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"Synthesis, Mesomorphic and DFT Studies of Chalcone Derived Room Temperature Liquid Crystal with Presence of Lateral Nitro and N, N-Dimethyl Amino Terminal Group"

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ABSTRACT

In this present article, we wish to report on the liquid-crystalline properties of chalcone-ester based homologous series of compounds having aliphatic chain length in n-alkoxy group (n = 1 to 10, 12, 14, 16, 18). The present series consisted thirteen compounds, in which comp.C₁ and C₂ shows nonliquid crystalline properties, while comp.C₃ to C₇ display SmC phase and comp.C₈ to C₁₈ exhibits only nematic phase. Textural pattern of presently synthesized compounds are schlieren and threaded type. All this compounds were well characterized by elemental analysis, FT-IR and ¹H NMR. Phase transition temperatures of present synthesised compounds were determined by optical polarising microscopy (POM), differential scanning calorimetric (DSC). Detailed XRD investigation endorses the presence of the nematic phase in higher homologues and SmC phase in lower homologues. It is shown that chalcone with ester as linking unit favors a calamitic liquid crystalline behaviour in molecules. To get more insights, the DFT based HOMO, LUMO studies are carried out which supports intramolecular charge transfer interactions in this class of mesogens. Chalconyl ester based compounds C_3 to C_{12} shows antibacterial as well as antifungal activity compared with corresponding standard drugs.

GRAPHICAL ABSTRACT



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KEY WORDS

Liquid crystal; nematic; chalcone; enantiotropic

1. Introduction

Study of liquid crystalline (LC) state 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. Calamitic molecules of conventional and unconventional liquid crystalline compounds have been intensively explored for scientific and technological potential applications such as biologically active materials, sensing materials and electronic display materials [5–6].

A number of chalcone having reported to exhibit a broad spectrum of anti-bacterial, antifungal, antiulcer, antimalarial, antitumor, anticancer, anti-inflammatory and antitubercular activity [7–10]. 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 [11–12]. 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 non-linearity and angle strain arising from the presence of keto (-C = O) group in chalcone [13]. Surprisingly, when -CO-CH = CH- linkage is linked with another linking group it becomes conductive to show LC property.

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 [14]. R.Gopalakrishnan et al. reported chalcone based single crystals, growth, and comparison of two new enone shifted chalcones and their NLO behaviour [15]. Tandel et al. studied the chain chalconyl polymers compounds to exhibiting threaded type nematic phases [16]. 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 [17]. Doshi et al. reported various homologous series based on chalconyl and vinyl ester linkage group and studied the effect on mesomorphism [18-20]. Furthermore, 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 [21]. Recently, Bhoya et al. reported a calamitic rod type homologous series containing vinyl ester and azomethine linkage groups [22-23]. 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 -OCH₃ substituted compounds exhibited greater mesophase stability as compare to halogen (-F, -Cl, -Br) [24]. Recently, we reported chalconyl ester based homologues series with different terminal group at tail part that affect the mesomorphic property [25-26].

In Present work, we planned to investigate a new chalcone based calamitic homologous series based on three phenyl rings and also study the effect of lateral nitro $(-NO_2)$ group on LCs property and reactivity with respect to $-N(CH_3)_2$ tail at one end and variable alkoxy terminal chain at another end. Comprehensive literature search on chalcone based room temperature LCs have so far not been reported till the date. Therefore, these synthesised newly compounds will help in considerate the structure-property relationship in the developing list of chalcone-based liquid crystalline compounds.

2. Experimental

2.1. 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 stage. ¹H NMR was recorded on a 400 MHz in Bruker Advance 400 in the range of 0.5 ppm-16 ppm using CDCl₃ solvent. The phase transition temperatures were measured using Shimadzu DSC-50 at heating and cooling rates of 10 °C min⁻¹. X-ray diffraction (XRD) measurements were performed on a Rigaku-Ultima IV powder diffractometer equipped with a Cu k α source ($\lambda = 1.5418$ A° and 1.6 kW, X-ray tube with applied voltage and current values as 40 kV and 30 mA power) and also Philips X'PERT MPD. 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. Geometry optimization and energy calculations were performed at the B3LYP/6-311 level in dichloromethane solution using the CPCM solvation method with default convergence criteria.

2.2. Materials

For present synthesized homologous series required materials: 4-hydroxy benzoic acid, alkyl bromide (R-Br) were purchased from SRL (Mumbai), 4-hydroxy, 3-nitro acetophenone, 4-N,N dimethyl amino benzaldehyde were purchased from (Sigma Aldrich), KOH (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

3. Result and discussion

In present article, we have synthesized newly chalcone based calamitic rod shaped homologous series contain chalcone and ester as central linking group with presence of left side changing alkoxy (-OR) group varying from methyl (C₁) to octadecyl (C₁₈) in presence of -nitro group on lateral side and N,N-dimethyl amino group at right terminal side. Here, we have study the effect of polar lateral group with changing alkyl chain length in terminal chain (-OR) on mesogenic property of liquid crystalline compounds. A newly chalconyl-ester derived series prepared from condensation of dimeric 4-nalkoxy benzoic acids and chalcone (α -4-hydroxy phenyl 3'-nitro benzoyl β -4"-N, Ndimethyl amino ethylene) is synthesized and evaluated their thermometric data to compare mesomorphic behaviours and the molecular structure through molecular rigidity and flexibility. The phase behaviour of all new synthesised compounds has been investigated by polarising optical microscope (POM) and differential scanning calorimetry (DSC), and X-ray diffraction (XRD).

3.1. Synthesis and characterisation

In order to study the influences of the different numbers of mesogens on mesomorphic properties, calamitic-shaped chalconyl ester derivatives were designed as target compounds having nitro group at lateral side with presence of N,N-dimethyl amino terminal group at one end and variable chain at another end. The synthesis of p-n-alkoxy benzoic acid (C) was carried out by reported method [28]. The (E)-3-(4-(dimethyl amino) pheny-1-(4-hydroxy-3-nitro phenyl) prop-2-en-1-one (chalcone) (D) was prepared by treating of 4-hydroxy 3-nitro acetophenone and 4-N, N-dimethyl amino benzaldehyde in ethanol [29]. The ¹H NMR of comp.D shows doublet of ethylene group 2H ($\delta = 7.54$ ppm and $\delta = 8.04$ ppm). From FT-IR, the peak found at 1640 cm⁻¹ signifying the presence of -C = O group. The final target compounds of series-1 were prepared by modified method using DCC and DMAP reagent for 24 hr to get the series of compounds [30]. The resultant crude residue was purified by using column chromatography on silica gel eluting with ethyl acetate: hexane as eluent (3:2). FT-IR results shows peaks at 1730 cm^{-1} and 1640 cm^{-1} correspondence to -COO- and -C=O group. While the results obtained from ¹H NMR supported to the corresponding structures of com. E_3 , E_4 , E_8 and comp. E_{14} . The synthetic route of series-1 is mentioned in Scheme 1.

3.2. POM investigation

We have studied comprehensively the effect of linking group, lateral group as well as changing alkyl chain length in left terminal chain (-OR) to form mesogens having calamitic rod-shaped. Here, in present investigation, we have synthesized newly chalcone (-CO-CH = CH-) and ester (-COO-) linkage group inbuilt between three phenyl ring and lateral nitro group based homologous series. In present series-1, we have prepared total thirteen compounds from C_1 (-OCH₃) to C_{18} (-OC₁₈H₃₇). Comp. C_1 , C_2 shows non-liquid crystalline property while comp. C3 to C5 shows SmC property and remaining comp. C_6 to C_{18} display only nematic mesophase. The observed data derived from POM and DSC study complemented to each other. All the synthesized compounds, except comp.C₁, C₂ exhibited mesogenic property in enantiotropically manner. Conversely, the type of the mesomorphic property depends upon the number of carbon atoms present in the aliphatic side chain in alkoxy (-OR) group. Comp.C₁, C₂ shows non liquid crystal (NLCs) property, this is due to the presence of short alkyl spacer methoxy (-OCH₃), ethoxy (-O-CH₂-CH₃) group at left side alkoxy terminal group. The crystallising tendency of short alkyl spacer compounds (C_1, C_2) are higher as compare to other compounds in present series-1 and so it directly transform into isotropic state when heating from solid state without exhibiting any LC property on heating and cooling condition. The transition temperature of present series is listed below in Table 1.

The plot of transition temperatures versus the number of carbon atoms present in terminal alkoxy chain showing Cr-SmC, SmC/N-l and N-I phase transition curve shown in Figure 1. The phase diagram shows descending tendency in all transition curve increasing from lower member to higher member in present series-1. The transition curve of Cr-SmC showing decreasing tendency from comp.C₃ to C₇. The Cr/SmC-I and N-I transition cure start decreasing as side alkoxy chain increases from comp.C₁ to C₁₈.



Scheme 1. Synthetic route of target compounds; (a) MeOH, conc.H₂SO₄, Reflux; (b) R-Br, KOH, MeOH, Reflux; (c) KOH, EtOH, Reflux; (d) KOH, EtOH, RT, 12 hr stirring; (e) DCC, DMAP, DCM, RT, 24 hr stirring.

No odd-even effect is seen in all phase transition present in present series-1. It can be seen that, as the methylene group increases in side alkoxy tail group (-OR), the linearity and polarizability of the molecules also increase which increases the flexibility of the molecules to induce mesomorphism at lower temperature. In present series-1, comp.C₁₂ to C_{18} shows nematic liquid crystalline property at room temperature, this is due to the presence of chain length (n = 12 to 18) which increases the flexibility of compounds and as a results LC property were seen at lower temperature or a room temperature. The presence of lateral polar nitro group in second phenyl ring which normally decrease the thermal stability of smectic and nematic mesophase, as a result of the

Table 1. Transition Temperature in °C by POM



	R = n-alkyl group	Transition temperatures in ^o C						
Sr.no		Cr	Sm	с	Ν		I	
1	C ₁		-	-	-	-	108.0	
2	C ₂		-	-	-	-	102.0	
3	C ₃		74.0		-	-	98.0	
4	C ₄		68.0	•	-	-	95.0	
5	C ₅		62.0	•	-	-	93.0	
6	C ₆		54.0	-	64.0		91.0	
7	C ₇		43.0	-	53.0		84.0	
8	C ₈		-	-	48.0		76.0	
9	C ₁₀		-	-	46.0		71.0	
10	C ₁₂		-	-	41.0		64.0	
11	C ₁₄		-	-	39.0		61.0	
12	C ₁₆		-	-	36.0		59.0	
13	C ₁₈		-	-	31.0	•	49.0	•

(Cr = solid crystal; Sm = Smectic C phase; N = nematic phase; I = Isotropic phase)

broadening effect that forcing the molecules and increases its polarity and polarizability [30]. The exhibition of smectic and nematic phase in comp.C₆ and C₇ is attributed to the optimum magnitudes of dipole-dipole interactions which control the suitable magnitudes of anisotropic forces and intermolecular cohesion and closeness to exhibited smectic and nematic phase in either reversible or irreversible manner [18]. The $-N(CH_3)_2$ group has significantly influenced the mesogenic properties and its charge transfer interfaces and broadening of molecule due to presence of $-CH_3$ group in $-N(CH_3)_2$ away from the plane.

In present series-1, the higher homologous display nematic phase with absence of any lamellar packing to exhibited only nematic property, this is due to the disalignment of molecules of an angle less than ninety degree under the externally exposed thermal vibrations of suitable magnitudes which matches with internal energy stored in a molecule (Δ H) as related to suitable magnitudes of anisotropic forces of intermolecular end to end attractions, as a consequence of favorable molecular rigidity and flexibility, which favorably arranges molecules to float on the surface in statistically parallel orientational order to maintain molecular two dimensional array [18, 31].

3.2.1. 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 2. POM observations reveal that comp.C₁₈ exhibited schlieren type texture with four brush pattern of nematic phase at 32.0 °C on heating condition. Comp. C₄ display focal conic texture image of SmC phase at 68.0 °C on cooling condition. Compound C₈ shows threaded type textural pattern of nematic



Figure 1. Phase diagram of series-1

phase at 48.0°C on cooling condition which was further confirmed by DSC analysis. Compound C_{16} exhibits threaded type textural pattern of nematic phase at 33.0°°C on heating condition. We have measure the phase sequence of compound C_8 on cooling condition as shown in Figure 3 which indicates (a) solid crystal, (b) commencement of nematic mesophase, (c-e) nematic mesophase at 38.0°C, 48.0°C, 49.0°C, (f) Isotropic mass appeared at 76.0°C. Observed phase sequence is repeated again during cooled condition and also confirmed by DSC analysis.

3.2.2. Comparative study

Some LC properties evaluated from thermotropic data of presently investigated newly series-1 with compared with structurally similar analogues series-2[32] as shown in Figure 4. Both the series-1 and series-2 are same with respect to two linkage group and terminally substituted N, N-dimethyl amino group and altering side chain at left terminal part. The linearity of both the series are same however the breadth of series-1 is higher as compare to series-2 due to presence of -nitro group at lateral side on second phenyl ring. The temperature range of mesophase in series-1 is lower as compare to series-2, this is due to the presence of nitro group which increasing the polarity and polarizability of molecules and also the presence of dimethyl amino group which increases the charge transfer interactions and flexibility caused by altering alkyl side chain in alkoxy group (-OR). Thus, changing in LC properties like thermal stability and temperature range, commencement of mesophase will be influenced by the magnitudes of changing features of homologous series-1 and series-2 taken under comparative study.

Figure 5 shows the ball-stick model of series-1 and series-2. It can be seen that, series-1 is more linear as compare to series-2 and it is differing from lateral side group on second phenyl ring in series-1. Both the series having ester (-COO-) and chalcone (-CO-CH = CH-) linkage group and shows LCs property at lower temperature. However, due to presence of



Figure 2. Microphotographs of (a) Nematic phase of comp. C_{18} at 32.0°C. (b) SmC phase of comp. C_4 at 68.0°C. (c) Nematic phase of comp. C_8 at 48.0°C. (d) Nematic phase of comp. C_{16} at 33.0°C.

nitro group in series-1 which effect on the thermal stability of mesophase and as a results mesophase appeared at lower temperature with poor thermal stability.

From the above Table 2, it indicates that presently investigated series-1 and series-X which was chosen for comparison are nematogenic in addition of smectogenic. Thermal stability of nematic phase in newly series-2 is higher as compare to series-1. However, the thermal stability of smectic phase in series-1 is higher as compare to series-2. Both the series shows mesomorphism in enantiotropical manner. The thermal stability of Cr-SmC and SmC-I phase transition in series-1 is higher as compare to series-2, while the SmC-N, Cr-N and N-I phase transition of series-1 is lower as compare to series-2. These observations are further established by using DSC analysis where phase transition associated with Cr-N, N-I in higher members, Cr-SmC, SmC-N, N-I in middle members while Cr-SmC, SmC-I in lower member of present series-1. Figure 6 represents the proposed mechanism to represents the arrangement of molecules to induce SmC phase in lower member (C_3 to C_7) and nematic mesophase in higher member (comp.C₆ to C_{18}) of present series-1. From Figure 6, It can be seen that the molecular length of higher member alkyl chain contain compounds is higher as compared to short alkyl

16 🕢 D. K. SHUKLA ET AL.



Figure 3. Phase sequence of comp.C₁₄ (heating cycle).



Figure 4. Structurally similar analogous series

spacer chain based compounds. Thus, due to the presence of higher alkyl chain in alkoxy terminal part increasing more flexibility to passing solid phase to nematic phase without exhibiting any smectic phase. Comp. C_1 and C_2 shows nonliquid crystalline property due to the presence of short alkyl spacer present in n-alkoxy terminal part.

3.3. Chemical reactivity

The nature of the electronic transition and frontier molecular orbital (FMO) distributions are investigated by using density functional theory (DFT) at the B3LYP/6-311 level in Dichloromethane solution using the CPCM solvation model with default convergence criteria. The calculated FMO distributions of comp.C₈ (series-1) compared with comp.C₈ (series-2) are presented in Figure 7 and Figure 8. It is shown that from Figure 7 that for comp.C₈ from series-1 and series-2, both HOMO and LUMO are



Figure 5. Ball-stick model of series-1, -2.

Table 2. Average thermal stability in °C

Series	Series-1	Series-2
SmC-I	95.33	81.66
SmC-N	58.56	59.64
Cr-N	68.03	82.01
Cr-SmC	60.02	52.85
N-I	69.37	76.66

localized on the chalconyl-phenyl unit having N,N-dimethyl amino terminal group. A close examination of these orbitals reveals that the HOMO of comp.C₄ from both series is predominantly localized on the second phenyl with chalconyl-phenyl unit while the LUMO is mostly concentrated on chalconyl-phenyl unit. Presence of N,N-dimethyl amino group at terminal side shows significant influence on the HOMO and LUMO orbitals. It can be noted that the electronic properties of $comp.C_8$ (series-1, series-2) could have originated from the chalconyl-phenyl unit substituted by N,N-dimethyl amino group at tail side. The energy difference between the HOMO and LUMO is termed as HOMO-LUMO gap. The HOMO-LUMO gap of comp.C₈ from both series is shown in Table 3. As careful observation of Table 3, the HOMO-LUMO gap of comp. C_8 (series-2) is 4.342 eV which is lower as compare to comp. C_8 (series-1). The presence of nitro group at lateral side effects the possibility of charge transfer of electron in the HOMO to the LUMO. The higher value of HOMO energy contributes negatively to the activity due to presence of N, N-dimethyl amino group as electron-donating group which increase the energy of the HOMO orbitals.

Figure 9 shows the planar structure along with carbon numbers and the geometry of present comp. C_8 -I and comp. C_8 -II were optimized using density functional theory (DFT) based method with Becker's three-parameter functional and the Lee-Yang-Parr



Figure 6. Proposed mechanism of present series-1.



Figure 7. The molecular orbitals and energy for the HOMO and LUMO of comp.C₈ (series-1).

functional (B3LYP) with 6-311 basis set [33]. The magnitude of dipole moment (4.77 D) of comp.C₈-I is higher as compare to comp.C₈-II due to presence of polar nitro group on lateral side is shown for geometry optimized structure. Further, the



Figure 8. The molecular orbitals and energy for the HOMO and LUMO of comp.C₈ (series-2).

overall length of the molecule (L) is found to be 28.275 Å (C₈-I) and 24.085 Å (C₈-II).

3.4. 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 10. In present study, DSC thermogram is traces in heating and cooling condition. An examination of crystal to mesophase transition temperatures reveal that with increasing alkyl chain length in left tail group, a decrease in transition temperatures. As a result, mesophase temperature range for compounds found lower and some of remaining compounds shows good mesophase range due to the presence of right terminal unaltered $-N(CH_3)_2$ group. Comp.C₁₈ shows endothermic peak at 35.68 °C on heating trace, which indicates the presence of crystal to SmC mesophase while on cooling condition, it trace at 36.02°C which reveal the presence of mesophase in enantiotropical manner. Comp.C₈ shows significant endothermic peaks at 49.27 °C on heating condition, which is nearly to the transition temperature observed by POM study while on cooling condition, it appeared at 50.62°C indicate the presence of Cr-N phase transition. Compound C₆ shows first endothermic peaks at 49.81°C for crystal to crystal phase and second endothermic peak appear at 72.09°C on heating condition and on cooling condition, it trace at 49.98°C and 73.12°C to confirm the presence of crystal to nematic phase which was further confirmed by POM analysis. For compound C_3 , the first endothermic peak trace at 35.68°C which shows the presence crystal to crystal phase and on further heating second endothermic peak trace at 72.68°C indicate crystal to smectic phase on heating condition while in cooling condition, endothermic peak

20 🕢 D. K. SHUKLA ET AL.

Table 3. HOMO-LUMO energy value of comp.C₈ (series-1, series-2).

Comp.	НОМО	LUMO	Energy gap
C ₈ -I (series-1)	—9.479 eV	—5.334 eV	4.145 eV
C ₈ -II (series-2)	—9.475 eV	—5.133 eV	4.342 eV



Figure 9. Energy optimized space filled model showing magnitude and direction of dipole moment.

trace at 80.02°C which specifies the presence of smectic mesophase and at 40.07°C smectic phase transform into crystal Transition temperature obtained by DSC analysis at heating condition and the value of enthalpy and entropy are listed in Table 4.

3.5. XRD study

The mesophase structures of novel chalconyl-ester LCs were further confirmed by X-ray diffraction (XRD) studies of comp.C₅ and comp.C₁₂ filled in Lindemann capillaries. The XRD pattern obtained for comp.C₅ and comp.C₁₂ at 62.0°C and 41.0°C corresponding to smectic C and nematic phase are shown in Figure 11 and Figure 12. The sharp reflection in the small angle region with d-spacing 14.924 Å of comp.C₅ which is slightly smaller than the molecular length 15.026 Å indicating the tilted organization of



Figure 10. DSC thermogram of (a) comp. C_{18} ; (b) comp. C_{8} ; (c) comp. C_{6} ; (d) comp. C_{3} on heating condition.

the molecules in the layers. The presence of sharp reflection in the small angle region is characteristic of layer ordering of smectic phase. No any diffuse peak is present at wide angle region. In comp. C_{12} , no any significant peak is present at lower angle region while the broad hump at higher angle region indicates the absence of in plane order and liquid like nature of molecules in the layer.

3.6. Biological Evaluation

In the present work, the focus has been drawn on designing new structural entities of chalcones inbuilt with 4-n-alkoxy benzoic acid to form chalconyl-vinyl ester scaffolds to evaluate the prospective effect on biological activity, particular antibacterial and antifungal activity. Newly synthesized bent core compounds based on chalconyl-vinyl ester 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 the broth dilution method.

Comp.	Transition	Heating scan(°C)	Cooling scan(°C)	ΔH (-Jg ⁻¹)	$\Delta H (Jg^{-1})$	Δ S (-J g ⁻¹ k ⁻¹)	$\Delta S (J g^{-1}k^{-1})$
C ₁₈	Cr-N	35.68	36.02	1.82	3.42	0.0059	0.0110
	N-I	>50.0	-	6.94	-	0.0214	-
C ₈	Cr-N	49.27	50.62	2.32	3.82	0.0072	0.0118
	N-I	>80.0	-	12.81	-	0.0362	-
C ₆	Cr-Cr'	49.81	49.98	3.34	3.43	0.0103	0.0106
	Cr'-N	72.09	73.12	14.73	21.82	0.0426	0.0630
	N-I	>100.0	-	2.74	_	0.0073	_
C₃	Cr-Cr'	35.68	72.68	5.32	1.42	0.0172	0.0041
	Cr'-SmC	40.07	80.02	11.43	7.32	0.0365	0.0207
	SmC-I	>100.0	-	8.21	-	0.0220	_
C₅	Cr-SmC	60.72	61.23	1.67	5.43	0.0050	0.0162
	SmC-I	>100.0	-	12.42	_	0.0333	_

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

(Cr-Cr' = solid to solid crystal; Cr-SmC = solid to SmC; Cr-N = solid to nematic; N-I = nematic to isotropic)



Figure 11. XRD patterns of compound C_5 at 62°C.

However, in case of antifungal activity, comp.C₃, C₄, C₆, C₇, C₈, C₁₀ and C₁₂ showed good results in *C.Albicans* at 500 μ g/mL which was equivalent to standard drug greseofulvin.

3.6.1. In vitro antibacterial activity

Table 4 shows that all the newly synthesised compounds were found to exhibit good to moderate activity against specific microbial strains. Initially, we screened all the synthesised compounds (C_3 to C_{12}) for their antibacterial activity *in vitro* by using both dilution methods [34]. The *in vitro* antibacterial results confirmed that some of the chalconyl-ester hybrids exhibited antibacterial activity against various strains of *E.coli*, *P.aeruginosa* (Gram-ve) and *S.aureus*, *S.pyogenus* (Gram + ve) as shown in Table 5. An antibacterial result was comparatively nearer to the standard drug ampicillin as compare to other drug. While, C_3 to C_{12} showed activity (62.5 µg/ml MIC and 100µg/ml MIC) against *E.coli*, which is nearer to the standard value of ampicillin. Furthermore,



Figure 12. XRD patterns of compound C₁₂ at 41°C.

	Table 5.	Result of	antibacterial	activity	of	the s	ynthesized	com	bound
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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	125	100	62.5		
2	C ₄	62.5	100	200	100		
3	C ₅	62.5	125	200	62.5		
4	C ₆	100	100	100	100		
5	C ₇	62.5	200	100	62.5		
6	C ₈	100	100	100	100		
7	C ₁₀	100	125	250	62.5		
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		

compound C₃, C₄, C₅, C₈, C₁₀ and C₁₂ having excellent growth inhibition at lower concentration (62.5µg/ml MIC) as compare to standard drug. Compound C₃ to C₁₂ showed activity against *P.aeruginosa* at (100 µg/ml MIC and 125 µg/ml MIC) which was further compare with the standard drug. However, compound C₅ (120 µg/ml MIC) and C₆ (125 µg/ml MIC) showed activity at higher concentration. Compound C₃, C₅, C₇ and C₁₀ showed good inhibitory activity with lower concentration (62.5 µg/ml MIC) against *S.Pyogenus* while remaining compound showed higher MIC value respectively.

3.6.2. In vitro antifungal activity

Antifungal activity data displayed in Table 6 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_4 , C_6 , C_8 and C_{10} at 500

24 🕒 D. K. SHUKLA ET AL.

ANTIFUNGAL ACTIVITY

Minimal Fungicidal Concentration							
Sr.No	Code. No.	C.Albicans MTCC 227	A.Niger MTCC 282	A.Clavatus MTCC 1323			
Microgramm / M	L						
1	C3	500	250	200			
2	C ₄	500	1000	250			
3	C ₅	250	250	200			
4	C ₆	500	250	250			
5	C ₇	250	1000	250			
6	C ₈	500	250	250			
7	C ₁₀	500	250	250			
Standard	Nystatin	100	100	100			
Standard	Greseofulvin	500	100	100			

Table 6. Result of antifungal activity of the synthesized compounds

 μ g/ml MIC which is equal to the concentration of standard drug Greseofulvin. However, compound C5 and C7 showed lower MIC as compared to other synthesized derivatives respectively. While inhibiting against *A.Niger*, *A.Clavatus* fungi by compound C₃, C₅, C₆, C₈ and C₁₀ at 250 μ g/ml MIC, while remaining compounds showed poor activity.

4. Conclusions

A new calamitic rod type chalcone-derived LCs compounds based on three phenyl rings as rigid core possessing two linking unit, lateral nitro group and N,N-dimethyl amino as terminal group at one end and other end with variable alkyl chain length in alkoxy group (-OR). Interestingly, it can be noted that seven compounds from this synthesized series showed good antimicrobial activity. The antibacterial and antifungal activity was determined by MIC (Broth dilution method). The POM and DSC measurements confirmed the presence of enantiotropic nematic as well as smectic mesophase. The lower member (comp.C₃ to C₅) shows enantiotropic smectic C phase while higher member (comp. C₆ to C₁₈) shows enantiotropic nematic phase at room temperature having lower value of thermal stability. The group efficiency order derived on the basis of (a) thermal stability, (b) early or late commencement of mesophase, (c) Temperature range of mesophase.

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26 🕒 D. K. SHUKLA ET AL.

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