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Synthesis of Liquid Crsytal Compoun With Azo Linakhe and Effect of Terminal Group on Liquid Crystal Properties

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ABSTRACT

The polar ester terminal group have an impact on the mesomorphic characteristics of the synthesized new LC. The 12 compounds in the current series, D-1 through D-16, are distinguished by their methylene groups. Out of the twelve compounds, five are nematic and seven are smectic. The mesophase behaviour was carried out by polarized optical microscope (POM). The structure of LC compound was confirm by ^{1}H-NMR, IR and Mass spectroscopy. The smectic thermal stability is 131.14 ^{0}C and nematic thermal stability is 181.40 ^{0}C. The mesophase length is 12.5 ^{0}C to 80.8 ^{0}C.

Keywords**:** Liquid crystal, Mesophase, Nematic, and Smectic.

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1. INTRODUCTION

The mesogens are materials that display liquid crystalline phases. The physical properties of mesogens that comprise the nematic phase are influenced by the link between their microscopic shape and the macroscopic symmetry of the phase. Therefore, influencing and especially enhancing molecular polarization is the goal when developing a molecular structure. The word "liquid crystal" is crucial to all aspects of existence [1-5]. A liquid crystal compound shouldn't have a branching structure. The behavior of liquid crystals is correlated with their molecular form. When heat is applied to molecules, the distinct phases can be distinguished by the kind of ordering that results. The isotropic phase at high temperatures is present in the majority of thermotropic liquid crystal compounds [6-10]. Due to the appearance of flexibility following the combination of two non-liquid crystalline moiety Int-A and Int-B, they unite to generate liquid crystalline behavior via distinct linkage groups. The individual parts Int-A and Int-B, lack this kind of adaptability. Because esters have a carbonyl group (C=O) in their structure, they are thought to be slightly polar. Esters are less polar than substances like alcohols and carboxylic acids, nevertheless, because of the surrounding hydrocarbon chains, which lessen their overall polarity.

2. EXPERIMENTAL

2.1. Synthesis of Int-A (4-Alkoxy-3-methoxy cinnamic acid)

The alkylation reaction to change 4-hydroxy-3-methoxy cinnamic acid into 4-Alkoxy-3-methoxy cinnamic acid by combining 4-hydroxy-3-methoxy cinnamic acid with an alkyl halide (R-X) in the presence of a base. This reaction replaces the hydroxyl group **(H-O-)** at the 4-position with an alkoxy group **(R-O-)**. 4-hydroxy-3-methoxy cinnamic acid (1 equivalent) was refluxed with combining n-alkyl bromides (1.5 equivalents) in the presence of potassium hydroxide (2 equivalents) and methanol as a solvent to produce 4-n-Alkoxy-3-methoxy cinnamic acid. TLC's reaction monitoring. A 10% KOH solution was added to the reaction mixture once the reaction was finished. In ice-cold water, the solid 4-n-alkoxy-3-methoxy cinnamic product separates from the reaction mass pore. To extract the crude product, the precipitate was filtered by vacuum filtration and dried. For later application, the crude product was recrystallised in ethanol. A Williamson ether synthesis is the name given to this process [11].

2.2. Synthesis of Int-B Ethyl-4-((4-hydroxyphenyl) diazenyl) benzoate

Ethyl 4-amino benzoate (1 equivalent) was weighed and mixed with water and HCl in a 500 mL beaker. In an ice bath, the mixture was agitated with a magnetic stirrer until the solid was dissolved. A suitable quantity of $NaNO_2$ was dissolved in water and cautiously added to the reaction. Now, stir the reaction mixture for an hour. On the other hand, NaOH and phenol (1 equivalent) were dissolved in the proper water. When the reaction mixture cooled, the two solutions were added cautiously and slowly. The mixture was agitated for over an hour, and at the end of the reaction, yellow precipitate started to flow out. Vacuum filtration was employed to remove this combination, and the crude product was then used after being recrystallized in ethanol. 93.5 % is the reaction yield [12].

Figure 1. Intermediate B.

2.3. Synthesis of Series-D (4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy phenyl azo-4’’-ethyl benzoate)

In 250 mL of single neck RBF, the 4-n-alkoxy-3-methoxy cinnamic acid (Int-A) (1 equivalent) dissolves in the proper dichloromethylene (DCM) solvent. After that, stir the reaction mixture for an hour at room temperature while adding DCC (1.2 equivalent) and a pinch of DMAP. Ethyl-4-((4-hydroxyphenyl) diazenyl) benzoate [Int-B] (1 equivalent) was then added, and the mixture was agitated for a full day at room temperature. TLC use for reaction monitoring. Following reaction completion, the solution was carefully filtered using vacuum filtration to remove the DCU precipitate, and the solvent was evaporated using a rotary evaporator. Ethanol recrystallized the crude product. The synthesis path way of novel Series-D (4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy phenyl azo-4’’-ethyl benzoate) mention in figure-2 [13].

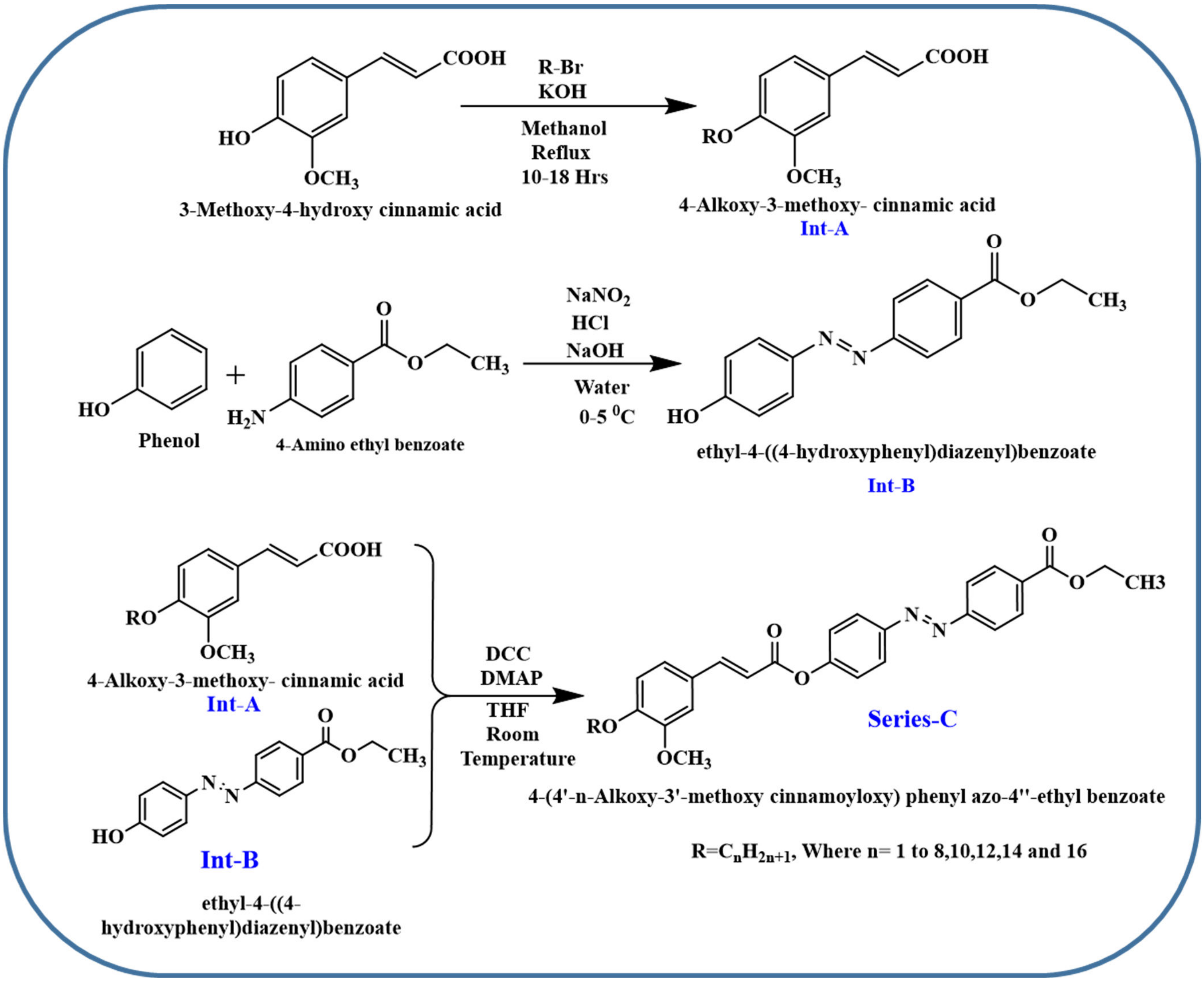

Figure 2. Synthesis route of novel series-C Series-D (4-(4'-n-Alkoxy-3'-methoxy cinnamoyloxy phenyl azo-4''-ethyl benzoate).

3. CHARACTERIZATION

On the EuroEA Elemental Analyser, elemental analysis was used to characterise a few series members. Using $CDCl_3$, NMR was recorded on a Bruker spectrometer, Shimadzu FTIR was used to record IR spectra, and Shimadzu GC Model No. QP-2010 was used to record mass spectra. The thermal behaviour was recorded using a Nikon Eclipse 400/TU Plan ELWD 20 X/0.40 mesomorphic properties recorder and a Shimadzu, Shinapore.

3.1. Analytical Data

3.1.1. D-2 compound

IR spectra in cm^{-1}:(KBr) 3063.06 (C-H stretching of alkene disubstituted), 2947.33 & 2839.31(C-H stretching of –(CH_2)- group of alkyl chain), 1705.13(C=O stretching of carbonyl carbon of ester), 1597.13 (C=C stretching of alkene), 1504.53 & 1458.23 (C=C stretching of aromatic ring), 1419.66 (-N=N- diazo), 1141.90(C-O stretching of ester group), 840.99(paradisubstiuted benzene ring), 810.13poly(-CH2-)n group).

Mass spectra: m/z (relative intensity %): 473.0 (M^+) (5%), 294.9(100%-ester linkage break), 269.9 (5%-ester linkage break).

3.1.2. D-7 compound

IR spectra in cm^{-1}:(KBr) 3063.06 (C-H stretching of alkene disubstituted), 2939.61 & 2862.46 (C-H stretching of –(CH_2)- group of alkyl chain), 1728.28 (C=O stretching of carbonyl carbon of ester), 1597.11(C=C stretching of alkene), 1512.24 & 1465.95 (C=C stretching of aromatic ring), 1419.66 (-N=N- diazo), 1126.47(C-O stretching of ester group), 840.99(paradisubstiuted benzene ring), 810.13 poly(-CH2-)n group).

Mass spectra: m/z (relative intensity %): 543.0 (M^+) (5%), 275.0 (100%-ester linkage break), 269.09 (5%-ester linkage break).

3.2. Elemental Analysis

Table 1. Elemental analysis of series-D.

Compound	Molecular Formula	Theoretical % (Found %)		
		C	H	O
D-2	$C_{27}H_{26}N_2O_6$	68.35 % (68.34%)	5.50 % (5.52%)	20.20 % (20.23%)
D-7	$C_{32}H_{36}N_2O_6$	70.52 % (70.57%)	6.62 % (6.66%)	17.58 % (17.62%)
D-8	$C_{33}H_{38}N_2O_6$	70.88 % (70.95%)	6.84 % (6.86%)	17.20 % (17.18%)

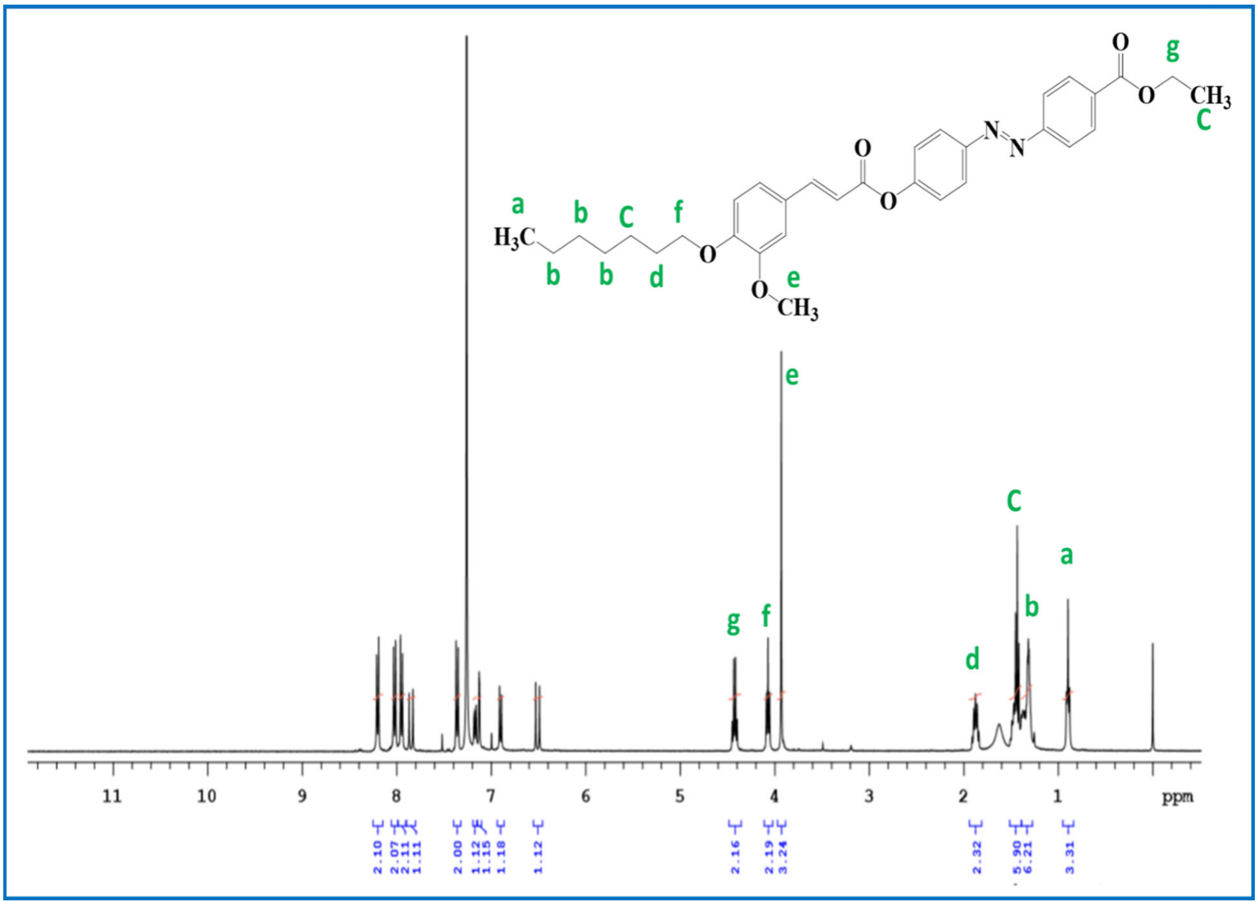

Figure 3. ^{1}H-NMR spectra of D-7 compound.

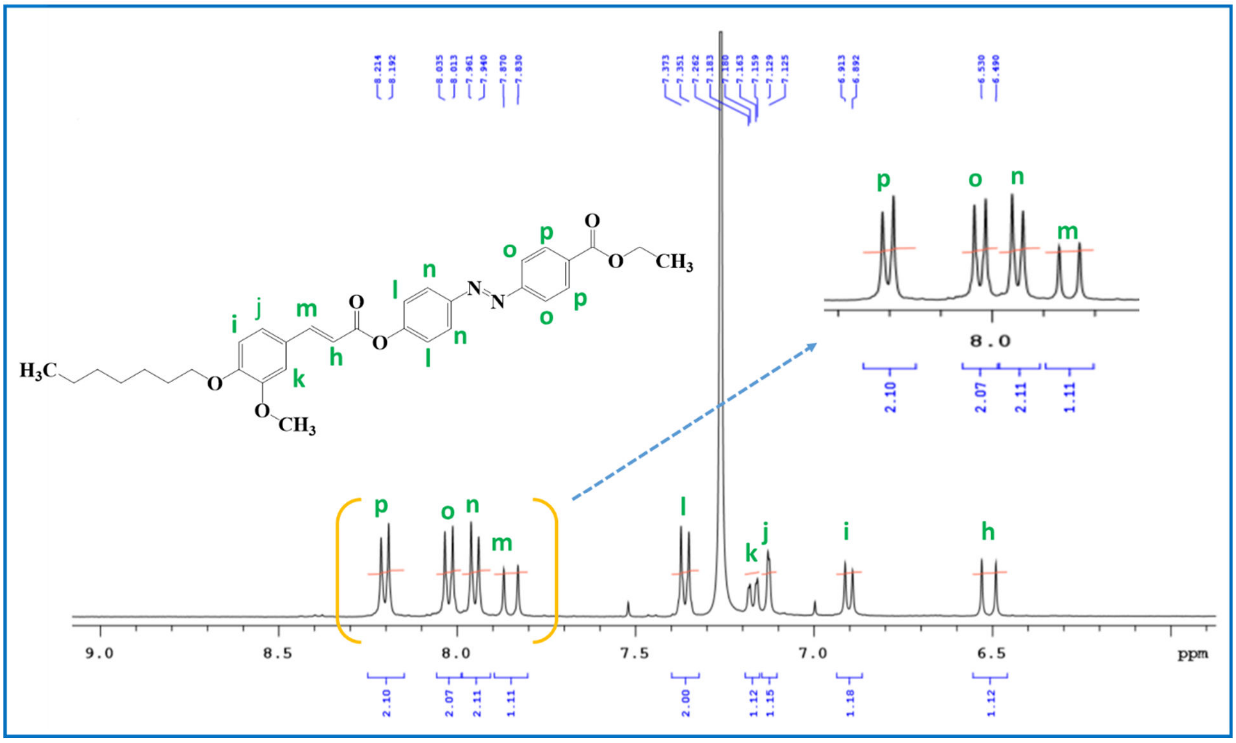

Figure 4. ^{1}H-NMR Aromatic region of D-7 compound.

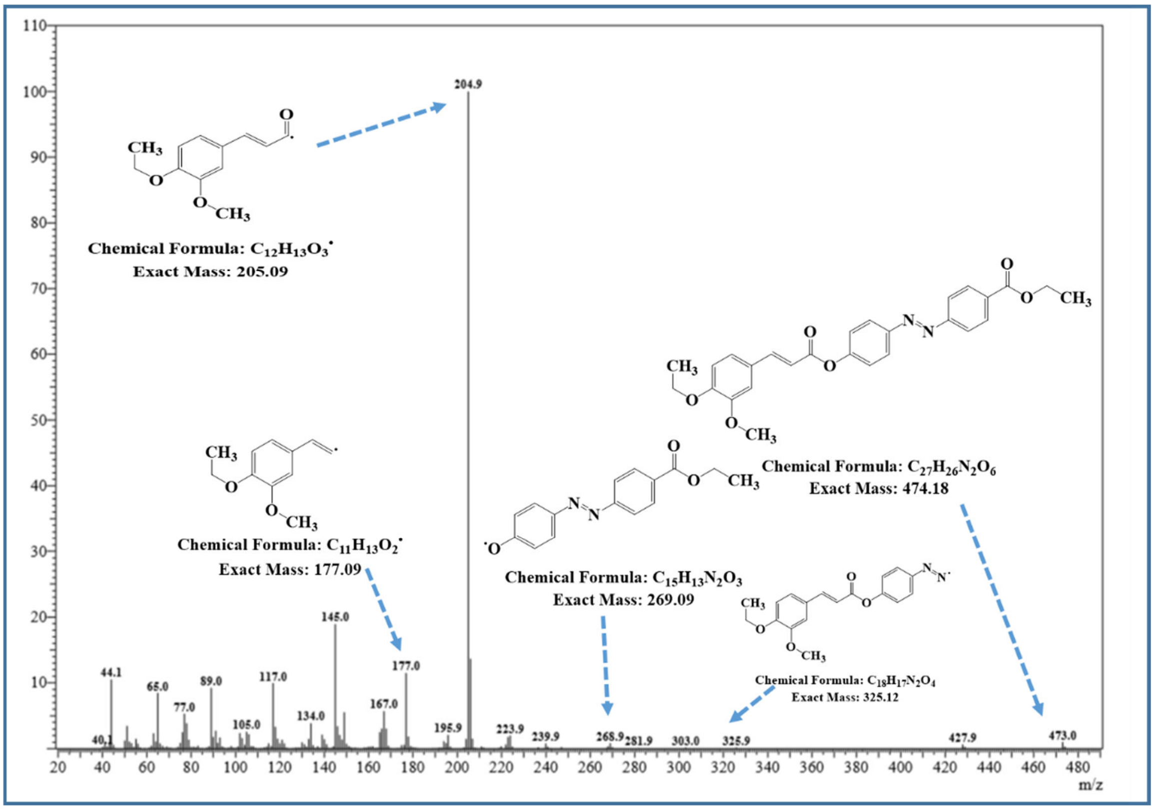

Figure 5. Mass spectra of D-2 compound.

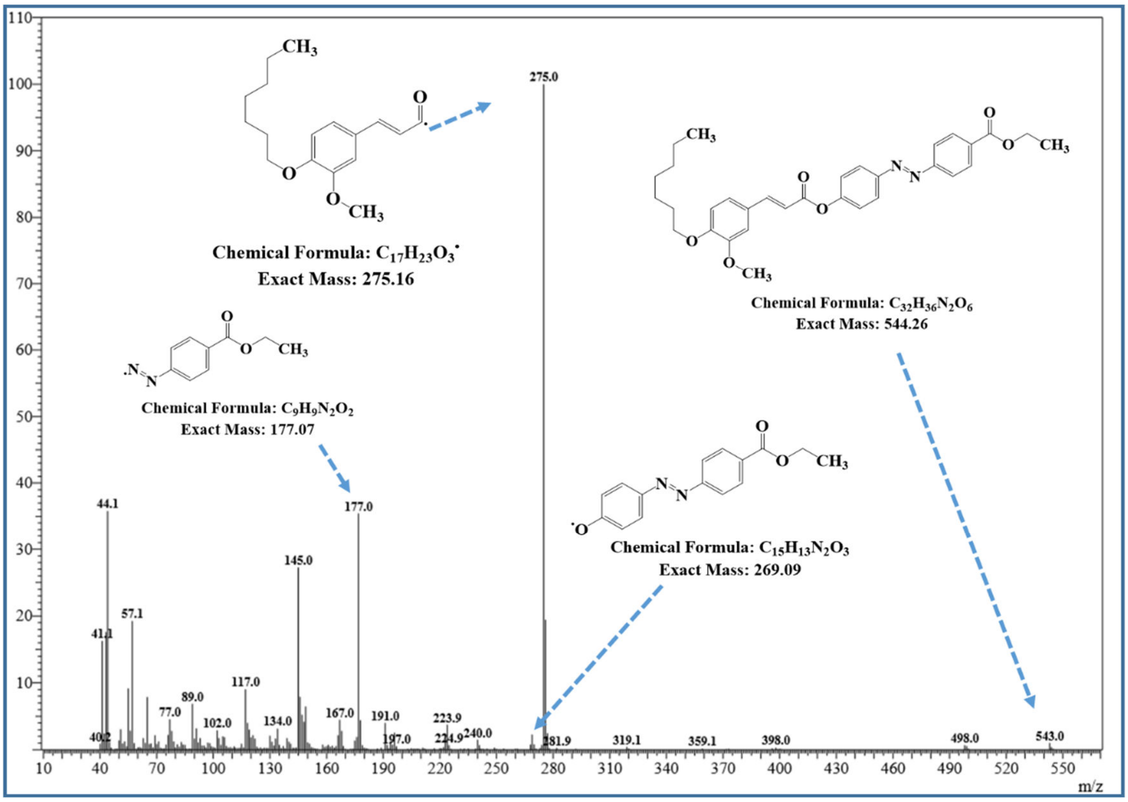

Figure 6. Mass spectra of D-7 compound.

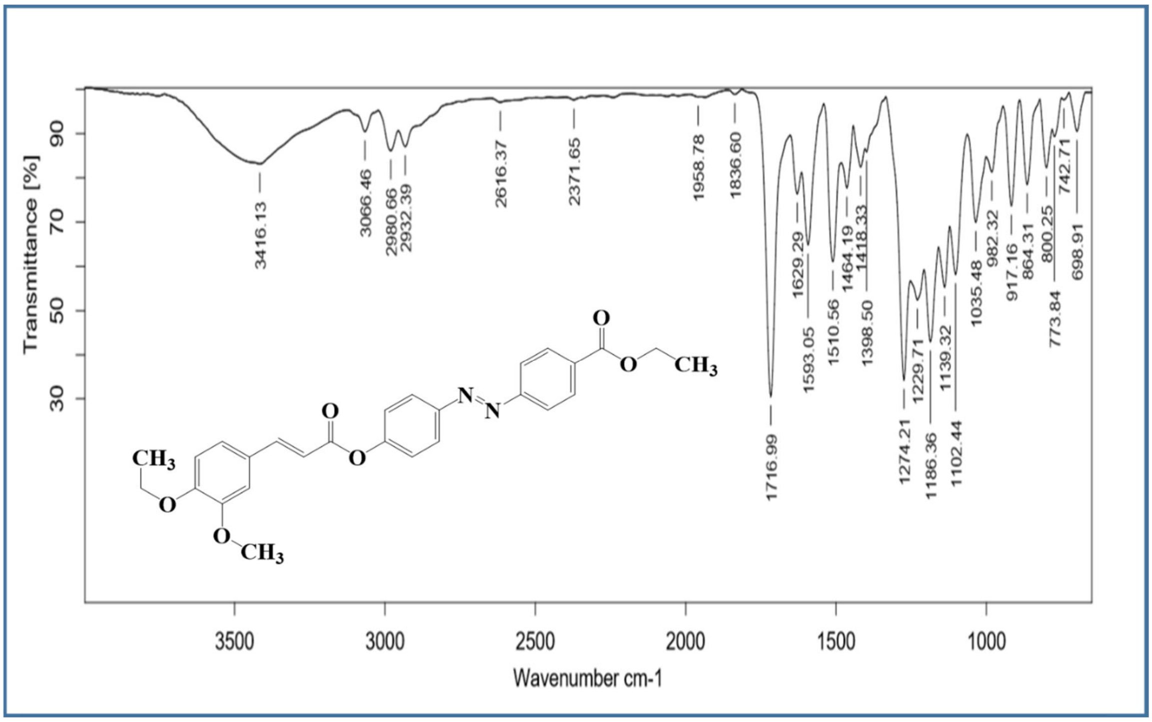

Figure 7. IR spectra of D-2 compound.

4. RESULT AND DISCUSSION

The behavior of LCs is strongly affected by polarity. Although conventional nematic LCs are typically thought of as apolar, the addition of polar molecules or the use of electric fields can result in a number of phenomena, such as spontaneous polarization, flexoelectricity, and ferroelectric effects, which are important for a number of applications, especially in electro-optical devices. The director is the direction in which the molecules in nematic liquid crystals have a tendency to align [14-17] This director alignment can be induced or reinforced by the introduction of an electric field or the presence of polar molecules. The optical characteristics of the LC may alter as a result of interactions between the molecules and the applied electric field. For the creation of different electro-optic devices, such as liquid crystal displays (LCDs) and other optical devices, polarity effects are essential. In a nematode liquid crystal phase, molecules orient themselves in a certain direction but lack positional order. Long, rod-like molecules that have a propensity to align parallel to one another along a preferred direction known as the "director" are what define them. They have special optical qualities like birefringence, where light bends differently depending on their polarization, because of this orientational order [18-20]. Nematic liquid crystals are a compound's most fundamental form. The elongated nematic molecule has a uniaxial optical index and is optically anisotropic. The figure 7 represent structure of series-D in first and second rigid core connected by cinnamates ester and second and second and third rigid core connected by azo linkage. The figure 7 represent binding connectivity of series-D structure. The present frame work consist right terminal alkoxy group (n=1 to 8, 10, 12, 14 and 16) and left terminal group ester, as well as methoxy as lateral group.

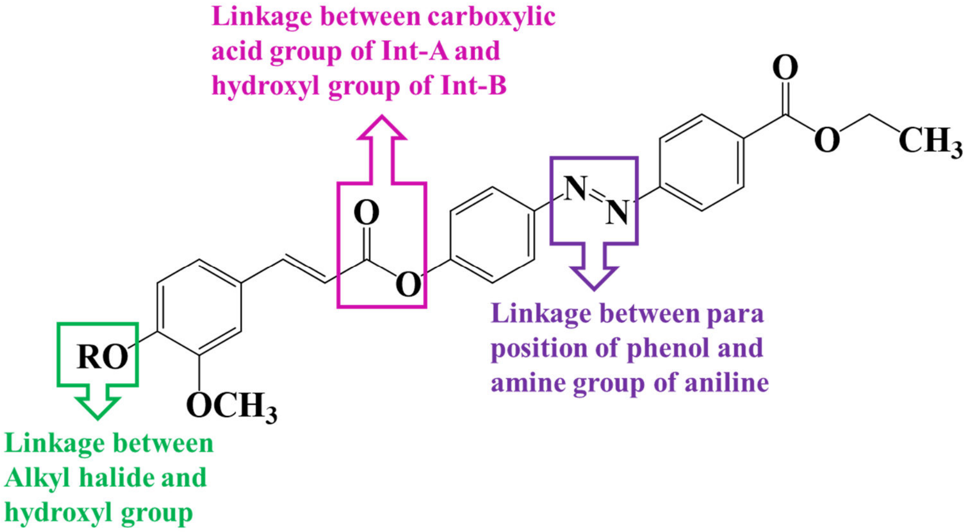

Figure 8. Structure of Series-D.

The novel series consist 12 homologue in which D-1 to D-16 behave nematogenic, D-6 to D-16 behave smectogenic liquid crystal compound. Among 12 compound, seven compound (D-6 to D-16) behave polymorphic nature mean D-6 to D-12 consist both nematic.

Table 2. Transition temperature of Series-D

No.	Compound	Transition temperature (^{0}C)		
		Smectic (Sm)	**Nematic (N)**	**Isotropic (I)**
1	D-1	-	162.2	207.7
2	D-2	-	122.4	200.3
3	D-3	-	125.8	195.3
4	D-4	-	117.8	198.6
5	D-5	-	137.8	193.3
6	D-6	112.3	138.6	173.2
7	D-7	97.4	132.7	189.4
8	D-8	98.2	128.1	186.9
10	D-10	100.8	113.7	151.4
12	D-12	72.3	127.3	162.3
14	D-14	88.2	140.3	166.7
16	D-16	104.2	137.3	151.8

A mesophase transition refers to the change of state from a solid or isotropic liquid to a mesophase, which is an intermediate state of matter between solid and liquid, often seen in liquid crystals. This transition can involve changes in molecular orientation, ordering, and structural arrangements. The mesophases exhibit properties like optical anisotropy, magnetic and electrical properties, and can be influenced by factors such as temperature, pressure, and the presence of external fields.

The figure-9 represent mesophase behaviour of series-D. The first transition (Blue line) in which Cr-N **(Crystalline to nematic transformation)** transition of D-1 to D-5 compound shows Zig-Zag pattern(Down-Up) and Cr-Sm **(Crystalline to smectic transformation)** transition of D-6 to D-16 compound shows continue decreasing pattern for D-6 to D-7, increasing pattern between D-8 to D-10, decreasing pattern between D-10 to D-12 and increasing pattern between D-12 to D-16.. The second transition (Red line) in which N-I **(Nematic to isotropic transformation)** transition of D-1 to D-5 compound shows continue decreasing pattern and Sm-N **(Smectic –Nematic transformation)** in which D-6 to D-10 shows decreasing pattern and D-12 to D-16 shows increasing pattern.

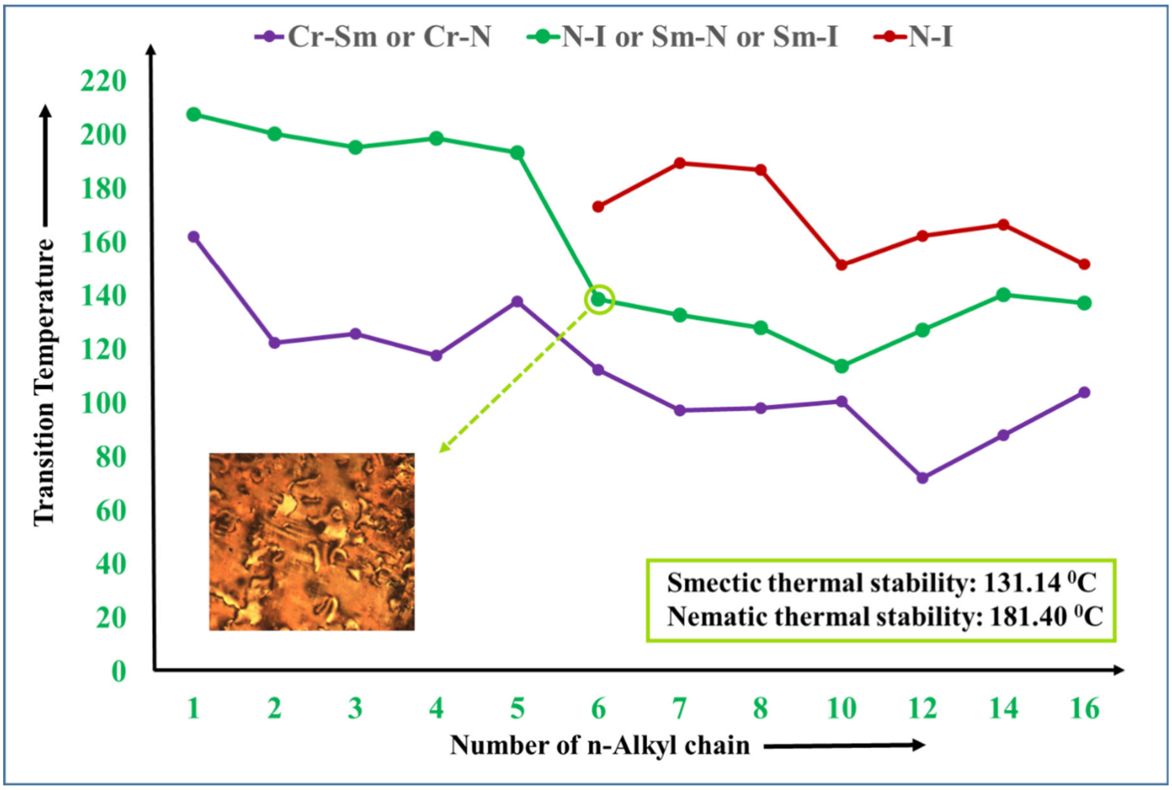

Figure 9. Mesophase behavior of series-D.

The unique texture of the current series as perceived by POM is mentioned in Figure 10 and 11. The compounds D-6 to D-16 showed both smectic and nematic texture, while compounds D-1 to D-5 showed nematic texture. Figure 10 on the heating cycle shows various optical photomicrographs of various compounds. The figure 10 in which figure-10(a) nematic texture of D-3 compound, figure 10(b) nematic texture of D-5 compound, figure 10(c) nematic texture of D-8 compound, figure 10(d) nematic texture of D-12 compound.

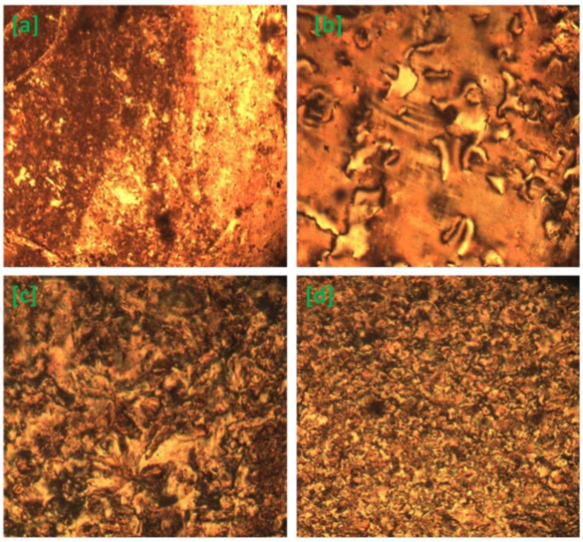

Figure 10. POM optical photomicrographs (a) Nematic texture of D-3 compound, (b) nematic texture of D-5 compound, (c) nematic texture of D-8 compound and (d) nematic texture of D-12 compound.

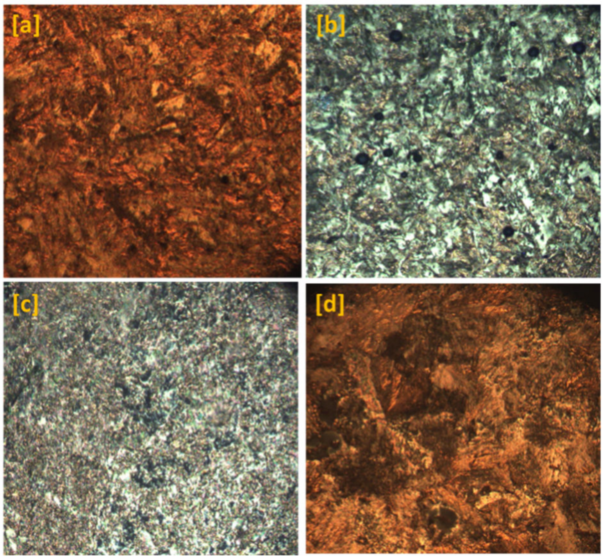

Figure 11. POM optical photomicrographs (a) Smectic texture of D-7 compound, (b) Smectic texture of D-8 compound, (c) Smectic texture of D-10 compound, and (d) Smectic texture of D-12 compound.

By examining the textural defects, it was determined that the uniaxial nematic mesophase is characterized by the existence of four-brush disclinations, whereas the biaxial nematic mesophase is characterized by the presence of just the so-called two-brush disclinations. To ascertain whether a phase is uniaxial or biaxial, texture alone is insufficient. Because of surface effects, how the liquid crystal sample molecules interact with the tiny plate walls, and how sample preparation affects the produced image, the microscopic approach is seen to be less elegant. It serves as an early technique for determining biaxial mesophase, but it needs to be used in conjunction with other techniques that don't require any disruptive outside influences.

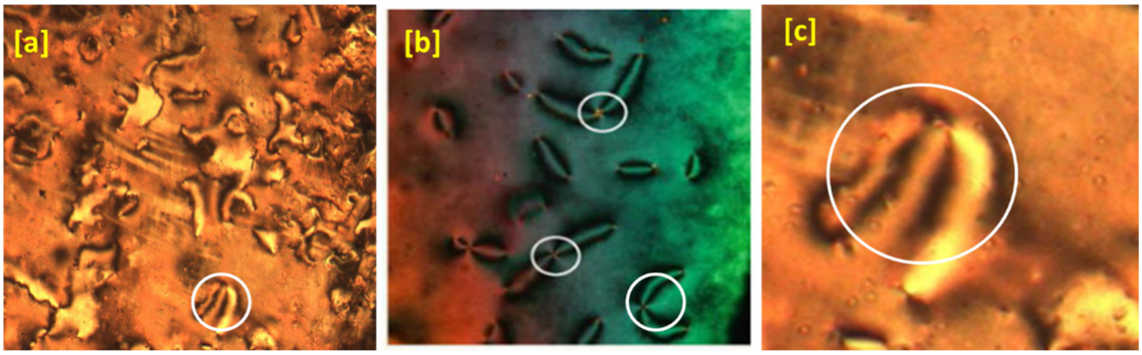

Figure 12. Schlieren texture of a presumably biaxial nematic phase (two-brush disclinations) of D-5 compound [21].

In terms of two phenyl rings, two central bridges (-CH=CH-COO- and -N=N-), and left terminal group homology from series to series, homologous series D and series X [22] chosen for comparison analysis are identical; nonetheless, they differ from the lateral group and right terminal group. Series-X lacks a lateral group, whereas series-D has a methoxy lateral group. The methoxy terminal group of series-X and the ester right terminal group of series-D are present. As the structure of LC's compound changes, so do the mesophase behavior, transition temperature, isotropic phase temperature, and mesophase length. The slight structural alteration causes a discernible change in LC's properties. Comparing the liquid crystal characteristics of series C and X with series to series and homologue to homologue is the focus of the current study. The clearing temperatures, phase types, and optical properties are only a few of the mesomorphic aspects of liquid crystal (LC) compounds that are greatly influenced by terminal groups. These groups can influence molecular alignment, intermolecular interactions, and ultimately the behavior of the LC molecule because they are affixed to its hard core. Terminal groups frequently influence the clearing temperature, which is the temperature at which a liquid crystal changes from the LC phase to an isotropic liquid. Different terminal groups, such as cholesteric, smectic, or nematic, may promote the development of distinct LC phases. For instance, polar groups can influence phase behavior and increase the "effective" molecule length by encouraging transitory antiparallel couplings. Intermolecular interactions can be strengthened or weakened by terminal groups, which impacts the LC molecules' capacity to self-assemble and create ordered structures. For instance, dimer formation via hydrogen bonding between terminal groups can effectively double the molecule length and affect the characteristics of LC.

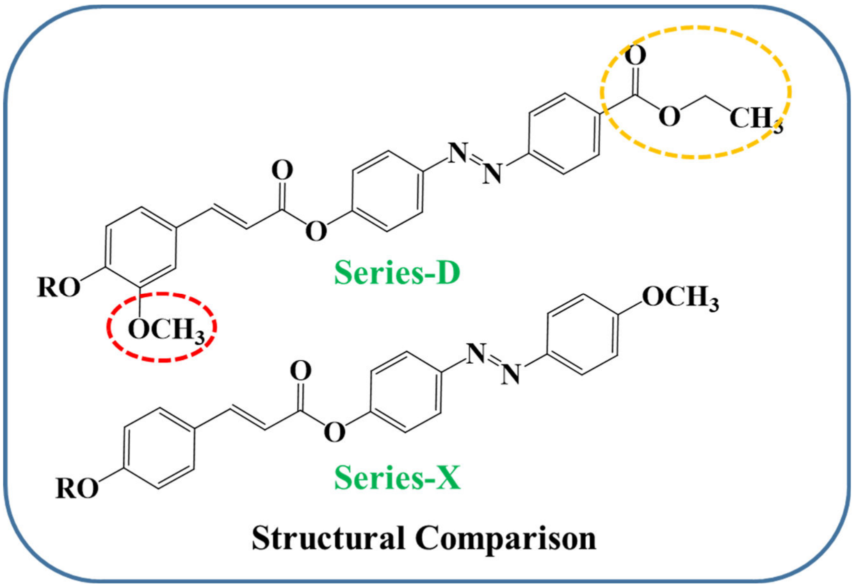

Figure 13. Structural comparison of Series-D and X.

Table 3. Relative thermal properties of Series-D and Series-X.

Series	**D**	**X**
Nematic-Isotropic	181.40 ^{0}C (C_1-C_{16})	251.7 ^{0}C (C_1-C_{14})
Commencement of Nematic phase	C_1	C_1
Smectic –Nematic or Smectic-Isotropic	131.14 ^{0}C (C_6-C_{16})	137.0 ^{0}C (C_{10}-C_{16})
Commencement of Smectic phase	C_6	C_{14}
Total mesophase length in ^{0}C	45.5 ^{0}C to 92 ^{0}C C_1 C_7	26.0 ^{0}C to 230.0 ^{0}C C_{16} C_1

From above table, we observe that

- Nematic thermal stability of Series-D is less than Series-X.
- Smectic thermal stability of Series-D is less than Series-X -X.
- The commencement of Nematic phase of both Series-D and Series-X are from C_1.
- The commencement of Smectic phase of Series-C and Series-X are from C_6 and C_{14} respectively.
- The minimum mesophase length of Series-C and Series-X are 45.5 ^{0}C and 26.0 ^{0}C respectively.
- The maximum mesophase length of Series-C and Series-X are 26.0 ^{0}C and 230 ^{0}C respectively.

5. CONCLUSION

The current study revealed how terminal polar groups affect the mesomorphic characteristics of LC chemicals. More research on structural alterations and their effects could lead to the development of more adaptable and efficient liquid crystalline materials. The study's findings provide valuable new information for the design and development of high-temperature-resistant liquid crystalline materials, which could result in innovations in fields like display technologies and optoelectronics.

- The smectic thermal stability is 131.14 ^{0}C and nematic thermal stability is 181.40 ^{0}C.
- The mesophase length is 45.5 ^{0}C to 92.0 ^{0}C.
- Smectic thermal stability: Series-D < Series-X.
- Nematic thermal stability: Series-D < Series-X.
- Commencement of Nematic phase: Series-C = Series-X.
- Commencement of smectic phase: Series-C < Series-X.
- The study's conclusions offer important new information for the design and development of liquid crystalline materials that can withstand high temperatures, potentially leading to breakthroughs in industries like optoelectronics and display technologies.

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