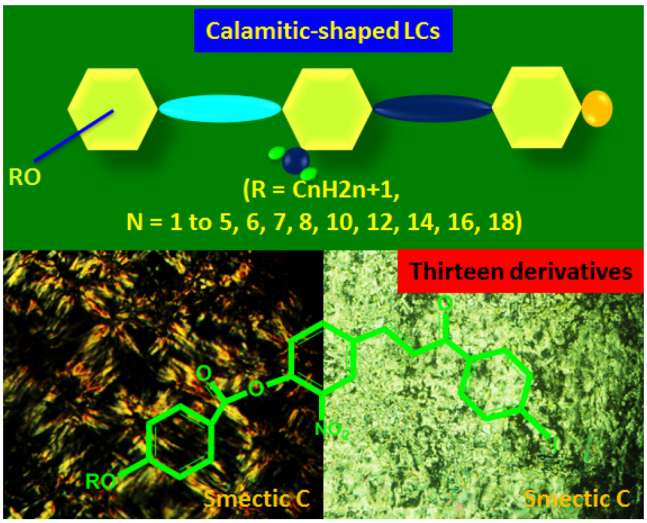
**ABSTRACT**

The mesomorphic properties of linear shaped homologous series based on two linkage group have been designed and synthesized with different side chain substituents (-OR) on the one end of terminal side with presence of lateral nitro group and second terminal iodo substituted group. Novel series consists thirteen members ($C_1$ to $C_8$, $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$). Compounds ($C_1$ to $C_6$) showed nonliquid crystalline properties while compound ($C_7$ to $C_{18}$) displayed smectic and nematogenic mesophase properties. The textures of smectic C and nematic phase are fan, schlieren and droplets type. All these compounds were characterized by spectroscopic techniques such as [FTIR] and $^1$H Nuclear magnetic resonance [NMR] spectroscopy. The mesomorphic properties of these compounds were observed by POM and further confirmed by DSC and XRD. Chalconyl ester based compounds ($C_3$ to $C_{12}$) shows good antibacterial as well as antifungal activity compared with corresponding standard drugs.




**KEYWORDS**

Chalcone; enantiotropic; mesogens; nematic; smectic C

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## 1. Introduction

Liquid crystal (LC) is an intermediate state of a matter in between the liquid and the crystal behaving with some typical properties of a liquid as well as some crystalline properties. There are many kinds of LC materials with different molecular structures, based on which LC could be divided into three categories, that is, calamatic liquid crystal, bent-shape liquid crystal and discotic liquid crystal. Calamatic LCs materials are widely used in a flat-panel display, smart windows, laser and other photonics. Liquid crystalline (LC) chalconyl ester derivatives play dual role useful in LC devices and pharmaceutical preparation and therapeutically treatment to cure diseases within definite range of concentration in solution state [1–5]. 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 [6–14].

Chalcone is an important class of chemical compound and is being studied extensively because of its significant use or application in various sectors. In the fields of biology and biochemistry, chalcone has been claimed to be one of the compounds that plays a vital role in anti-tumor [15,16], anti-inflammatory [17,18], and anti-malarial [19] activities. It has also been documented that the chalcone possesses a remarkable nonlinear optical (NLO) property, which is an essential element for optical communication devices [20]. The other importance of this compound is its high photosensitivity and thermal stability, which are used in development of various crystalline electro-optical devices [21–23]. The effects of laterally substituted group on mesogens are considerable interesting because these compounds deviate from the classical rod-like shape [24–31].

In literature, similar homologous series based on ester-chalcone groups has been reported till the date. R.Gopalakrishnan et al. reported chalcone based single crystals, growth, and comparison of two new enone shifted chalcones and their NLO behavior [32]. Tandel et al. studied the chain chalconyl polymers compounds to exhibiting threaded type nematic phases [33]. Doshi et al. reported chalconyl ester and chalconyl vinyl ester linkage group inbuilt between three phenyl rings and studied the effect on mesomorphism by substituted groups at terminal and lateral side [34,35]. Shah et al. studied a nonlinear homologous series based on ester and chalcone linkage group [36]. Patel et al. reported rod type homologous series having chalconyl ester central linkage group and hexyloxy tail group [37].Gallardo and his coworkers reported polycatenar liquid crystals series based on bent shaped chalcone and cyanopyridine molecules [38]. S.Kumar et al. reported chalcone based LCs compounds possessing short alkyl chain at one end and other end with variable chain lengths. These derivatives were reported to exhibit SmC, SmA and nematic phase [39]. Rai et al. reported unsymmetrical liquid crystalline compounds based on chalcones and 3,5-disubstituted isoxazoles derivatives [40]. Karawi et al. reported chalcone based pyrazoles liquid crystals and also studied their photo-luminescent behaviors [41]. On continues working on to design chalcone based LCs, we have reported homologous series based on three phenyl rings bonded through –CH = CH-COO- and –CO-CH = CH- linking groups as well as varying left n-

alkoxy terminal end group and a fixed tail part at right side ended group and various halogen group [42–47]. Very recently, we have reported chalcone biphenyl amine functionalized calixarene based blue-light emitting supramolecular liquid crystal and investigated their OLEDs application [48].

In present research article, we have planned to synthesized chalcone-based homologues series and study the effects of tail group (-OR) and lateral group (-$NO_2$) on LCs properties of present synthesized iodo based mesogens. Further, the structure-function relationship was further studied with structural similar reported series by our group. The liquid crystalline behavior is preliminary checked by polarizing optical microscopy (POM) and further confirmed by differential scanning calorimetry (DSC) and PXRD analysis respectively. In the present synthesized few selected derivatives showed good antibacterial and antifungal activity.

## 2. Experimental

### 2.1. Materials

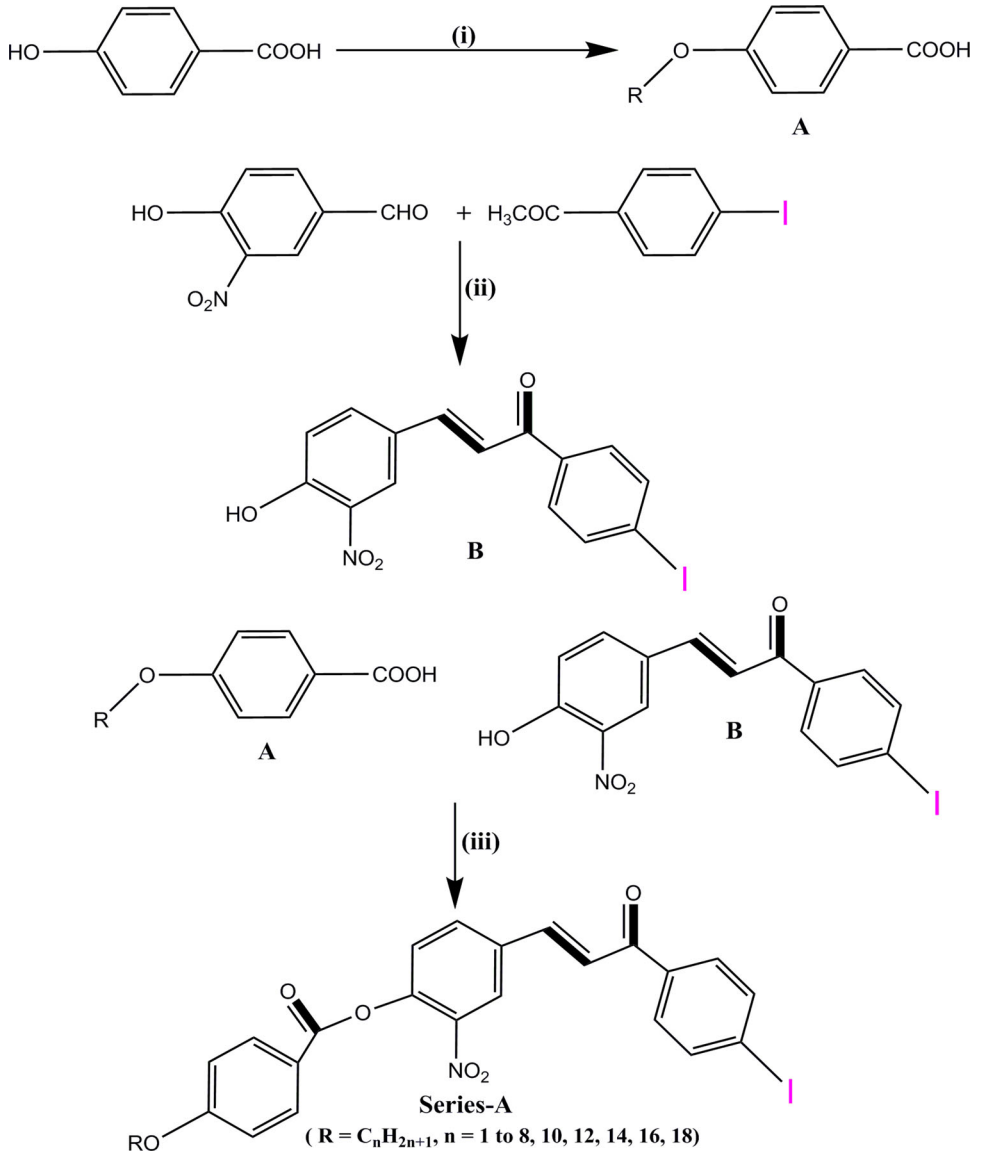
For present synthesized homologous series required materials: 4-iodo acetophenone, 4-hydroxy benzoic acid, (Lancaster, England, SRL Mumbai), 2-nitro, 4-hydroxy benzaldehyde was purchased from (Sigma Aldrich), Anhydrous $K_2CO_3$, KOH were purchased from (Finar Chemicals, India), N,N-dimethyl amino pyridine (DMAP) and Dicyclohexylcarbodiimide (DCC) was purchased from Fluka Chemie (Switzerland). R-Br (alkyl halide) ($R = C_nH_{2n+1}$, $n = 1$ to 8, 10, 12, 14, 16, 18) were purchased from S.R.L. Chemicals (Mumbai). 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 analyzer. The texture images were studied on a trinocular optical polarizing microscope (POM) equipped with a heating plate and digital camera. $^1H$ NMR spectra and $^{13}C$ NMR were recorded on a 400 MHz in 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 ($\Delta H$) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed. For the POM analysis, the synthesized compound is sandwiched between to glass slide and cover slip and heating and cooling rate is (2°C/min).

### 2.3. Synthesis

4-n-alkoxy benzoic acids **(A)** prepared by reported method [36]. 1-(4-hydroxy-3-nitrophenyl)-3-(4-(iodo) phenyl) prop-2-en-1-one **(B)** was prepared by usual established method [34]. Final target chalcone-ester derivatives (series-A) were synthesized by a




**Scheme 1.** (i) R-Br, KOH, MeOH, Reflux; (ii) EtOH, KOH, r.t. Stirring, 24 hr; (iii) DCC, DMAP, DCM, r.t. 48 h.

method reported in literature [47]. 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 benzoic acid (A)*

4-hydroxy benzoic acid alkylated by alkylating agent (R-Br), KOH, MeOH ($C_1$ to $C_8$) and Ethanol ($C_{10}$ to $C_{16}$), increasing reflux time period with increasing chain to yield

corresponding 4-n-alkoxy benzoic acids (**A**), which was confirmed by IR and $^{1}$H NMR study [36].

### 2.3.2. Synthesis of chalcone (B)

Chalcone (**B**) was prepared by usual established method reported in the literature [34].

### 2.3.3. Synthesis of ester derivatives (Series-A)

The compound has been prepared by esterification of the appropriate 4-n-alkoxy benzoic acid (A) (1.0 mmol) and chalcone (B) (1.02 mmol), dicyclohexylcarbodiimide (DCC) (1.22 mmol) and dimethylaminopyridine (DMAP) in catalytic amount (0.2 mmol) in dry $CH_2Cl_2$ (DCM) (30 ml) was stirred at room temperature for 48 h. 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: methanol, recrystallization from methanol: chloroform (2:3) until constant transition temperatures were observed [47].

## 2.3.4. Reaction scheme

### 2.3.4.1. *Analytical* data

**Chalcone (B):** FT-IR (KBr) in $cm^{-1}$: 3016-3030 (-C-H- str in $CH_3$), 1510-1450 (N-O str bands), 1450 (N-O str bands), 1365 and 1219 (>C = O str), 940 (trans, -CO-CH = CH-, -CH = CH), 802 disubstituted aromatic ring (para), 1640 (-C = O) group. $^{1}$H NMR: $\delta$H ($CDCl_3$, 400 MHz): 8.02 (d, $J$ = 15.1 Hz, 1H, -CO-CH = CH-), 7.53-7.55 (d, $J$ = 15.1 Hz, 1H, -CO-CH = CH-), 6.94-6.94 & 7.62-7.61 (2H, $J$ = 7.5 Hz, second phenyl ring) , 8.44, 827 & 7.40, (4H, $J$ = 7.1 Hz, first phenyl ring), 5.30 (1H, -OH group).; $^{13}$C NMR ($CDCl_3$): $\delta$ ppm 14.0 ($CH_3$ of $-OC_5H_{11}$ chain), 22.72–29.36 ($CH_2$ aliphatic), 68.67 (-$OCH_2$), 114.31, 129.78, 131.21, 120.22, 137.41, 137.42, 157.84 (Ar-C), 120.32 ($\alpha$ carbon of -CO–CH = CH), 144.98 ($\beta$ carbon of CO–CH = CH), 185.52 (C = O group of chalcone).

**Butyloxy ($C_4$):** FT-IR (KBr): 636 Polymethylene (-$CH_2$-)n of $-OC_5H_{11}$, 839 (–C-H- def. di-substituted-para), 759 Polymethylene (-$CH_2$-) of $-OC_4H_9$, 920 (–C-H- def. hydrocarbon), 1028 and 1068(>C = O str), 1197 and 1250 (>C = O str) in $-(CH_2)_n$ chain, 1427 (-C-H- def. in $CH_2$), 1510-1450 (-N-O str bands), 1514 (-C = C-)str, 1658 (-C = O group), 1740 (-COO- ester group), 2840 and 2960 (-C-H str in $CH_3$). $^{1}$H NMR ($CDCl_3$): $\delta$ ppm 0.88-0.90 (t, 3H, -$CH_3$ of $-OC_5H_{11}$ & $-OC_4H_9$), 1.31 & 1.45 (q, 2H, -$CH_2$ of -$OC_4H_9$), 1.76 (P, 2H of $-OC_4H_9$ group), 4.06 (t,2H,-O-$CH_2$-$CH_2$-of -$OC_4H_9$), 7.56 (d, 1H, $J$ = *15.1 Hz,* -CO-CH = CH-), 8.32 (d, 1H, $J$ = *15.1 Hz*, -CO-CH = CH-), 7.14-7.15 & 8.11-8.12 (d, 4H, left side phenyl ring), 7.82 & 8.68, 8.51 (3H, central phenyl ring), 7.62-7.61 & 6.94-6.92 (d, 4H, terminal phenyl ring).

**Pentyloxy ($C_5$):** FT-IR (KBr): 636 Polymethylene (-$CH_2$-)n of $-OC_4H_9$, 839 (–C-H- def. di-substituted-meta), 781 Polymethylene (-$CH_2$-) of $-OC_5H_{11}$, 952 (–C-H- def. hydrocarbon), 1028 and 1068(-C-O-) Str, 1197 and 1228 (>C = O str in $-(CH_2)$n chain,

1440 (-N-O str.), 930 (Trans, -CH = CH-)str, 1604 and 1666 (>C = O group), 1726 (-COO- ester group), 2850 and 2970 (-C-H str in $CH_3$). $^1$H NMR ($CDCl_3$): $\delta$ ppm 0.88-0.90 (t, 3H, -$CH_3$ of –$OC_5H_{11}$), 1.31 (q, 2H, -$CH_2$ of -$OC_5H_{11}$), 1.76 (P, 2H of –$OC_5H_{11}$ group), 4.06 (t, 2H,-O-$CH_2$-$CH_2$-of -$OC_5H_{11}$), 7.58 (d, 1H, *J = 15.1 Hz,* -CO-CH = CH-), 8.04 (d, 1H, *J = 15.1 Hz,* -CO-CH = CH-), 7.14-7.15 & 8.11-8.12 (d, 4H, left side phenyl ring), 7.82 & 8.68, 8.51 (3H, central phenyl ring), 7.62-7.62 & 6.94-6.93 (d, 4H, terminal phenyl ring).

**Hexyloxy ($C_6$):** FT-IR (KBr): 636 Polymethylene (-$CH_2$-)n of –$OC_4H_9$, 839 (–C-H- def. di-substituted-meta), 688 Polymethylene (-$CH_2$-) of –$OC_6H_{13}$, 951 (–C-H- def. hydrocarbon), 1028 and 1068(>C = O) str, 1197 and 1440 (-N-O- str.), 1514 (-C = C-)str, 1604 and 1666 (>C = O group), 1726 (-COO- ester group), 2850 and 2970 (-C-H str in $CH_3$). $^1$H NMR ($CDCl_3$): $\delta$ ppm 0.88-0.90 (t, 3H, -$CH_3$ of –$OC_6H_{13}$), 1.39-1.43 (t, 2H, -$OC_6H_{13}$), 1.23-1.28 (m, 6H, -$CH_2$ of -$OC_6H_{13}$), 1.76 (P, 2H of –$OC_6H_{13}$ group), 4.06 (t, 2H,-O-$CH_2$-$CH_2$- of -$OC_6H_{13}$), 7.58 (d, 1H, *J = 15.1 Hz,* -CO-CH = CH-), 8.02 (d, 1H, *J = 15.1 Hz,* CO-CH = CH-), 7.14-7.15 & 8.11-8.12 (d, 4H, left side phenyl ring), 7.81 & 8.68, 8.51 (3H, central phenyl ring), 7.62-7.61 & 6.94-6.93 (d, 4H, terminal phenyl ring).

**Heptyloxy ($C_7$):** FT-IR (KBr): 636 Polymethylene (-$CH_2$-)n of –$OC_4H_9$, 839 (–C-H- def. di-substituted-meta), 701 Polymethylene (-$CH_2$-) of –$OC_7H_{15}$, 952 (–C-H- def. hydrocarbon), 1028 and 1068(>C = O) str, 1197 and 1228 (>C = O str) in –($CH_2$)n chain, 1440 (-N-O- str.), 1514 (-C = C-)str, 1604 and 1660 (>C = O group), 1760 (-COO- ester group), 2850 and 2970 (-C-H str in $CH_3$). $^1$H NMR ($CDCl_3$): $\delta$ ppm 0.88-0.90 (t, 3H, -$CH_3$ of –$OC_7H_{15}$), 1.26 (m, 6H, -$OC_7H_{15}$), 1.76 (P, 2H of –$OC_7H_{15}$ group), 4.06 (t, 2H,-O-$CH_2$-$CH_2$-of -$OC_7H_{15}$), 7.58 (d, 1H, *J = 15.1 Hz,* -CO-CH = CH-), 8.06 (d, 1H, *J = 15.1 Hz,* -CO-CH = CH-), 7.14-7.15 & 8.11-8.12 (d, 4H, left side phenyl ring), 7.81 & 8.68, 8.51 (3H, central phenyl ring), 7.62-7.62 & 6.94-6.93 (d, 4H, terminal phenyl ring).

**Decyloxy ($C_{10}$):** FT-IR (KBr): 637 Polymethylene (–$CH_2$–)n of –$OC_4H_9$, 839 (–C–H– def. di-substituted-meta), 821 Polymethylene (-$CH_2$-) of –$OC_{10}H_{21}$, 952 (–C-H- def. hydrocarbon), 1028 and 1068(>C = O) Str, 1197 and 1228 (>C = O str in –($CH_2$)n chain, 1440 (-N-O- str.),1514 (–C = C–)str, 1666 (>C = O group), 1730 (-COO- ester group), 2850 and 2970 (-C-H str in $CH_3$). $^1$H NMR ($CDCl_3$): $\delta$ ppm 0.88-0.90 (t, 3H, -$CH_3$ of –$OC_{10}H_{21}$), 1.29 (m, 12H, of –$OC_{10}H_{21}$), 1.76 (P, 2H of –$OC_{10}H_{21}$ group), 4.06 (t,2H,-O-$CH_2$-$CH_2$- of -$OC_{10}H_{21}$), 7.58 (d, 1H, *J = 15.1 Hz*, -CO-CH = CH-), 8.02 (d, 1H, *J = 15.1 HZ,* -CO-CH = CH-), 7.14-7.15 (d, 4H, left side phenyl ring), 7.82 & 8.68, 8.51 (3H, central phenyl ring), 7.62-7.61 & 6.94-6.92 (d, 4H, terminal phenyl ring).

**Dodecyloxy ($C_{12}$):** FT-IR (KBr): 636 Polymethylene (–$CH_2$–)n of –$OC_4H_9$, 839 (–C–H– def. di-substituted-meta), 759 Polymethylene (–$CH_2$–) of –$OC_{12}H_{25}$, 952 (–C–H– def. hydrocarbon), 1028 and 1068(>C = O) Str, 1197 and 1228 (>C = O str.) in $(–CH_2)_n$ chain, 1440 (–N–O– str.),1514 (–C = C–)str, 1640 (>C = O group), 1726 (-COO- ester group), 2850 and 2970 (–C–H str in $CH_3$). $^1$H NMR ($CDCl_3$): $\delta$ ppm 0.88–0.90 (t, 3H, -$CH_3$ of –$OC_{12}H_{25}$), 1.29 (m, 14H, of –$OC_{12}H_{25}$), 1.31 (q, 4H, -$CH_2$ of -$OC_{12}H_{25}$), 1.76 (P, 2H of –$OC_{12}H_{25}$ group), 4.06 (t, 2H,–O–$CH_2$–$CH_2$-of –$OC_{12}H_{25}$), 7.58 (d, 1H, *J = 15.1 Hz*, –CO–CH = CH-), 8.02 (d, 1H, *J = 15.1 HZ,*–-CO–CH = CH–), 7.14–7.15 & 8.11–8.12 (d, 4H, left side phenyl ring), 7.82 & 8.68, 8.51 (3H, central phenyl ring), 7.61–7.62 & 6.93–6.92 (d, 4H, terminal phenyl ring).

## 3. Result and discussion

### 3.1. Pom analysis

In order to investigate the influence of the central linkage group with respect to lateral nitro and terminal substituted iodo group with varying left alkoxy variable side chain on the mesomorphic properties of the present synthesized chalconyl materials. In this present investigation, we have prepared calamitic rod-shaped homologous series with total thirteen compounds ($C_1$ to $C_8$, $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$). In this present study, we have find out liquid crystalline materials with good thermal stability. In series-A, compounds $C_1$ to $C_6$ shows nonmesomorphic properties and directly passes through isotropic liquid from solid state, this is mainly due to short alkyl spacer in left side chain causes more crystallinity and directly converted into isotropic phase without displaying LC phase either heating or cooling condition.

The nonmesomorphicity of $C_1$ to $C_6$ homologous is attributed due to the appearance of low magnitudes intermolecular dispersion forces and low magnitudes of dipole-dipole interfaces leading to high crystallizing tendency due to short alkyl chain length as result it causes hasty breaking of crystal lattices because of unsuitable magnitudes of anisotropic forces of intermolecular desirability [2–4]. Thus, improper breaking of crystal lattices which directly melts at reaching its isotropic temperature on heating and on further cooling the solidification is taking place without displaying of liquid crystalline phase [3]. One can see that, higher chain substituted compounds ($C_7$ to $C_{18}$) showed liquid crystalline properties with good mesophase temperature range respectively. Cr-SmC, SmC-N and N-I is plotted against the phase transition temperature versus the number of carbon atoms in n-alkyl chain at (left alkoxy side chain) as shown in Figure 1. All phase transition curves showed descending behavior till the last homologue, this is due to the higher flexibility of the molecule along with polarity. Presence of lateral substituted polar nitro group at lateral position along with terminal iodo group on central phenyl ring, increases molecular aromaticity, polarity and polarizability of molecules [34,35]. The phase transition temperature of series-A is shown in Table 1.

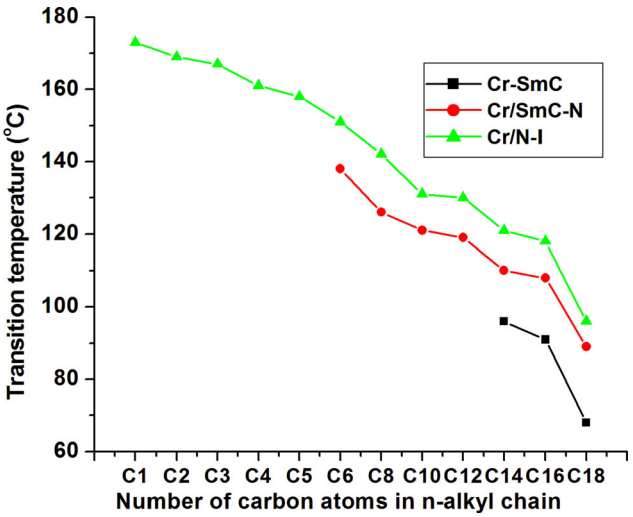



Figure 1. Phase diagram of newly synthesized Series-A.

**Table 1.** Transition Temperature in °C by POM.

| | | Transition temperatures in $^0$C | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sr.no | R = n-alkyl group | Cr | | **Smectic** | | | **Nematic** | | | **Isotropic** | |
| 1 | $C_1$ | · | – | – | – | – | 173.0 | · | | | |
| 2 | $C_2$ | · | – | – | – | – | 169.0 | · | | | |
| 3 | $C_3$ | · | | – | – | – | 167.0 | · | | | |
| 4 | $C_4$ | · | – | – | – | – | 161.0 | · | | | |
| 5 | $C_5$ | · | – | – | – | · | 158.0 | · | | | |
| 6 | $C_6$ | · | – | · | – | · | 151.0 | · | | | |
| 7 | $C_7$ | · | – | · | 138.0 | · | 142.0 | · | | | |
| 8 | $C_8$ | · | – | · | 126.0 | · | 131.0 | · | | | |
| 9 | $C_{10}$ | · | – | · | 121.0 | · | 130.0 | · | | | |
| 10 | $C_{12}$ | · | – | · | 119.0 | · | 123.0 | · | | | |
| 11 | $C_{14}$ | · | 96.0 | · | 110.0 | · | 121.0 | · | | | |
| 12 | $C_{16}$ | · | 91.0 | · | 108.0 | · | 118.0 | · | | | |
| 13 | $C_{18}$ | · | 68.0 | · | 89.0 | · | 96.0 | · | | | |

The presence of odd-even parity on n-alkyl chain create variation in phase transition temperatures, this is due to the odd and even number of methylene units present in the n-alkyl side chain of left n-alkoxy chain group. The exhibition of smectic C phase in present synthesized higher homologues ($C_{14}$, $C_{16}$, $C_{18}$), due to the formation of molecular lamellar packing of in crystal lattices which maintains sliding layered molecular arrangement in floating condition under the influence of exposed thermal vibrations on heating and cooling conditions [36]. The exhibition of nematic property from $C_7$ homologue to $C_{18}$ homologue is attributed due to the presence of suitable magnitudes of anisotropic at end to end side intermolecular attractions and appropriate permanent dipole moment across the long molecular axis., dispersion forces, dipole-dipole interactions, shape, size, magnitudes of polarity and polarizability etc., which maintains floating of the homologue in statically parallel orientational order to adopt nematogenic character, under exposed thermal vibrations; either directly or via smectic phase in enantiotropic manner [37]. Texture images of some selected compounds are mention in Figure 2 respectively. Compound $C_{12}$ showed needle type texture pattern of SmC phase at 96.0 °C which on further heating, exhibited nematic mesophase at 119.0 °C and finally converted into isotropic liquid at 123.0 °C. Compound $C_{18}$ with octadecyloxy tail group exhibited needle type texture image of smectic C phase at 68.0 °C on heating conditions respectively, which was further confirmed by DSC analysis. Similar texture patterns are found for other synthesized chalconyl-ester derivatives.

### 3.2. DSC study

DSC is a valuable method for detecting phase transitions. The thermal behavior of novel homologues series was confirmed by using DSC measurement shown in Figure 3. DSC thermogram traces under heating and cooling condition. Compound $C_{18}$ showed three endothermic and exothermic peaks on heating and cooling condition. On heating condition, three endothermic peaks are traced at 62.5 °C, 84.5 °C and 109.8 °C corresponding to Cr-SmC, SmC-N and N-I phase transition. While on

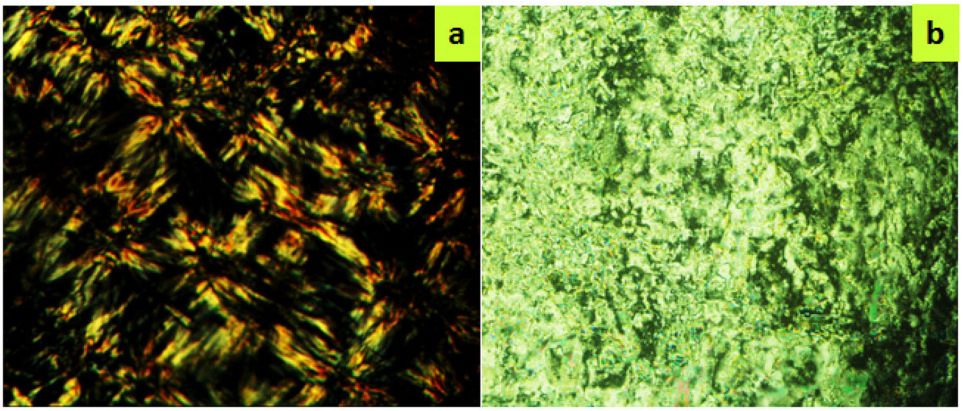



**Figure 2.** Texture image of Series-A observed between cross polarizers: (a) SmC of $C_{12}$ homologue at 96.0˚C; (b) SmC of $C_{18}$ homologue at 68.0˚C.

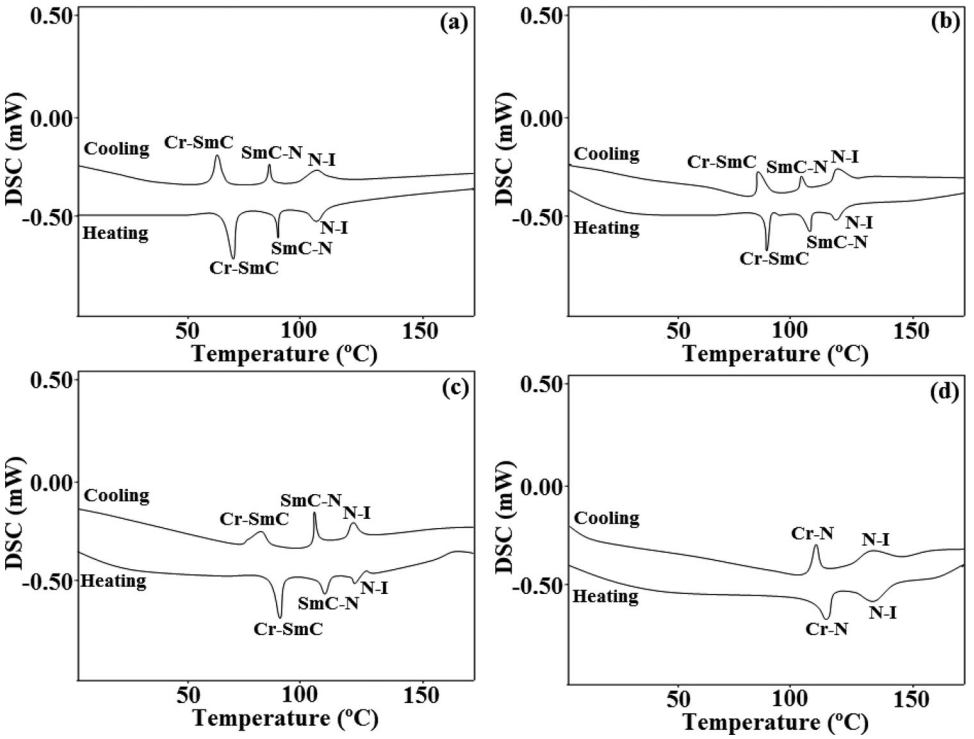



**Figure 3.** DSC thermogram of conpound (a) $C_{18}$; (b) $C_{16}$; (c) $C_{14}$; (d) $C_{12}$ homologues on heating and cooling condition.

cooling condition, three exothermic peaks are traced at 107.1 °C, 81.2 ˚C and 57.2 ˚C. For $C_{16}$ homologue, three significant peaks is observed at 90.4 °C, 106.2 ˚C and 121.6 ˚C corresponding to three phase transition, while on cooling condition it again revealed at 123.2 ˚C, 104.6 ˚C and 69.4˚C respectively. This is nearly to the transition temperature observed by POM investigation. Similarly compound $C_{14}$ showed three

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

| 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 | 62.5 | 57.2 | 9.11 | 7.63 | 0.0271 | 0.0231 |
| | SmC-N | 84.6 | 81.3 | 10.14 | 12.73 | 0.0283 | 0.0359 |
| | N-I | 109.8 | 107.1 | 5.12 | 6.45 | 0.0134 | 0.0169 |
| $C_{16}$ | Cr-SmC | 90.4 | 83.5 | 7.82 | 4.48 | 0.0215 | 0.0125 |
| | SmC-N | 106.2 | 104.6 | 16.14 | 17.35 | 0.0425 | 0.0459 |
| | N-I | 121.6 | 123.2 | 6.43 | 7.56 | 0.0162 | 0.0190 |
| $C_{14}$ | Cr-SmC | 92.1 | 82.4 | 10.06 | 7.49 | 0.0275 | 0.0210 |
| | SmC-N | 120.4 | 117.4 | 18.39 | 16.01 | 0.0467 | 0.0410 |
| | N-I | 126.8 | 127.6 | 3.78 | 6.98 | 0.0094 | 0.0174 |
| $C_8$ | Cr-N | 123.4 | 121.3 | 14.22 | 12.54 | 0.0358 | 0.0318 |
| | N-I | 134.8 | 135.9 | 8.62 | 7.67 | 0.0211 | 0.0187 |
| $C_{10}$ | Cr-N | 116.8 | 112.3 | 9.17 | 10.78 | 0.0235 | 0.0279 |
| | N-I | 134.6 | 137.9 | 4.04 | 7.89 | 0.0099 | 0.0192 |

endothermic peaks at 92.1 °C, 120.4 °C and 126.8 °C on heating and three exothermic peaks at 127.6 °C, 117.4 °C and 82.4 °C on cooling condition corresponding to three phase transition observed on enantiotropical manner respectively. One can see that, higher chain substituted derivatives showed lamellar type of molecular arrangement and showed smectic C type of molecular arrangements. Compound $C_{12}$ showed two endothermic peaks at 123.4 °C and 134.8 °C corresponding to Cr-N and N-I phase transition while on cooling condition, it again traced at 135.9 °C and 121.3 °C which was further confirmed by POM study. Two endothermic peaks traced for $C_{10}$ homologue at 117.4°C and 139.1°C on heating condition. Transition temperature obtained by DSC analysis at heating and cooling condition and the values of enthalpy and entropy is mention in Table 2. 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 [35]. The liquid crystalline phase obtained enantiotropical manner in present series is smectogenic and nematogenic respectively.

### 3.3. Thermal stability of mesophase

Some LC parameters evaluated from thermotropic data of presently synthesized novel series-A is compared with structurally similar series-X which was previously reported by our research group [49] is mention in Figure 4. The linearity of the both series is different at lateral group so their magnitudes of combined effects of molecular rigidity and polarity may effect on liquid crystalline properties with respect to commencement of mesophase and its temperature range respectively. Presences of $-NO_2$ group at lateral side in present series which may increase the polarity and polarizability of molecule as compared to previously reported series-X. It can be noted that the presence of nitro group in series-A decrease the thermal stability of mesophase in both phase transition (Sm-N and N-I) as compared to series-X. The thermal stability parameters were studied

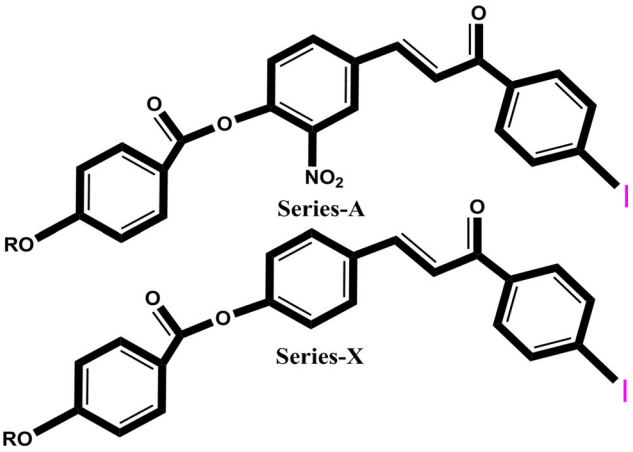



**Figure 4.** Structurally similar series-A with series-X.

from DSC analysis data and POM data obtained from synthesized chalcogens materials. The stability of Sm-N and N-I phase transition in series-A are 102.3 ˚C and 123.0 ˚C which are lower as compared to series-X (155.0 ˚C and 180.7 ˚C).

### *3.4. XRD investigation*

To investigate the structure of the observed smectic and nematic phase in present synthesized chalconyl-ester derivatives, we have performed high temperature XRD to correlate with the results obtained from DSC and POM investigation to further understand the molecular arrangement at phase transition temperature state respectively. The XRD data of comp. $C_{14}$, $C_{12}$, $C_{10}$ are shown in Figure 5 which indicates the X-ray pattern shows the diffraction peaks in the small angle diffraction region corresponded to a smectic C and further at higher temperature single diffraction peak appeared which confirmed the nematic type molecular reorganization. A sharp peaks ($2\theta = 10–20''$) were observed during X-ray investigation. The reflections for the small-angle area correspond to a smectic layer structure. The *d*-spacing for $C_{14}$ at $2\theta = 8.71$ Å, 6.34 Å and 5.48 Å and reflections observed at 10.18˚, 14.21˚ and 16.32˚ occur at 96.0˚C further at 110.0˚C, comp.$C_{14}$ traced only one diffuse peak at 24.98˚ and the calculated d-spacing is 3.64 Å . In addition, comp. $C_{16}$ showed three reflections at $2\theta = 11.26$, 16.04 and 19.42 and the calculated d-spacing value is found to be 7.88 Å, 5.57 Å and 4.3 Å. Compound $C_{12}$ showed single diffuse reflections at 21.28˚ with 4.24 Å d-spacing length indicates the absence of any well-ordered smectic type molecular arrangement. It is observed that the presence of higher alkyl chain at left terminal side group in $C_{14}$, $C_{16}$ and $C_{18}$ homologues may increase the arrangement of molecules in ordering layered and formation of molecules in smectic mesophase. The arrangement of molecule is isomeric calamatic rod type shape. The lower member of the present series showed nematic type mesophase while higher members of the present series showed smectic C type mesophase. This is due to the molecular packing of the alkyl chains with linking groups oriented tilted way directions and nitro group substituted at lateral side in smectic layers structure and effect of flexibility to induce smectic mesophase. The theoretical

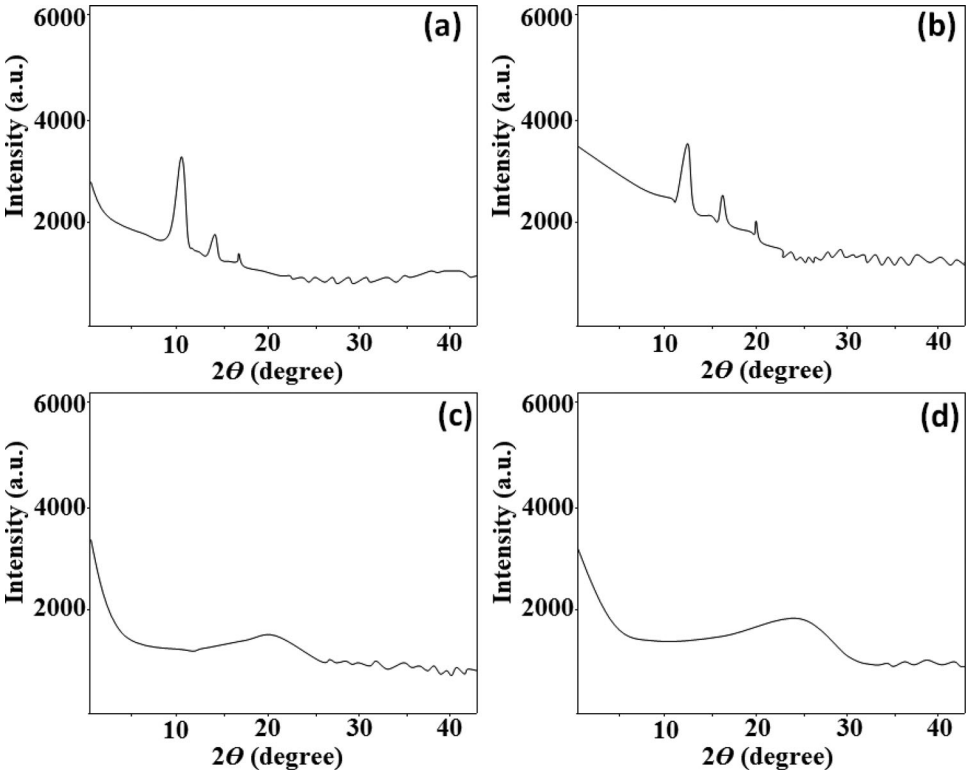



**Figure 5.** XRD traces of compound $C_{14}$ (a); $C_{16}$ (b); $C_{10}$ (c); $C_{14}$ (d) measured at transition Temperature obtained from POM study.

calculated d-spacing length of compound $C_{14}$ is near to the observed or experimental d-spacing length as shown in Figure 6. According to the graphical proposed mechanism, the molecular are arranged in lamellar order, although, the long axes of the molecules are tilted to the layers planes shown in Figure 7.

### 3.5. Biological evaluation

In the present work, the focus has been drawn on designing new structural entities of iodo based nitro substituted chalcones inbuilt with 4-n-alkoxy benzoic acid to form chalconyl-ester derivatives to evaluate the prospective effect on biological activity, particularly antibacterial and antifungal activity. Newly synthesized mesogens with two lateral side groups were examined for antimicrobial activity against four pathogenic micro-organism viz. *E.coli, P.aeruginosa* (Gram –ve) and *S.aureus*, *S.pyogenus* (Gram + ve) bacterial strains. The antifungal activities were carried out with *C.albicans*, *A.niger* and *A.clavatus* at various concentrations. The synthesized compounds showed good activity results against *E.coli*, *P.aeruginosa* (Gram–ve) and *S.aureus*, *S.pyogenus* (Gram + ve). The ampicillin, gentamycin, chloramphenicol, ciprofloxacin, nystatin and greseofulvin were used as the standard drug for gram-positive, gram-negative and fungal strains, respectively. The minimum inhibitory concentration (MIC) was evaluated by

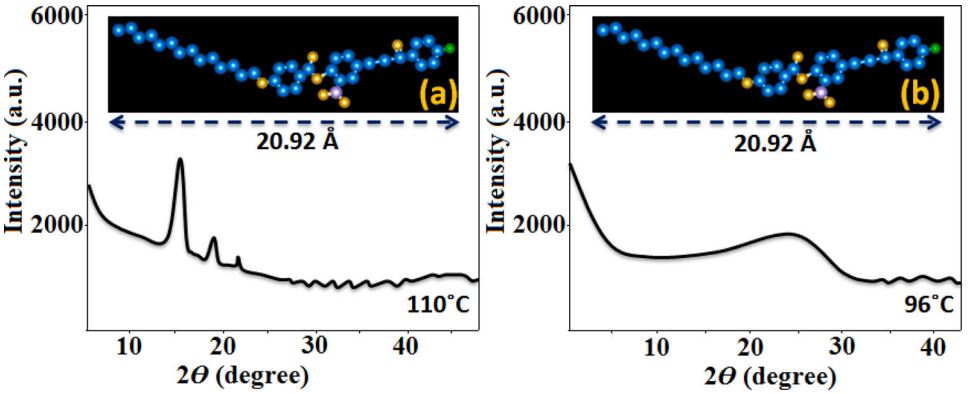



**Figure 6.** XRD traces of compound $C_{14}$ (a) and $C_{14}$ (b) measured at 96.0° and 110.0°C.

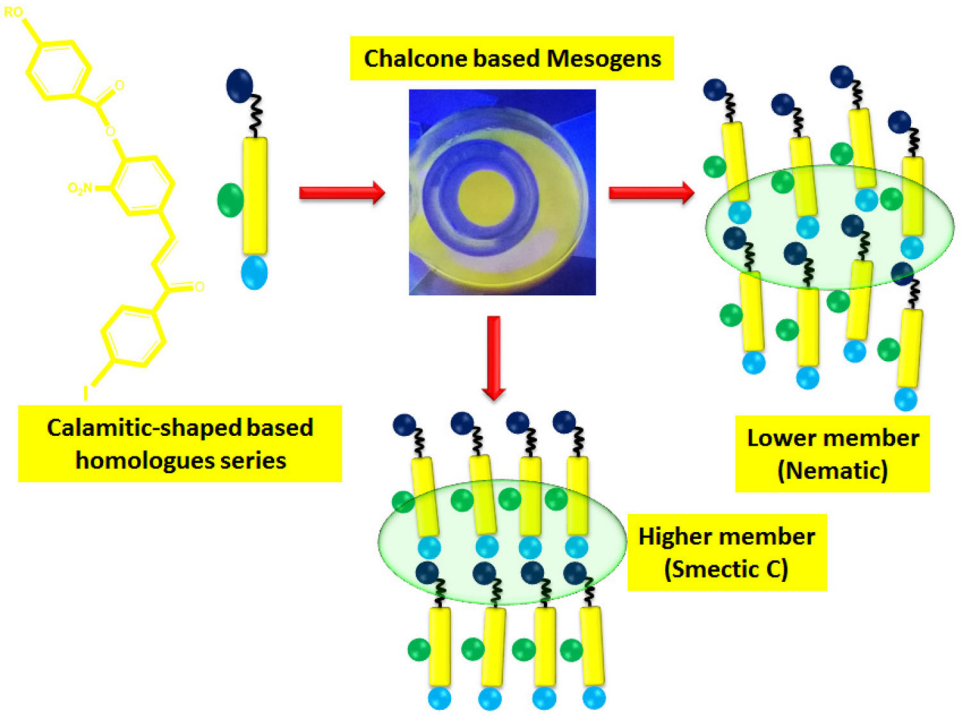



**Figure 7.** Proposed molecular packing in present Series-A.

the broth dilution method. All the selected compounds ($C_3$, $C_4$, $C_5$, $C_6$, $C_7$, $C_{10}$ and $C_{12}$) showed good results and further compared with standard drugs.

### *3.5.1. In vitro antibacterial activity*

Table 3 shows that all the newly synthesized compounds were found to exhibit good to moderate activity against specific microbial strains. Initially, we screened few selected synthesized mesogens ($C_3$ to $C_{12}$) for their antibacterial activity *in vitro* by using both

**Table 3.** Result of antibacterial activity of the synthesized compounds.

| ANTIBACTERIAL ACTIVITY | | | | | |
|---|---|---|---|---|---|
| | | Minimal Inhibition Concentration | | | |
| Sr.No | Code No. | *E.Coli* MTCC 443 | *P.Aeruginosa* MTCC 442 | *S.Aureus* MTCC 96 | *S.Pyogenus* MTCC 442 |
| **Microgramm / ML** | | | | | |
| 1 | $C_3$ | 62.5 | 100 | 100 | 62.5 |
| 2 | $C_4$ | 62.5 | 125 | 100 | 200 |
| 3 | $C_5$ | 62.5 | 100 | 250 | 100 |
| 4 | $C_6$ | 62.5 | 100 | 100 | 100 |
| 5 | $C_7$ | 100 | 125 | 250 | 62.5 |
| 6 | $C_{10}$ | 100 | 200 | 100 | 100 |
| 7 | $C_{12}$ | 100 | 125 | 100 | 100 |
| **Standard** | **Ampicillin** | 100 | 100 | 250 | 100 |
| **Standard** | **Gentamycin** | 0.05 | 1 | 0.25 | 0.5 |
| **Standard** | **Chloramphenicol** | 50 | 50 | 50 | 50 |
| **Standard** | **Ciprofloxacin** | 25 | 25 | 50 | 50 |

**Table 4.** Result of antifungal activity of the synthesized compounds.

| | | Antifungal activity Minimal fungicidal concentration | | |
|---|---|---|---|---|
| Sr.No | Code. No. | C.Albicans | A.Niger | A.Clavatus |
| | | **MTCC 227** | **MTCC 282** | **MTCC 1323** |
| **Microgramm / ML** | | | | |
| 1 | $C_3$ | 500 | 250 | >1000 |
| 2 | $C_4$ | 1000 | 1000 | 250 |
| 3 | $C_5$ | 500 | 250 | 1000 |
| 4 | $C_6$ | 1000 | 250 | 250 |
| 5 | $C_7$ | 500 | 1000 | >1000 |
| 6 | $C_{10}$ | 1000 | 1000 | 250 |
| 7 | $C_{12}$ | 500 | 250 | >1000 |
| **Standard** | **Nystatin** | 100 | 100 | 100 |
| **Standard** | **Greseofulvin** | 500 | 100 | 100 |

dilution methods. It is interesting to note that all selected mesogens showed excellent antibacterial activity. The *in vitro* antibacterial results confirmed that some of the chalcone hybrids exhibited antibacterial activity against various strains of *E.coli*, *P.aeruginosa* (Gram–ve) and *S.aureus*, *S.pyogenus* (Gram + ve). An antibacterial result was comparatively nearer to the standard drug ampicillin as compare to other drug. Comp. $C_3$ to $C_6$ having excellent activity (62.5 µg/ml MIC) against *E.coli*. Furthermore, compound $C_7$, $C_{10}$ and $C_{12}$ showed growth inhibition at lower concentration (62.5 µg/ml MIC) as compare to standard drugs. Compound $C_3$ to $C_{12}$ showed good activity against *P.aeruginosa* at (100 µg/ml MIC and 125 µg/ml MIC) which was further compared with the standard drug. However, comp.$C_4$ (120 µg/ml MIC) and $C_5$ (125 µg/ml MIC) and comp. $C_{12}$ showed activity at higher concentration. Compound $C_3$ and $C_7$ exhibited good inhibitory activity with lower concentration (62.5 µg/ml MIC) against *S.Pyogenus*.

### *3.5.2. In vitro antifungal activity*

Antifungal activity data displayed in Table 4 which indicates the results of compound $C_3$ to $C_{12}$ showed adaptable degrees of inhibition against the tested fungi *C.Albicans*,

*A.Niger*, *A.Clavatus*. *C.Albicans* fungi were inhibited by $C_3$, $C_5$, $C_7$ and $C_{12}$ at 500 µg/ml MIC which is equal to the concentration of standard drug Greseofulvin. While inhibiting against *A.Niger*, *A.Clavatus* fungi by compound $C_3$, $C_5$, $C_6$ and $C_{12}$ at 250 µg/ml MIC, while all the other derivatives exerted moderate to poor activity profiles.

## 4. Conclusions

A new calamitic chalconyl-ester mesogens based on two linking groups and three benzene core as rigid core possessing one lateral group with variable alkoxy side chain group (-OR). The liquid crystalline properties of the synthesized mesogens were carried out by using POM, DSC and XRD techniques which revealed the occurrence of enantiotropic nematic as well as smectic C phase. The lower member comp. ($C_1$ to $C_6$) shows non-mesogenic nature due to the presence of short alkoxy side spacer in left side terminal group. Further, comp. $C_7$ to $C_{12}$ showed only enantiotropical nematic phase while comp. ($C_{14}$ to $C_{18}$) shows nematic as well as smectic C properties. Higher chain substituted members ($C_{14}$, $C_{16}$ and $C_{16}$) showed well-ordered smectic C as well as nematic properties. The group efficiency order derived on the basis of (a) mesophase thermal stability, (b) early or late commencement of mesophase, (c) Temperature range of mesophase. The antibacterial and antifungal activity was determined by MIC (Broth dilution method). All the synthesized mesogens exhibited good antibacterial as well as antifungal activity.

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