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Synthesis and characterization of novel rod-like ester-based liquid crystalline homologous series: Effect of *tert*-butyl tail on mesomorphism

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ABSTRACT

A new rod-like homologous series consisting twelve compounds with central ester linkage and terminal *tert*-butyl group, *tert*-butyl [4-(4'-*n*-alkoxybenzoyloxy)benzoates] has been synthesized and characterized through standard spectroscopic techniques like UV, FT-IR, ¹HNMR, DSC, POM, and XRD. Methoxy and ethoxy derivatives are nonmesogenic. Nematic mesophase commences as enantiotropy from propyloxy derivative and persists up to the octadecyloxy derivatives. Smectic A mesophase commences as monotropy from propyloxy to the octadecyloxy derivatives. The mesomorphic properties of present series are compared with other structurally related series to evaluate the effect of terminal *tert*-butyl group on mesomorphism. Two derivatives are subjected to *in vitro* antimicrobial activity.

KEYWORDS

Enantiotropic; *in vitro* activity; liquid crystal; nematic; smectic A; *tert*-butyl group

1. Introduction

A liquid crystalline state [1] is a state which is an intermediate state between liquid and solid and is of great importance to universal bodies in different areas of relating science and other technological applications [2, 3]. Some substances exhibit an intermediate state of matter with molecular ordering in between that of conventional crystalline solid and isotropic liquid phases, and this state of matter is called a liquid crystal state or mesomorphic state [4, 5]. Because of the peculiar physical properties and different ranges of temperature, the nematic phase behavior in liquid crystal plays an important role in generation of new liquid crystal displays (LCDs). A small change in the molecular arrangements is affected by the mesomorphic behavior of organic compounds. The theoretical study of many series was very informative to have an idea about chemical constitution in nematogenic and smectogenic compounds [6, 7]. The orientation of molecule in nematic phase is toward a particular direction. The molecular orientation can be achieved in portable approach after applying an electric or magnetic field [8]. Calix [4] arene core was prepared by condensing Schiff base derivatives of 4-*n*-alkoxybenzaldehyde and 4-aminobenzoic acid at lower rim of *tert*-butyl calix [4] arene and studied the mesomorphic properties of calix [4] arene Schiff base ester derivatives along

with the biological investigations [9]. Calixarene with tunable 3D shaped cavities which helps in creating supramolecular platform after crown ether and cyclodextrin [10]. A review on lower rim substituted calixarenes along with their applications was reported by Menon *et al.* [11]. Recently, antimicrobial activity of p-tetra nitro calix [4] arene derivatives was reported by Menon *et al.* [12]. Doshi *et al.* synthesized homologous series containing ester and vinyl ester linkage group [13, 14]. Vinay *et al.* reported the effect of tail or lateral group on mesomorphism for various homologous series containing alkoxy benzoates and alkoxy cinnamates [15–19]. Earlier mesogenic esters with straight and branched alkyl chains have been reported [20–22]. Calix [4] arene-based chemosensors with high sensitivity and power were reported to sense analytes [23]. Calix [4] arene system with fluorescence mechanism is mainly PET [24], FRET [25], PCT [26], and ICT [27] for molecular recognition. E. Šinkovec *et al.* reported a liquid–liquid phase transfer catalyzed (PTC) esterification reaction of 4-*t*-butylphenol in aqueous phase and 4-methoxybenzoyl chloride in organic phase with product 4-*t*-butylphenyl 4-methoxy benzoate in a micro channel under parallel laminar flow conditions by using tetra butyl ammonium bromide as PTC developing a 3D mathematical model considering convection in the flow directions and diffusion in spatial directions [28].

From earlier researches, Wang *et al.* [29], Asai *et al.* [30], Wang *et al.* [31], Bhattacharya *et al.* [32], and Yang *et al.* [33] reported about interfacial mass transfer and mathematical modeling. For estimating diffusion coefficients, Wilke–Chang’s empirical correlation was used as follows:

$$D_{AB} = 7.4 \times 10^{-8} \frac{\sqrt{\Psi_B M W_B T}}{\eta_B \bar{V}_A^{0.6}}$$

where A and B denote solute and solvent (Li and Carr [34]).

Ju Hyun Kim *et al.* reported a CO-gas-free alkoxy carbonylation of aryl iodides in presence of [Rh(COD)Cl]₂DPEPhos catalytic system and an alcohol with/without an aldehyde [35]. Presence of both alcohol and aldehyde leads to high yield of alkoxycarbonylated products while without these two, leads to have moderate yield. Also, phenol leads to phenoxy-carbonylation products with high yields. Esters from aryl iodides and various alcohols in phenoxy-carbonylation reaction in which aldehyde acted as a sole source of CO yield a product 4-*t*-butylphenyl 4-methoxy benzoate (30%) as one of the substrate leads to a conclusion that phenyl hydroxyl groups is more reactive than benzyl hydroxyl group and electron-deficient phenols are more reactive than electron-rich phenols [36]. A plausible reaction can be drawn for alkoxycarbonylation of an aryl halide with rhodium compound, an alcohol and an aldehyde [37–39]. Recently, some studies have been reported [28, 35], and the research group reported various aspects related to their research field but no mesomorphic properties were mentioned for LC. In our present studies, we have synthesized newly ester-based homologous series with varying left alkoxy (-OR) side chain while keeping the group fixed at terminal *tert*-butyl tail showing great mesogenic properties related to LC studies.

2. Experimental

2.1. Materials

For present synthesized homologous series, 4-hydroxy benzoic acid was purchased from S.R.L., Mumbai and para *tert*-butyl phenol from Sigma–Aldrich. N-bromo alkanes

(S.R.L., Mumbai), methanol, pure thionyl chloride (SOCl_2), potassium hydroxide (Finar Chemicals, India), and pyridine, required for synthesis, were used as received along with previously dried and purified solvents.

2.2. Measurements

Microanalysis of the compounds was performed on a Coleman Carbon/Hydrogen analyzer. The FT-IR spectral data were obtained for KBr pellets, using Shimadzu IR-408 spectrophotometer. ^1H NMR spectral data were recorded on a Perkin-Elmer R-32 spectrometer using tetramethylsilane (TMS) as internal reference standard. The chemical shifts are shown in δ (ppm) downfield from the reference, and CDCl_3 was used as solvent. The beautiful images were captured on a trinocular optical polarizing microscope (POM) (Leitz Laborlux 12 POL) fitted with heating plate and a digital camera. The transition enthalpies were recorded by cryo-DSC model DSC 822 $^\circ$, Mettler Toledo, Switzerland, having star $^\circ$ software system at a heating and cooling rate of 5°C min^{-1} with pure indium as a standard for calibration. The compound is sand-witched between the two glass slides and a cover slip at heating, and cooling rate is 2°C min^{-1} , respectively.

The synthetic route to compounds of Series I is illustrated in [Scheme 2](#).

2.3. Synthesis

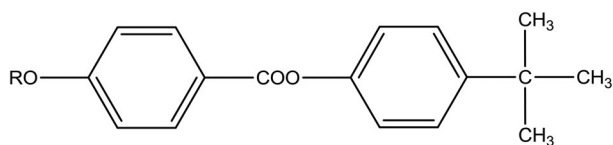
4-*n*-alkoxy benzoic acids (A) were prepared from 4-*n*-hydroxy benzoic acids by applying a Williamson's ether synthesis protocol [40] by refluxing the mixture of 4-*n*-hydroxy benzoic acid (one equiv.) with corresponding *n*-alkyl bromide (1 equiv.) in presence of KOH (1.5 equiv.) and methanol as a solvent [40]. 4-*n*-alkoxy benzoyl chloride (B) was prepared by heating corresponding acids with excess of thionyl chloride under reflux for 2 hrs [41]. The *tert*-butyl phenol (15 mmol) was dissolved in dry pyridine (10 ml), and a cold solution of an appropriate 4-*n*-alkoxy benzoyl chloride (15 mmol) (B) was added slowly while stirring in an ice bath. Before acidification with cold 1:1 aq. HCl, the mixture kept undisturbed overnight at room temperature. The insoluble was removed through filtration. The elute was obtained after the removal of excess solvent using TLC plates (thin layer + chromatography Merck Kiesel gel 60 F₂₅₄ pre-coated plates) for purity check. After extraction, the obtained residue was separated by column chromatography on silica gel using proportion (95:5) of petroleum ether and ethyl acetate, and then, it was crystallized repeatedly from methanol till constant transition temperature was obtained. All twelve synthesized compounds of present Series I are confirmed by using spectral and analytical techniques like UV, FT-IR, $^1\text{HNMR}$, and XRD (*n*-dodecyloxy derivative of Series I), and were found to be satisfactory with the proposed structure.

Typical spectral data of various compounds of Series I are as follows:

Series I: *tert*-butyl [4-(4'-*n*-hexyloxy) benzoate]

UV Spectrum (MDC) nm: 280.

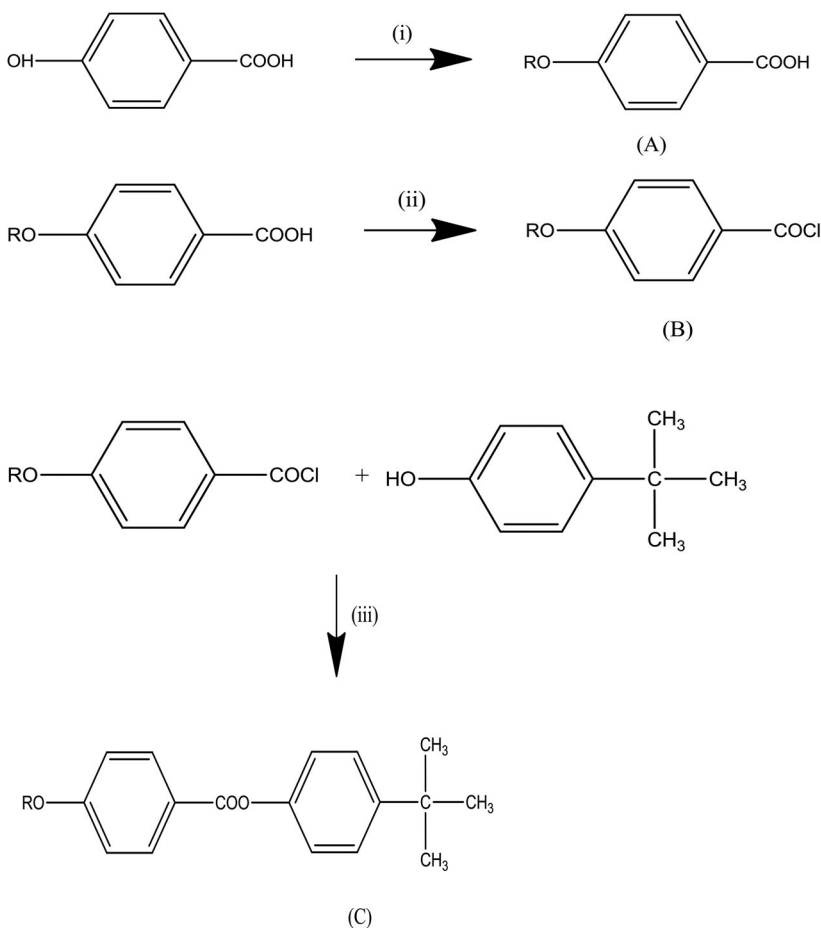
IR spectrum (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2932, 1724 ($-\text{COO}-$), 1627, 1258, 846,643.



tert-butyl [4-(4'-*n*-alkoxybenzoyloxy) benzoates],

$R = C_nH_{2n+1}$; $n = 1$ to 8, 10, 12, 14, 16 and 18

Scheme 1. The general formula is shown.



$R = C_nH_{2n+1}$; $n = 1$ to 8, 10, 12, 14, 16 and 18

Reagents and conditions: (i) R-Br, potassium hydroxide (KOH), dry methanol ; (ii) Excess SOCl₂; (iii) Dry pyridine, cold aq. HCl.

Scheme 2. Synthetic route to Series I compounds.

¹H NMR: δ H(CDCl₃, 400 MHz): 0.89 (t, 3H, -CH₃), 1.32-1.48 (m, 6H, 3 × -CH₂), 1.32 (s, 9H, -C(CH₃)₃), 1.80 (p, 2H, -CH₂), 4.03 (t, 2H, -OCH₂), 6.93 (d, 2H, ArH), 7.71 (d, 2H, ArH), 7.91 (d, 2H, ArH), 8.05 (d, 2H, ArH).

Series I: *tert*-butyl [4-(4'-*n*-decyloxy)benzoate]*UV Spectrum (MDC) nm:* 280.*IR spectrum (KBr) ν_{max}/cm^{-1} :* 2918, 1732 (-COO-), 1601, 1515, 1464, 1286, 1249, 1160, 816. 1H NMR: $\delta H(CDCl_3, 400\text{ MHz})$: 0.88 (t, 3H, -CH₃), 1.24-1.47 (m, 14H, 7 $\times$ -CH₂), 1.31 (s, 9H, -C(CH₃)₃), 1.80 (p, 2H, -CH₂), 4.03 (t, 2H, -OCH₂), 6.93 (d, 2H, ArH), 7.14 (d, 2H, ArH), 7.45 (d, 2H, ArH), 8.05 (d, 2H, ArH).**Series I:** *tert*-butyl [4-(4'-*n*-dodecyloxy)benzoate]*UV Spectrum (MDC) nm:* 270.*IR spectrum (KBr) ν_{max}/cm^{-1} :* 2926, 1735 (-COO-), 1607, 1511, 1465, 1254, 1168, 1069, 842. 1H NMR: $\delta H(CDCl_3, 400\text{ MHz})$: 0.88 (t, 3H, -CH₃), 1.27-1.56 (m, 18H, 9 $\times$ -CH₂), 1.31 (s, 9H, -C(CH₃)₃), 1.79 (p, 2H, -CH₂), 4.04 (t, 2H, -OCH₂), 6.97 (d, 2H, ArH), 7.11 (d, 2H, ArH), 7.61 (d, 2H, ArH), 8.15 (d, 2H, ArH).**Series I:** *tert*-butyl [4-(4'-*n*-tetradecyloxy)benzoate]*UV Spectrum (MDC) nm:* 260.*IR spectrum (KBr) ν_{max}/cm^{-1} :* 2918, 1732 (-COO-), 1601, 1515, 1464, 1286, 1249, 1160, 816. 1H NMR: $\delta H(CDCl_3, 400\text{ MHz})$: 0.88 (t, 3H, -CH₃), 1.26-1.47 (m, 22H, 11 $\times$ -CH₂), 1.31 (s, 9H, -C(CH₃)₃), 1.80 (p, 2H, -CH₂), 4.02 (t, 2H, -OCH₂), 6.92 (d, 2H, ArH), 7.12 (d, 2H, ArH), 7.43 (d, 2H, ArH), 8.03 (d, 2H, ArH).**Series I:** *tert*-butyl [4-(4'-*n*-hexadecyloxy)benzoate]*UV Spectrum (MDC) nm:* 260.*IR spectrum (KBr) ν_{max}/cm^{-1} :* 2918, 1732 (-COO-), 1601, 1515, 1464, 1286, 1249, 1160, 816. 1H NMR: $\delta H(CDCl_3, 400\text{ MHz})$: 0.88 (t, 3H, -CH₃), 1.26-1.45 (m, 26H, 13 $\times$ -CH₂), 1.31 (s, 9H, -C(CH₃)₃), 1.80 (p, 2H, -CH₂), 4.00 (t, 2H, -OCH₂), 6.91 (d, 2H, ArH), 7.09 (d, 2H, ArH), 7.42 (d, 2H, ArH), 8.05 (d, 2H, ArH).**Series I:** *tert*-butyl [4-(4'-*n*-octadecyloxy)benzoate]*UV Spectrum (MDC) nm:* 250.*IR spectrum (KBr) ν_{max}/cm^{-1} :* 2918, 1736 (-COO-), 1604, 1511, 1470, 1255, 1205, 1167, 844. 1H NMR: $\delta H(CDCl_3, 400\text{ MHz})$: 0.80 (t, 3H, -CH₃), 1.18-1.41 (m, 30H, 15 $\times$ -CH₂), 1.31 (s, 9H, -C(CH₃)₃), 1.76 (p, 2H, -CH₂), 3.96 (t, 2H, -OCH₂), 6.88 (d, 2H, ArH), 7.04 (d, 2H, ArH), 7.34 (d, 2H, ArH), 8.06 (d, 2H, ArH).

3. Results and discussion

3.1. Optical microscopy studies

On the basis of earlier attempts, the optical microscopic studies conclude that the mesophases exhibited by the compounds of Series I and Series A. The structurally related

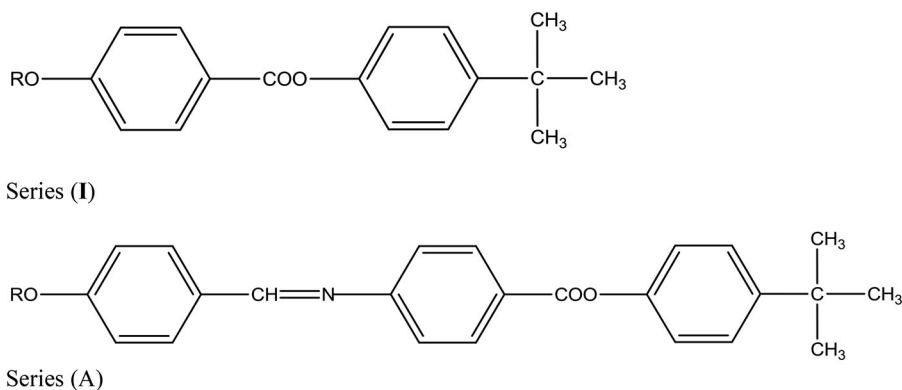


Figure 1. Structurally similar Series I and Series A.

Series I and comparative Series A are shown in Figure 1. The space filling diagrams of both Series I and Series A are shown in Figure 2. *n*-Methoxy and *n*-ethoxy derivatives are nonmesogenic and change directly into liquid state, that is enantiotropy (no mesophase exists) due to the possibility of high rate of crystallization because of high melting point.

The non-mesomorphicity of *n*-methoxy and *n*-ethoxy derivatives with short alkyl chain length might be because of the lower intermolecular dispersion forces and lower dipole-dipole interfaces providing great isotropic crystallizing tendency. Thus, during heating, irregular and further splitting of crystal lattices directly reach to its isotropic phases, while during cooling conditions, freezing starts from isotropic conditions without showing any liquid crystalline phases. The present investigation includes the effect of terminal-side *tert*-butyl group with linear chalconyl ester group with variable flexibility on mesomorphism. In addition, compounds showing classical schlieren pattern of the nematic mesophase commence as enantiotropy from *n*-propyloxy and persist up to the *n*-octadecyloxy derivative of the series. Smectic A mesophase with focal conic pattern commences as monotropy from *n*-propyloxy and persists up to the *n*-octadecyloxy derivative of the series. Using optical polarizing microscope, phases can be seen by making thin film samples by sandwiching novel compound between glass slide and cover slip. Nematic phase can be observed as enantiotropy, and all the compounds from *n*-propyloxy to *n*-octadecyloxy show droplet-type texture. On cooling, isotropic liquids of Series I compounds show the classical schlieren texture of the nematic phase like in form of small droplets in Figure 3a.

On further cooling, all the compounds from *n*-propyloxy to the *n*-octadecyloxy exhibit focal conic texture of SmA mesophase in Figure 3b and c. While in Series A, nematic mesophase starts from *n*-tetradecyloxy to *n*-octadecyloxy homologous, in *n*-tetradecyloxy, fan-like rod nematic mesophase in heating and cooling conditions and droplet-type texture of nematic mesophase in *n*-hexadecyloxy and rod-like texture of nematic phase in *n*-octadecyloxy, respectively. SmA phase with broken fan-like texture can be seen from methoxy to *n*-dodecyloxy along with the SmC mesophase in all the thirteen compounds [42]. The existence of nematic mesophase is due to greater terminal attractions. As the number (*n*) increases, alkyl chain length increases and polarizability increases with the increase in intermolecular van der Waals attractions. But the lateral

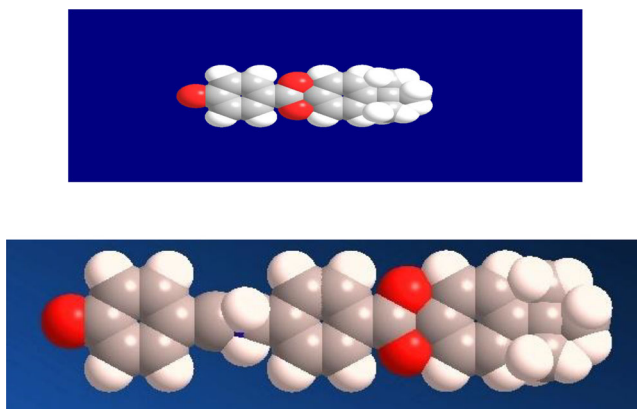


Figure 2. Space filling diagrams of Series I and Series A.

attractions are more predominant over terminal attractions [43]. Thus, molecules achieve layered structure in fluid conditions while heating further increases in temperature, weakens the strict adherence to layered form due to greater thermal vibrations, thus achieving more fluid nature. At a certain temperature, breaking of layered structure occurs but still maintains end-to-end parallel orientation which leads to give nematic-threaded texture to the homologous. But at a certain temperature, SmA mesophase exists due to the increase in the alkyl chain length at one end and as ratio of terminal to lateral attractions decreases, there are less chances of achieving nematic mesophase and at that particular stage there are more chances of achieving SmA mesophase only.

Figure 4 shows the plot of transition temperature and number of carbon atoms. A sharp decrease in crystal-mesophase/isotropic transition temperature can be seen as the length of terminal alkyl chain(-OR) increases giving enantiotropic behavior from third member of Series I. Due to the change in (-R) group from *n*-methoxy to last member *n*-octadecyloxy, there exists a change in the mesomorphic properties while keeping the central ester group at the same position.

Nematic-isotropic (N-I), (SmA-N) as well as SmA-I transition temperatures decrease exhibiting the usual odd-even effect. Also, in comparative Series A, the same odd-even effect can be seen [42] in phase diagram.

Gray et al. described a view on higher nematic phase transition curve with the increase in anisotropy of the polarizability and increase in intermolecular cohesive forces due to the increase in the side chain of the molecule. The molecule becomes strained as oxygen atom will bump into the nonbonded side of the adjacent hydrogen of ring causing twist around the carbonyl bond. This will make the molecule broad, and benzene ring of Series I becomes out of plane [43].

The nematic mesophase exists due to the thermal vibrations (ΔH), also due to the anisotropic end-to-end intermolecular attractions helping the molecules to move on the surface in parallel orientation which can be seen on the top of slide [44].

For confirmation of the phase transition and thermal behavior, DSC is most widely used and a valuable tool. Thermograms obtained in heating and cooling conditions are in close agreement with the microscopic temperature values in heating and cooling conditions. For Series I, on heating cycle, the compound **8** showed three peaks at 99.46 °C

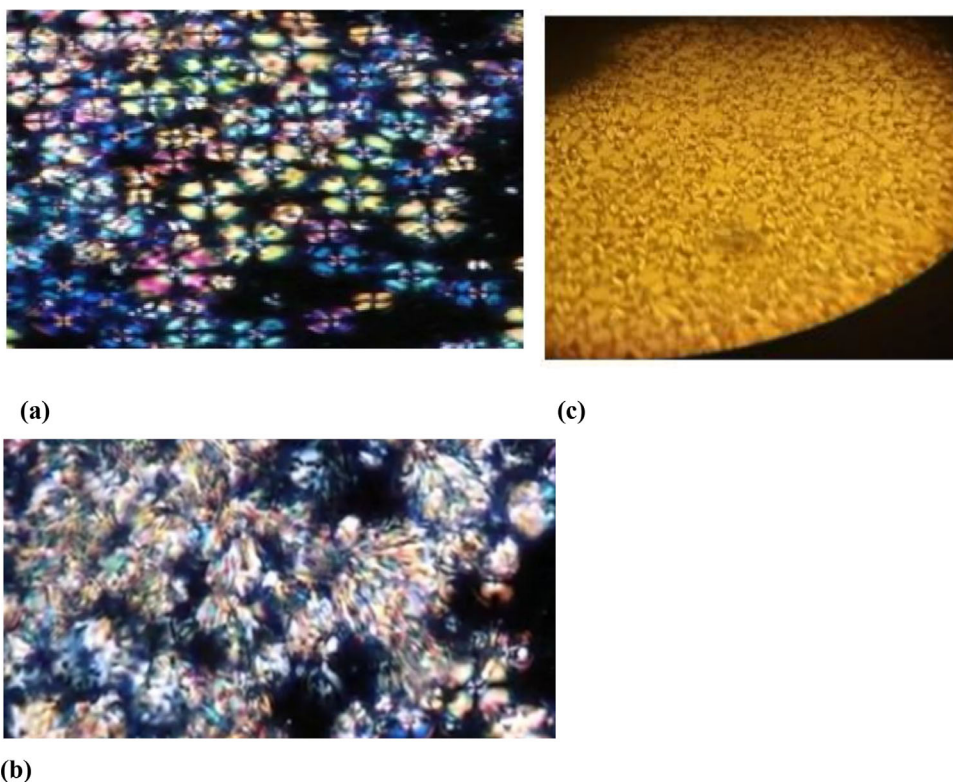


Figure 3. Optical textures of the compounds of the present series. Optical textural photographs of (a) schlieren texture of nematic mesophase (Series I; $n = 14$) at 99°C , (b) focal conic texture of SmA mesophase (Series I; $n = 14$) at 95°C on cooling, and (c) focal conic texture of SmA mesophase (Series I; $n = 18$) at 75°C on cooling.

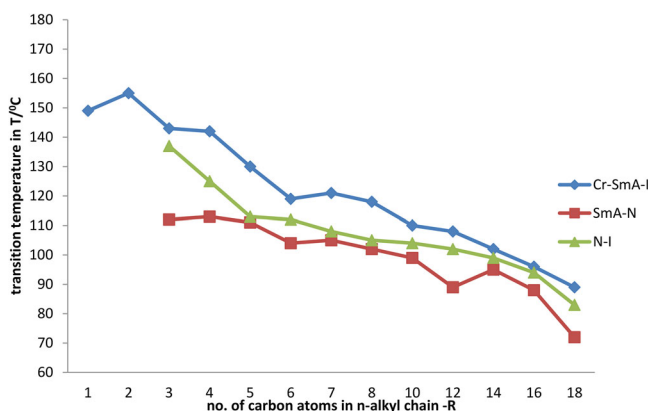


Figure 4. Phase diagram of Series I.

($\Delta H = 89.15 \text{ J/g}$), 102.16°C ($\Delta H = 68.40 \text{ J/g}$), and 118.00°C ($\Delta H = 70.22 \text{ J/g}$), which corresponds to the Cr-SmA, SmA-N, and N-I transitions, respectively. For Series I, on heating cycle, the compound 13 showed three peaks at 61.61°C ($\Delta H = 61.49 \text{ J/g}$), 72.50°C ($\Delta H = 58.34 \text{ J/g}$), and 90.00°C ($\Delta H = 61.56 \text{ J/g}$), which corresponds to the

Table 1. Transition temperatures ($^{\circ}\text{C}$) of the Series I compounds.

Compound No.	$R = \text{C}_n\text{H}_{2n+1}$ $n =$	Cr	SmA	N	I
1	1	149	–	–	•
2	2	151	–	–	•
3	3	143	(• 112)	• 137	•
4	4	142	(• 113)	• 125	•
5	5	130	(• 111)	• 113	•
6	6	119	(• 104)	• 112	•
7	7	121	(• 106)	• 108	•
8	8	118	(• 102)	• 105	•
9	10	110	(• 99)	• 104	•
10	12	108	(• 89)	• 102	•
11	14	108	(• 95)	• 99	•
12	16	96	(• 88)	• 94	•
13	18	89	(• 72)	• 83	•

() = monotropic value; Cr = crystalline solid; SmA = smectic A phase; N = nematic phase; I = isotropic liquid phase; •, phase exists; –, phase does not exist.

Table 2. Transition temperature ($^{\circ}\text{C}$), and enthalpy ($-\text{Jg}^{-1}$) and entropy ($-\text{Jg}^{-1}\text{K}^{-1}$) change by DSC measurement of Series I and of comparative Series A. DSC data for Series I and A compounds.

Series	Compound	Transition	Peak temp/ $^{\circ}\text{C}$	$\Delta H/\text{Jg}^{-1}$	$\Delta S/\text{Jg}^{-1}\text{K}^{-1}$
I	8	Cr–SmA	99.46	89.15	0.2393
		SmA–N	102.16	68.40	0.1556
		N–I	118	70.22	0.1795
	18	Cr–SmA	61.61	61.49	0.1837
		SmA–N	72.50	58.34	0.1688
		N–I	90.00	61.56	0.1695
A	8	Cr–SmC	105.02	37.92	0.1003
		SmC–SmA	113.12	9.21	0.0227
		SmA–I	>140	11.34	0.0274
	18	Cr–SmC	85.91	32.29	0.0899
		SmC–N	98.23	7.53	0.0202
		N–I	>110	9.62	0.0251

Cr–SmA, SmA–N, and N–I transitions, respectively. On cooling also, the compound **13** showed significant peaks for the I–N, N–SmA, and SmA–Cr transitions, respectively, which was further confirmed by POM studies.

The results are recorded in Table 2.

On heating, hexyloxy homolog shows endothermic peak at 112°C indicates presence of nematic phase, and on cooling, two endothermic peaks can be seen at 111°C and 104°C confirming the nematic phase as well as SmA mesophase. On heating, decyloxy homolog shows endothermic peak at 104°C indicates presence of nematic phase, and on cooling, two endothermic peaks can be seen at 102°C and 99°C confirming the nematic phase as well as SmA mesophase. On heating, dodecyloxy homolog shows endothermic peak at 102°C indicates presence of nematic phase, and on cooling, two endothermic peaks can be seen at 101°C and 89°C confirming the nematic phase as well as SmA mesophase. On heating, tetradecyloxy homolog shows endothermic peak at 99°C indicates presence of nematic phase, and on cooling, two endothermic peaks can be seen at 97°C and 95°C confirming the nematic phase as well as SmA mesophase. On heating, hexadecyloxy homolog shows endothermic peak at 94°C indicates presence of nematic phase, and on cooling, two endothermic peaks can be seen at 90°C and 88°C confirming the nematic phase as well as SmA mesophase. Reference to Table 3 shows that the mesophase length and thermal stabilities of Series I are 15 and 119 while

Table 3. The mesophase length, phase transition, and comparative molecular structure of *n*-hexyloxy derivative of Series I and A.

Series No.	Compound	Mesophase range	Thermal stabilities SmA-I	Commencement of smectic A phase	Commencement of nematic phase
I	C ₆	(15)	119	C ₃	C ₃
A	C ₆	14	134	C ₁	C ₁₄

Table 4. Result of antimicrobial activity of synthesized compounds.

Compound name	<i>E. coli</i> MTCC 443	<i>Aureus</i> MTCC 96	Name of organism
C12 <i>tert</i> -butyl recrystallized	700	700	<i>E. coli, S. aureus</i>
C18 <i>tert</i> -butyl recrystallized(F2)	400	400	<i>E. coli, S. aureus</i>
C18 <i>tert</i> -butyl recrystallized(F1)	200	200	<i>E. coli, S. aureus</i>
Standard amoxicillin & clavulanic acid	240	240	

in Series A, the mesophase length and thermal stabilities of Series A is 14 and 134. In Series I, the mesophase range exists as monotropy and the difference is of only 1 °C, respectively, while in Series A, the mesophase range exists as enantiotropy. Reference to the molecular structure, both the compounds differ only at the central linkage. The Series A has additional central (-CH=N-) linkage whereas the Series I only central ester (-COO-) linkage. Series I compounds are showing lower readings, and readings exist as monotropy and mesophases exist as in heating as well as in cooling conditions which are quite in close agreement with the DSC readings taken. Therefore, the smectic and nematic mesophase range and thermal stability of present Series I can be explained in terms of the polarizability of the molecule resulting from (-COO-) ester group in the central linkage and terminal *tert*-butyl chain in Series I.

4. XRD analysis

In order to verify the results obtained from POM and DSC, we have performed XRD of *n*-dodecyloxy (Series I) to confirm the structure of various phases present at transition temperature. The XRD patterns at their transition temperature are shown in Figure 5.

The recorded pattern contains a sharp peak. The obtained reflection pattern [45] and microscopic textural observations confirm the presence of nematic phase as well as smectic phase.

5. *In vitro* antibacterial activity

A sensitivity analysis is a test that determines the sensitivity of bacteria to an antibiotic. It also determines the ability of the drug or a compound to kill the bacteria.

Two compounds at different test concentrations were tested for its antibiotic properties or effect against gram-positive and gram-negative bacteria, namely *E. coli* MTCC 443 and *S. aureus* MTCC 96. Clavum (amoxicillin and clavunilic acid) was used as control standard in all the plates. Amoxicillin and clavunilic acid are used for the treatment of many infections caused by bacteria. Amoxicillin inhibits the growth of bacteria. Significant zone of inhibition could be observed for control standard in all the plates of

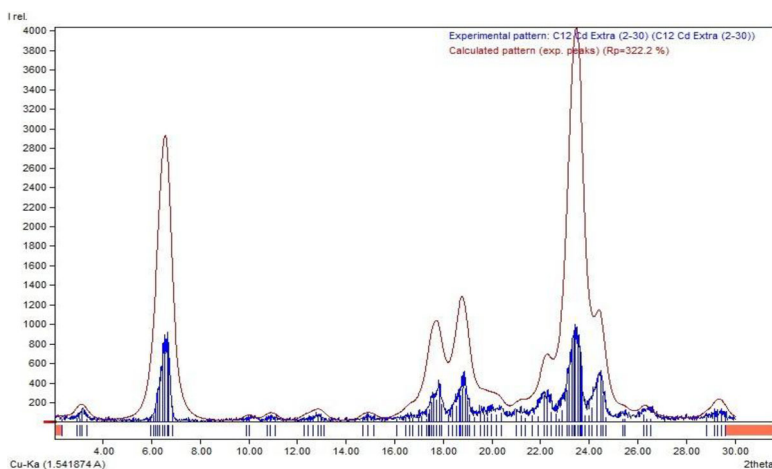


Figure 5. Diffraction pattern graphics XRD pattern of compound C₁₂-Series I at 102 °C.

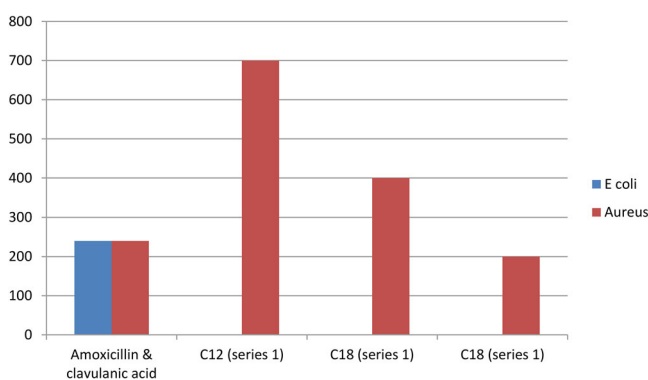


Figure 6. Antimicrobial activity at various concentrations with standard drug.

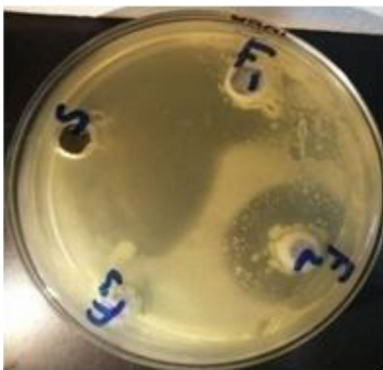


Figure 7. Zone of inhibition.

E. coli as well as *S. aureus*. None of test compounds showed zone of inhibition against *E. coli*, and only *n*-dodecyloxy and *n*-octadecyloxy compounds showed inhibition zone against *S. aureus* at two concentrations.

From the above experiment, it can be concluded that compound *n*-dodecyloxy showed zone of inhibition at minimum inhibitory concentration 700 ($\mu\text{g/ml}$) and compound *n*-octadecyloxy showed zone of inhibition at 200 minimum inhibitory concentration ($\mu\text{g/ml}$), respectively, against *S. aureus*, whereas no compounds showed zone of inhibition against *E. coli*. The zone of inhibition observed for two compounds against *S. aureus* was less compared to control standard but satisfactory.

Conclusion

We have synthesized a homologous series with terminal *tert*-butyl and alkoxy side chain. The presence of terminal *tert*-butyl group and the ester (-COO-) group at center leads to have mesophases. The classical schlieren pattern of the nematic mesophase commences as enantiotropy from *n* -propyloxy, and smectic A mesophase with focal conic pattern commences as monotropy from *n* -propyloxy and persists up to the *n*-octadecyloxy derivative of the series with great thermal stability. The methoxy and ethoxy derivatives are non-mesogenic due to the presence of short alkyl spacer. The mesogenic behavior was studied using POM, DSC, and XRD. Further, antimicrobial activities of few compounds were performed, and results show that the derivatives may be bioactive.

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References

- [1] F. Reintzier, *Monastsh. Chem.* **9**, 421 (1888).
- [2] G. W. Gray and P. A. Winsor, Liquid crystals and plastic crystals, Chapter 6.2. In *The Role of Liquid Crystal in Life Processes*, Stewart, G. T. (Eds.), Vol. 1, pp. 308.
- [3] E. Hertz, B. Lavorel, and O. Faucher, *Nature Photon.* **5** (2), 78 (2011). doi:10.1038/nphoton.2011.6
- [4] G. W. Gray and P. A. Winster, Liquid crystals and plastic crystals, Chapter 6.2. In *The Role of Liquid Crystal in Life Processes*, Stewart, G. T. (Eds.), Vol. 1, pp. 308–326.
- [5] M. Hird *et al.*, *Liq. Cryst.* **15** (2), 123 (1993). doi:10.1080/02678299308031946
- [6] (a) G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press, London and New York, 1962);(b) M. Hird, K. J. Toyne, G. W. Gray, S. E. Day, D. G. M. Donell. *Liq. Cryst.* **15**, 123–150 (1993); (c) M. Hird, J. W. Goodby, N. Gough, K. J. Toyne. *J. Mater. Chem.* **11**, 2732–2742 (2001) doi:10.1039/b102988f; (d) G. W. Gray, M. Hird, D. Lacey, K. J. Toyne. *J. Chem. Soc.*, **2**, 2041–2053 (1989).
- [7] J. S. Dave *et al.*, *Mol. Cryst. Liq. Cryst.* **14** (3–4), 307 (1971). doi:10.1080/15421407108084645
- [8] a) J. A. Castellano, *Liq. Cryst. Today* **1** (1), 4 (1991);b) G. Nordendorf, J. Schmidtke, D. Wilkes, and H. Kitzerow, *J. Mater. Chem. C* **5**, 518 (2017). doi:10.1080/13583149108628568

- [9] V. S. Sharma *et al.*, *Chem. Sel.* **2** (27), 8596 (2017). Wiley Online Library Chem Pub Soc Europe, doi:[10.1002/slct.201701306](https://doi.org/10.1002/slct.201701306)
- [10] C. D. Gutsche *et al.* *Calixarenes in Action* (Imperial College Press, London, 2000) doi:[10.1021/jo00419a052](https://doi.org/10.1021/jo00419a052)
- [11] P. Jose and S. K. Menon, *Bioinorg. Chem. Appl.* **2007**, 1 (2007). doi:[10.1155/2007/65815](https://doi.org/10.1155/2007/65815)
- [12] S. Muneer *et al.*, *Polycycl. Aromat. Compd.* **35**, 1 (2015).
- [13] R. P. Chaudhari *et al.*, *Mol. Cryst. Liq. Cryst.* **569**, 49 (2012). doi:[10.1080/15421406.2013.794672](https://doi.org/10.1080/15421406.2013.794672)
- [14] D. M. Suthar and A. V. Doshi, *Mol. Cryst. Liq. Cryst.* **569** (1), 64 (2012). doi:[10.1080/15421406.2012.698235](https://doi.org/10.1080/15421406.2012.698235)
- [15] V. S. Sharma and R. B. Patel, *Mol. Cryst. Liq. Cryst.* **633** (1), 37 (2016). doi:[10.1080/15421406.2016.1177880](https://doi.org/10.1080/15421406.2016.1177880)
- [16] V. S. Sharma and R. B. Patel, *Mol. Cryst. Liq. Cryst.* **630** (1), 58 (2016). doi:[10.1080/15421406.2016.1146866](https://doi.org/10.1080/15421406.2016.1146866)
- [17] V. S. Sharma and R. B. Patel, *Mol. Cryst. Liq. Cryst.* **630** (1), 162 (2016). doi:[10.1080/15421406.2016.1146938](https://doi.org/10.1080/15421406.2016.1146938)
- [18] R. B. Solanki *et al.*, *ILCPA Sci. Press* **58**, 144 (2015). doi:[10.18052/www.scipress.com/ILCPA.58.144](https://doi.org/10.18052/www.scipress.com/ILCPA.58.144)
- [19] V. S. Sharma *et al.*, *ILCPA* **54**, 240 (2016). doi:[10.18052/www.scipress.com/ILCPA.59.115](https://doi.org/10.18052/www.scipress.com/ILCPA.59.115)
- [20] V. Vill, *Liquid Crystals 2.0. Database of Liquid Crystalline Compounds for Personal Computers* (Fijitsu Kyushu System (KOS) Ltd., Fukuoka, 1996).
- [21] D. Demus, H. Zashcke, *Flussige Kristalle in Tabellen II* (VEB Deutscher Verlag Fur Grundstoffindustrie, Leipzig, 1984).
- [22] H. Kelker, *Handbook of Liquid Crystals*, Kelker, H. and Hatz, R. (Eds.) (VCH, Weinheim, 1980).
- [23] (a) C. D. Gutsche, *Calixarenes Revisited* (The Royal Society of Chemistry, Cambridge, England, 1998);(b) P. G. Sutariya, A. Pandya, V. A. Rana, S. K. Menon, *Liq. Cryst.* **40** (3), 374–383 (2013) doi:[10.1080/02678292.2012.749305](https://doi.org/10.1080/02678292.2012.749305); (c) P. G. Sutariya, N. R. Modi, A. Pandya, V. A. Rana, S. K. Menon, *RSC Adv.* **3**, 4176–4180 (2013).
- [24] (a) T. Jin *et al.*, *J. Chem. Soc. Chem. Commun.* **1771** (1991). doi:[10.1039/c39910001771](https://doi.org/10.1039/c39910001771)
- [25] M. A. Hossain, H. Mihara, and A. Ueno, *J. Am. Chem. Soc.* **125**, 1178 (2003).
- [26] J. D. Van Loon, W. Verboom, and D. N. Reinhoudt, *Org. Prep. Proced. Int.* **24** (4), 437 (1992). doi:[10.1080/00304949209356227](https://doi.org/10.1080/00304949209356227)
- [27] A. Dhir, V. Bhalla, and M. Kumar, *Org. Lett.* **10** (21), 4891 (2008). doi:[10.1021/ol801984y](https://doi.org/10.1021/ol801984y)
- [28] E. Šinkovec, A. Pohar, and M. Krajnc, *Microfluid. Nanofluid.* **14** (3–4), 489 (2013). doi:[10.1007/s10404-012-1067-7](https://doi.org/10.1007/s10404-012-1067-7)
- [29] M. L. Wang and H. S. Wu, *J. Org. Chem.* **55** (8), 2344 (1990). doi:[10.1021/jo00295a021](https://doi.org/10.1021/jo00295a021)
- [30] H. S. Wu, *Ind. Eng. Chem. Res.* **32** (7), 1323 (1993). doi:[10.1021/ie00019a006](https://doi.org/10.1021/ie00019a006)
- [31] M.-L. Wang and S.-W. Chang, *Ind. Eng. Chem. Res.* **33** (6), 1606 (1994). doi:[10.1021/ie00030a022](https://doi.org/10.1021/ie00030a022)
- [32] A. Bhattacharya, *Ind. Eng. Chem. Res.* **35** (3), 645 (1996). doi:[10.1021/ie950483t](https://doi.org/10.1021/ie950483t)
- [33] H.-M. Yang, *Ind. Eng. Chem. Res.* **37** (2), 398 (1998). doi:[10.1021/ie960346b](https://doi.org/10.1021/ie960346b)
- [34] J. W. Li and P. W. Carr, *Anal. Chem.* **69** (13), 2530 (1997). doi:[10.1021/ac961005a](https://doi.org/10.1021/ac961005a)
- [35] J. H. Kim, H. Park, and Y. K. Chung, *RSC Adv.* **7** (1), 190 (2017). doi:[10.1039/C6RA25723B](https://doi.org/10.1039/C6RA25723B)
- [36] C. Ramesh *et al.*, *Synthesis* **501** (2003).
- [37] J. H. Park, Y. H. Cho, and Y. K. Chung, *Angew. Chem. Int. Ed. Engl.* **49** (30), 5138 (2010). doi:[10.1002/anie.201001246](https://doi.org/10.1002/anie.201001246)
- [38] J. H. Park, S. M. Kim, and Y. K. Chung, *Chemistry* **17** (39), 10852 (2011). doi:[10.1002/chem.201101745](https://doi.org/10.1002/chem.201101745)
- [39] Z. Shen *et al.*, *Angew. Chem. Int. Ed.* **51**, 8607 (2012). doi:[10.1002/anie.201203556](https://doi.org/10.1002/anie.201203556)
- [40] J. S. Dave, R. A. Vora, J. F. Johnson, and R. S. Porter. *Liquid Crystals and Ordered Fluids* (Plenum Press 6, New York, Vol. 477, 1970).

- [41] A. K. Prajapati and H. M. Pandya, *J. Chem. Sci.* **117** (3), 255 (2005). doi:[10.1007/BF02709295](https://doi.org/10.1007/BF02709295)
- [42] V. S. Sharma and R. B. Patel, *Mol. Cryst. Liq. Cryst.* **643** (1), 178 (2017). doi:[10.1080/15421406.2016.1264234](https://doi.org/10.1080/15421406.2016.1264234)
- [43] G. W. Gray, *Molecular Structure and Properties of Liquid Crystals* (Academic Press, London, 1962).
- [44] S. L. Arora, J. L. Fergason, and T. R. Taylor, *J. Org. Chem.* **35** (12), 4055 (1970). doi:[10.1021/jo00837a708](https://doi.org/10.1021/jo00837a708)
- [45] B. Xu and T. M. Swager, *J. Am. Chem. Soc.* **117** (17), 5011 (1995). doi:[10.1021/ja00122a039](https://doi.org/10.1021/ja00122a039)