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Schiff Base Liquid Crystals and Ester Mesogens: Synthesis, Characterization and Phase Behavior

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ABSTRACT
A novel homologous series of ortho - pera Schiff's bases, RO-C_6H_4-CH=CH-COO-C_6H_4-CH=N-C_6H_3-CH_3(Br), has been synthesized and studied in order to understand and establish the effects of molecular structure on mesomorphic properties and to provide a source of novel liquid crystalline (LC) materials. The series contains 12 homologues (C_1 to C_8, C_{10}, C_{12}, C_{14}, and C_{16}). The multifarious features of Schiff base liquid crystals generated from cinnamic acid derivatives are investigated in this study, which combines the elegance of liquid crystal phases with the potential for biological activity. The average thermal stabilities of smectic and nematic materials are 100.16°C and 150°C, respectively. The mesomorphism is measured by using POM and DSC.
***Keywords:** Mesogen; mesophase; nematic; smectic*

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I. INTRODUCTION

Many researchers find liquid crystal (LC) materials [1] beneficial in a variety of applications [2-6], either thermotropically or lyotropically. A distinct physical state of matter known as liquid crystal (LC), mesomorphic, or mesogenic state.[7] This material, which is neither totally solid crystalline nor fully isotropic liquid, is useful in the production of electronic display devices, light-emitting materials, and other electronic applications. Aromatic esters, on the other hand, are known for their thermal stability, ease of synthesis, and relative resistance to hydrolysis; also, the conjugation connections of ester groups between the two phenyl rings[8-10]. Mesogenic features or behaviors of the current new series will be understood using molecular rigidity and flexibility as a foundation. Several homologous series and other LC materials have been reported to date [11-12], but the proposed novel series will consist of three phenyl rings and two central bridges, -CH=CH-COO- and -CH=N- with flexible n-alkoxy (-OR) and laterally substituted 2,methyl,4 Bromo groups at the first and last phenyl rings, respectively. In liquid crystals, lateral substitution broadens the molecules, so lateral substitution plays a role[13-14]. The thermotropic LC compound most study in research. The thermotropic liquid crystal further classified in two types: Smectic(Sm)and Nematic (N) base on arrangement of molecular after heating on POM [11-16]. The Schiff base (-CH= N-) acts as a link between the rigid core moieties. Despite its stepped core structure, it retains molecular linearity.resulting in increased thermal stability and the formation of phases . A large number of low molecular weight mesomorphic Schiff base/esters LC materials have recently been created and their biological potential assessed.[18,19] Furthermore, using a 1,3-dihydroxybenzene core with two symmetric wings that each contain three benzene rings connected by esteric, azomethinic, and azo groups, Scutaru et al. have created bent-core liquid crystals.

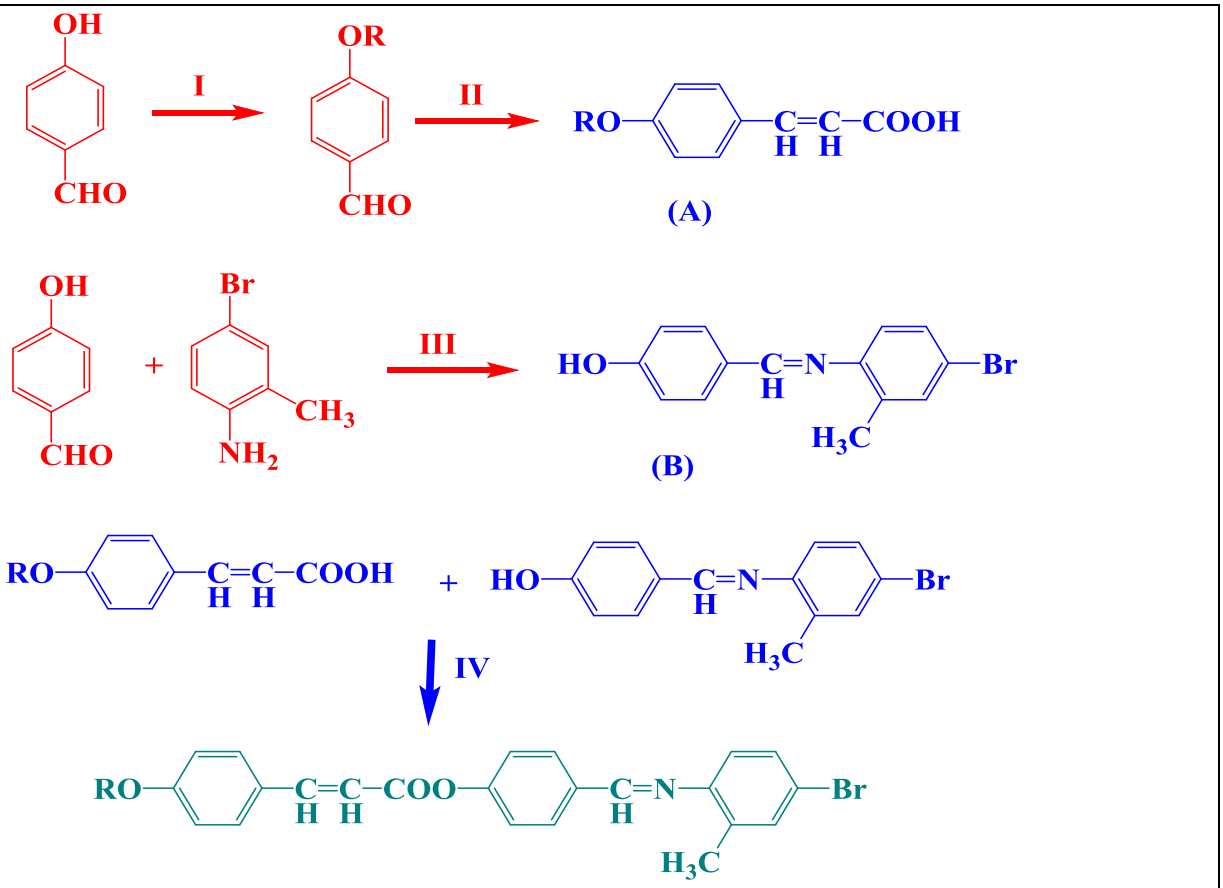
II. MATERIALSANDMETHODS

All other chemicals and reagents used in our experiments were of analytical grade. Avra Synthesis Private Ltd., Hyderabad, India, supplied 4-hydroxybenzaldehyde, alkyl bromides of C_1 to C_{16} n-alkyl chains, 4-bromo-3-methylaniline and anhydrous K2CO3. S. D. Fine-Chem. Ltd., Mumbai, provided acetone, dichloromethane, N,N'-Dicyclohexylcarbodiimide (DCC), and dimethylamino pyridine (DMAP). For each experiment, double-distilled water was used. Merck, India, supplied the TLC plates (silica gel 60 F254 silica-aluminum plates).

III. RESULTAND DISCUSSIONS

By refluxing 4-hydroxybenzaldehyde (1 equivalent) with corresponding n-alkyl bromides (1 equivalent) in the presence of potassium carbonate (1 equivalent) and acetone as a solvent, 4-n-Alkoxybenzaldehydes were created[17]. The resulting 4-n-alkoxybenzaldehydes were then reacted with 1-2

drops of piperidine as a catalyst and pyridine as a solvent to yield the corresponding trans-4-n-alkoxy cinnamic acids. Malonic acid (1.2 equiv.) was also present. A well-established procedure was used to prepare {(4-bromo-2-methylaniline phenyl) imino} methyl] phenol . Steglich esterification is used to couple compound A and B, yielding 4-(4-n-Alkoxycinnamoyloxy) benzal and 4-bromo-2-methylaniline. Scheme 1 describes the synthetic pathway leading to the new homologous series of Schiff's base cinnamoyl ester derivatives. Scheme 1.



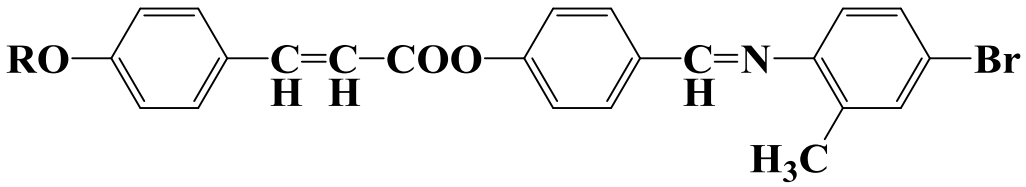
Where ,R = C_nH_{2n+1} , n= 1 to 8 ,10, 12 ,14 and 16

(I).+RX ,Acetone ,K_2CO_3 ,4-5 hrs ,reflux. (II).Pyridine ,1-2 drops piperidine , Malonic acid

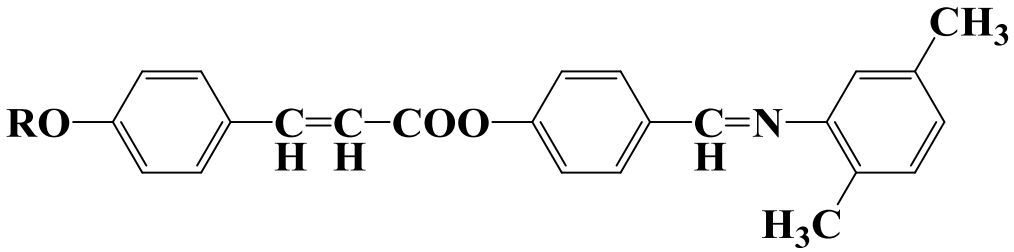
(III).MeOH, $MgSO_4$,heat to boil (VII) .CH_2Cl_2 ,DCC, 5 mol % DMAP

The homologous series in this investigation-1 and the series –X that was selected for comparison are identical with regard to two functional groups, either -CH_3 or –CH_3, as their mesogenic group efficiencies are nearly equal. They are also identifiable with regard to three phenyl rings and a left n-alkoxy terminal end group for same homologue[27]. Due to the equivalent group polarities of –CH3 ≈ –Br, both central bridges contribute to the overall molecular rigidity while maintaining nearly identical molecular flexibility, which accounts for the differences between series-1 and X. Since both central bridges—CH=CH–COO– or –COO– and –CH=N– or –N=N– in the case of series-1 and X, respectively, for the same homologue from series to series and from homologue to homologue in the same series—change and depend upon varying magnitudes of intermolecular dispersion forces as a consequence of changing a part of molecular rigidity. This means that the properties of liquid crystals (LC) and the degree of mesomorphism are dependent upon the thermodynamic quantity enthalpy (ΔH) of molecular structure.

Siries 1



Siries :X



The LC family's novel Schiff's base homologous series is primarily nematogenic and partially smectogenic, with a relatively short mesophase length, a transition temperature that ranges from 100°C to 150.0°C. Mesogenic properties are dependent of the effects due to central bridges.

1.Characterization

Thermal analysis was carried out using differential scanning calorimetry (DSC) on a Perkin Elmer Thermal Analyzer at a heating rate of 10 degrees Celsius per minute. Fourier-transform infrared (FT-IR) spectra were obtained using the KBr pellet method and analyzed using a Bruker TENSOR 27 in the range of 3500-500 cm-1. Proton-Nuclear Magnetic Resonance (1H-NMR) spectra were collected using a Bruker Advance (400 MHz) in $CDCl_3$ Solvent and tetramethylsilane (TMS) as an internal standard. The mesophase is identified using a polarizing optical microscope (POM) equipped with a temperature-controlled heating stage, such as the Nikon Eclipse LV-100 POL.

Spectral Data:

FT-IR (KBr): νmax/cm-1.

Sample C_8: ~1045, ~1160 & ~1211 (-C-H hydrocarbon), ~1288 & ~1253 (C-H bending of alkene), ~1201(C-O str. of ether linkage), ~1144 (C-N), ~1509 & ~1602 (aromatic ring), ~1724 & ~1703 (-COO, ester linkage), ~2922and ~2854 (-C-H str),C-Br~519,~774 and ~715 (p-di substituted phenyl ring), and ~990 and ~818 poly(-CH2-)n.

Sample C_{10}: ~1145, ~1168& ~1207 (-C-H hydrocarbon), ~1293& ~1257 (C-H bending of alkene), ~1201(C-O str. of ether linkage), ~1143 (C-N), ~1509 & ~1601 (aromatic ring), ~1725 & ~1703 (-COO, ester linkage), ~2921and ~2853(-C-H str),C-Br~519,~774 and ~987 and ~819 poly(-CH2-)n.

^{1}H-NMR ($CDCl_3$):

Sample C_{14}: 0.90 (3H, t; –CH3 of -$OC_{14}H_{29}$ group), 1.28-1.77 (2H, m; -CH2-CH2-O-), 4.01(2H, t; -CH2-O-), 7.32–7.38 (4H, m; middle phenyl ring), 7.51(1H, d; -CH=CH-COO-), 6.50-6.51 (1H, d; -CH=CH-COO-), 8.34 (1H, s; –N=CH-), 7.55–7.96 (4H, m; phenyl ring), 6.8, 6.9 and 8.1 (p-di substituted phenyl ring).

Sample C_{16}: 0.88 -0.90 (3H, t; –CH3 of –$OC_{16}H_{33}$ group), 1.27-1.80 (2H, m; -CH2-CH2-O-), 4.007-4.023 (2H, t; -CH2-O-), 7.32–7.55 (4H, m; middle phenyl ring), 7.51-7.85(1H, d; -CH=CH-COO-), 6.54-6.51 (1H, d; -CH=CH-COO-), 8.35 (1H, s; –N=CH-), 7.38–7.96 (4H, m; phenyl ring), 6.94, 6.96 and 7.99 (p-di substituted phenyl ring).

CHN Analysis

Table 1. CHN Analysis

Samples	**Molecular Formula**	**Elements % Found (% Calculated)**		
		C	**H**	**N**
C_1	$C_{24}H_{20}BrNO_3$	63.99 (64.01)	4.45 (4.48)	3.07 (3.11)
C_2	$C_{25}H_{22}BrNO_3$	64.51 (64.66)	4.59 (4.78)	3.01 (3.02)
C_3	$C_{26}H_{24}BrNO_3$	65.19 (65.28)	5.01 (5.06)	2.81 (2.99)
C_4	$C_{27}H_{26}BrNO_3$	65.71 (65.86)	5.28 (5.32)	2.79 (2.84)
C_5	$C_{28}H_{28}BrNO_3$	66.31 (66.41)	5.49 (5.57)	2.69 (2.77)
C_8	$C_{31}H_{34}BrNO_3$	67.79 (67.88)	6.19(6.25)	2.48 (2.65)
C_{10}	$C_{33}H_{38}BrNO_3$	68.61 (68.74)	6.53 (6.64)	2.39 (2.43)

3. 1 POMand DSC investigation

Figure 3&4 shows examples of the DSC curves for the prepared compounds $C_8$and C_{10} during heating and cooling scans. Figure 1 illustrates that upon heating and cooling scans, both compounds displayed two endotherm peaks of the crystal–mesophase and mesophase–isotropic transitions. For the SmA phase, the POM displayed a focal conic fan characteristic, and for the N phase, it displayed spread schlieren (Figure 1&2). To verify the stability of the prepared compounds, two heating-cooling cycles of DSC measurements were carried out. These compounds' thermal analyses were all captured from the second heating scan.

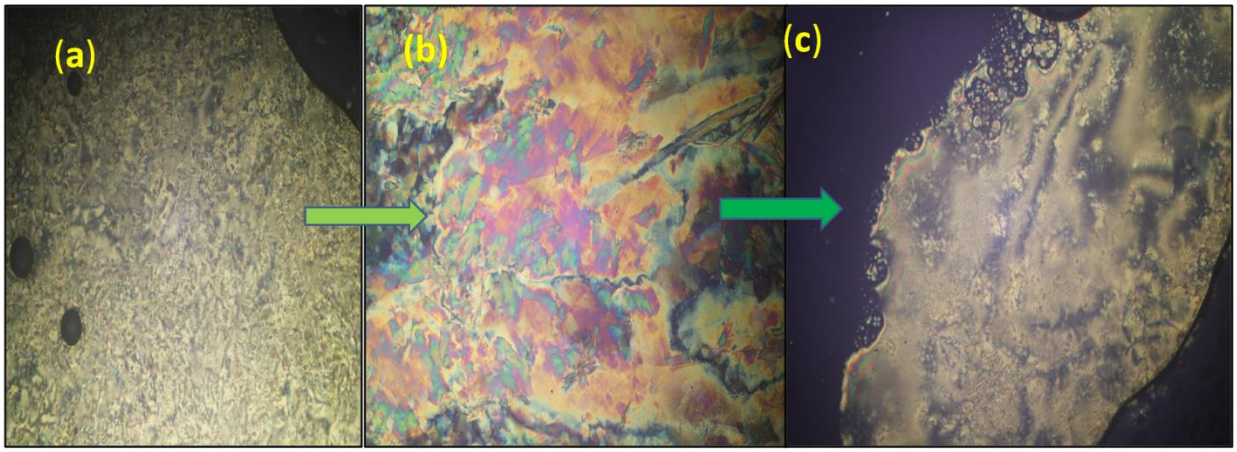


Figure 1. Microphotographs of
(a) Solid phase of sample C_8 **(b)** Nematic phase of sample C_8 at78.0˚C.**(c)**Nematic phase of sample C_{10} at 121.

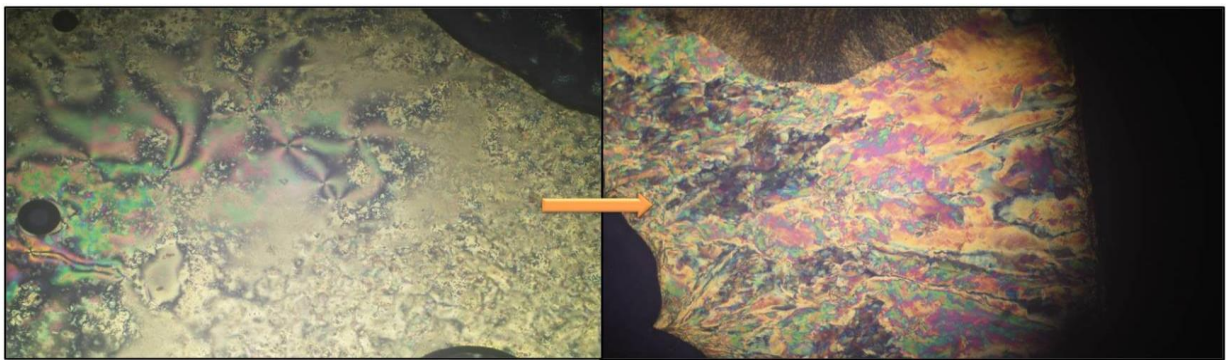
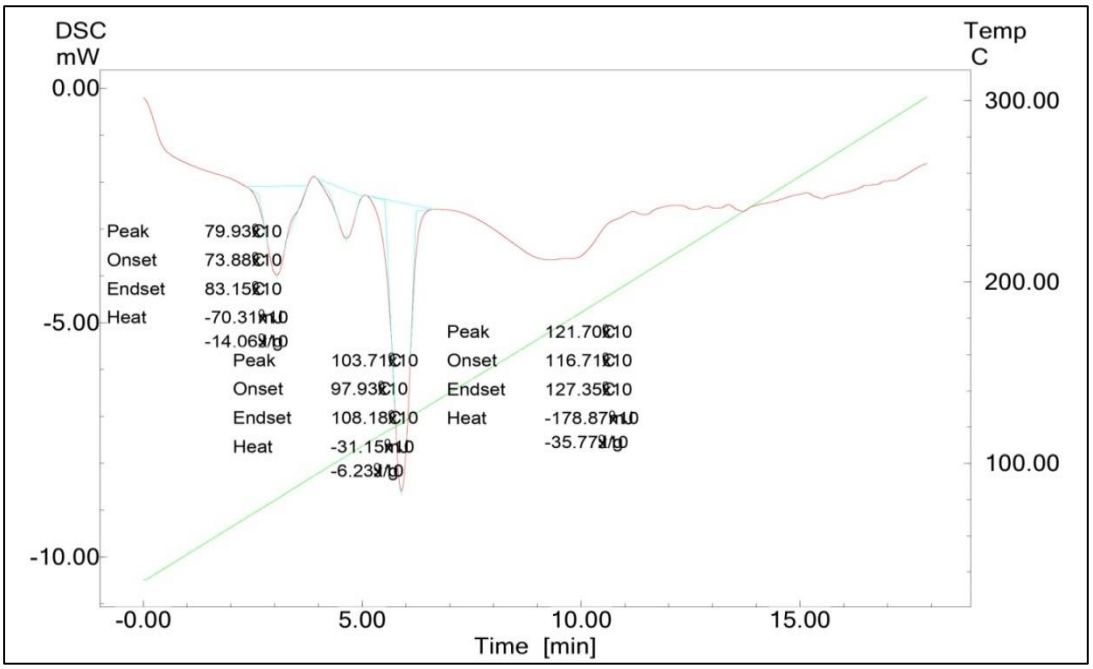
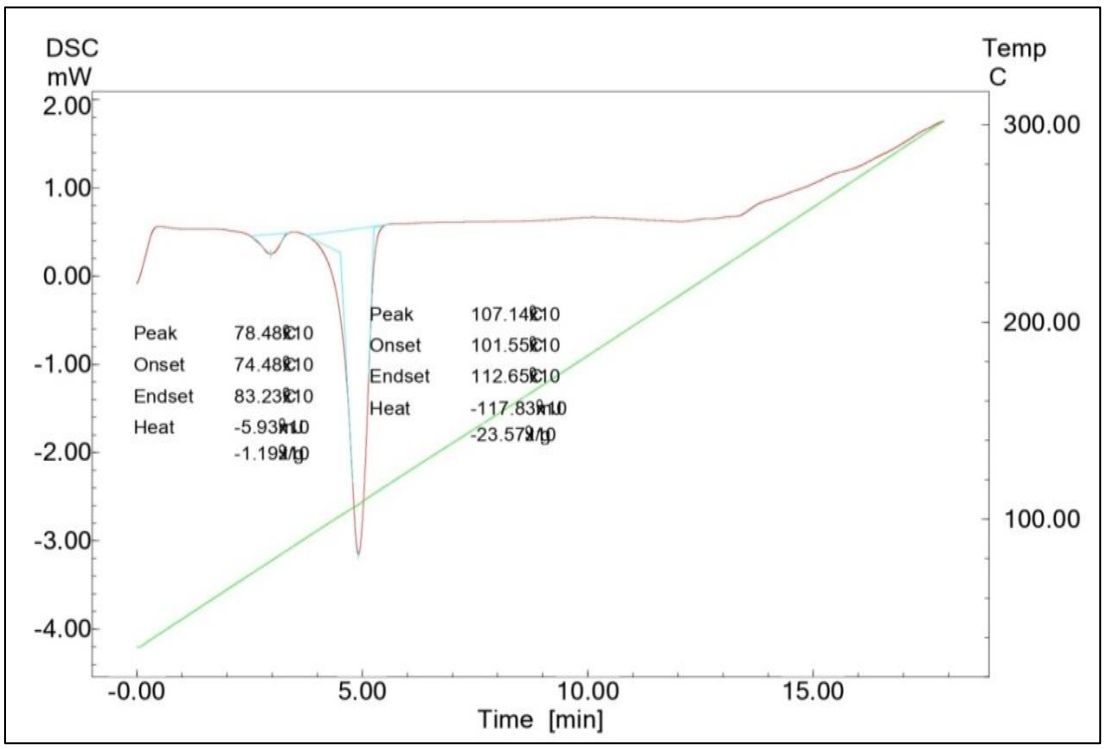


Figure 2. Nematic phase of sample C_{14} at120˚C.



Figures 3.DSC data ofcompound C_8



Figures 4.DSC data ofcompound C_{10}

Table 2. Phase transition temperatures (°C) of the synthesized LC samples

Samples	Smectic	Nematic	Isotropic
C_1	--	--	254
C_2	--	--	240
C_3	--	--	252
C_4	--	165	235
C_5	--	--	226
C_6	--	153	215
C_7	--	--	212
C_8	78	121	178
C_{10}	--	107	135
C_{12}	-	126	166
C_{14}	-	120	141
C_{16}	--	112	139

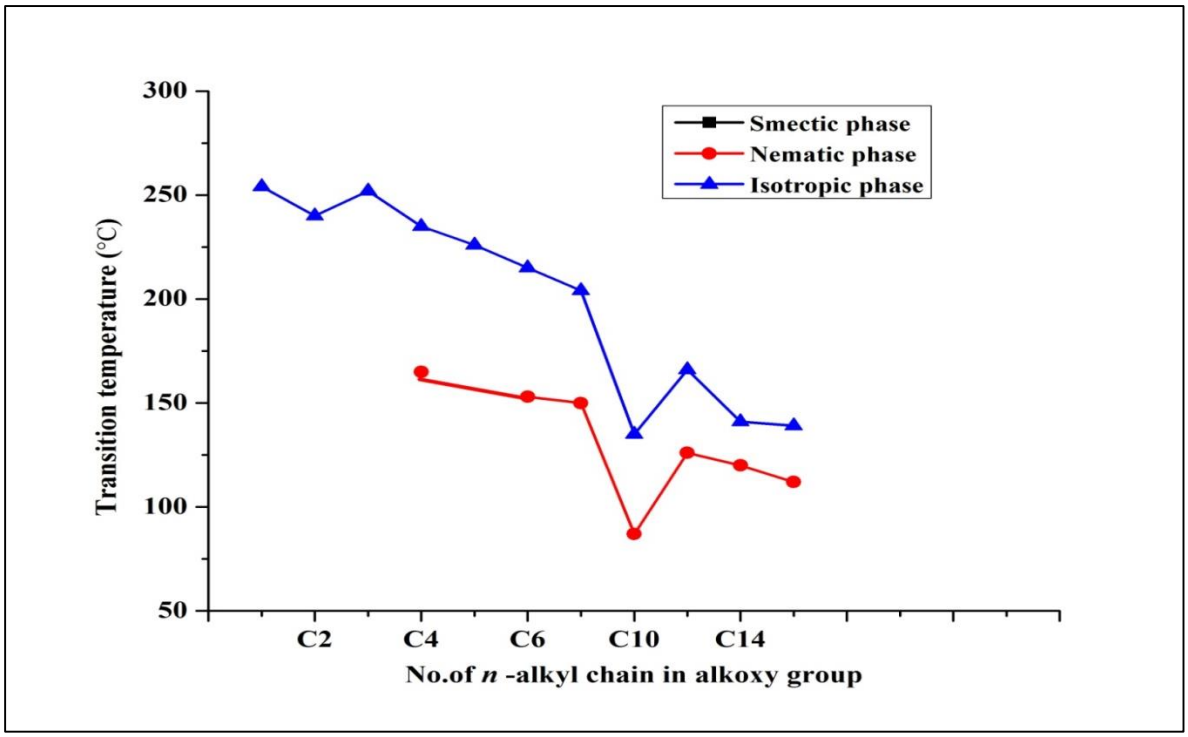


Figure 5. Phase transition temperatures

3.2 Biological Evaluation.

Using Gram negative (E. coli and P. aeruginosa) and Gram positive (S. aureus and S. pyogenus) bacterial species and fungal species (C. albicans, A. niger, and A. clavatus) as test subjects for biological potential evaluation experiments, the antibacterial and antifungal activity of the study has been investigated. Using the examination data that was collected. (Table 3).

Table 3. Data of antimicrobial activity

Minimal Inhibition Concentration ($\mu g \cdot mL^{-1}$) for the synthesized samples				
Samples	**E. Coli MTCC 443**	**P. Aeruginosa MTCC 1688**	**S. Aureus MTCC 96**	**S. Pyogenus MTCC 442**
C_4	50	62.5	100	62.5
C_{10}	100	125	250	100
Minimal Inhibition Concentration ($\mu g \cdot mL^{-1}$) for standard drug samples				
Gentamycin	0.05	1.0	0.25	0.5
Ampicillin	30.0	--	40.0	25.0
Chloramphenicol	50.0	50.0	50.0	50.0
Ciprofloxacin	25.0	25.0	50.0	50.0
Norfloxacin	10.0	10.0	10.0	10.0

*MTCC: Microbial Type Culture Collection

Table 4. Data of antifungal activity

Minimal Fungicidal Concentration ($\mu g \cdot mL^{-1}$) for the synthesized samples			
Samples	**C. Albicans MTCC 227**	**A. Niger MTCC 282**	**A. Clavatus MTCC 1323**
C_4	1000	500	1000
C_{10}	500	1000	1000
Minimal Fungicidal Concentration ($\mu g \cdot mL^{-1}$) for the Standard Drug samples			
Nystatin	100	100	100
Greseofulvin	500	100	100

*MTCC: Microbial Type Culture Collection

IV. CONCLUSION

In conclusion, we created an azo ester-based homologous series (C1-C12) by veering twelve alkyl chains on the terminal of moieties. By esterification in the last stage, all compounds were produced with high yield. FTIR and NMR studies confirmed the identity of all derivatives. POM was used to assess the liquid crystalline behavior of compounds, which was corroborated by DSC analysis. The homologous series is fully nematogenic, with a narrow range of liquid crystallinity and smectic phase show. The current investigation supports the previous position and lends weight to the previously acquired ideas. According to the findings, these mesogens could be valuable for further research and LC construction.

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