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Synthesis and Characterization of New Thermotropic Liquid Crystalline Compounds with Bromo-Substituted Terminal Group and Azo Vinyl Ester Linkages

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ABSTRACT

A novel series of liquid crystal (LC) materials based on azo-vinyl ester, specifically $\text{RO-C}_6\text{H}_3(-\text{OCH}_3)-\text{CH}=\text{CH}-\text{COO}-\text{C}_6\text{H}_3(-\text{CH}_3)-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{Br}$, has been synthesized and investigated to understand the influence of molecular structure on liquid crystal properties. This series aims to provide novel thermotropic LC materials to the scientific and technological research community. The series includes 12 members (C_1 to C_8 , C_{10} , C_{12} , C_{14} & C_{16}), out of these some compounds exhibit enantiotropic smectic & nematic phase and some compounds monotropic liquid crystal behavior. Transition temperatures and textures of the homologues were determined using a polarizing optical microscope (POM) equipped with a heating stage. The phase transition curves (Cr-I/M, Sm-N/I, N-I or I-N) in the phase diagram followed expected patterns. Analytical and spectral data confirmed the molecular structures of the homologues. Thermal stabilities of the smectic and nematic phases were 101.2°C and 115.2°C , respectively, with the total mesophase lengths ranging from 4.4°C to 39.5°C . The liquid crystal properties of this novel series were compared with those of structurally similar series.

Keywords: Mesophase, Nematic, Smectic, Monotropic, Homologue

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1. INTRODUCTION

Studies of liquid crystal substances, both thermotropic and lyotropic, have garnered significant interest due to their beneficial applications for humanity[1]. These substances exhibit unique properties: they flow like liquids yet exhibit optical behavior akin to crystals, making them valuable in display devices [2], [3] and biological systems, including various biochemical reactions within the body [4 - 10], which play a crucial role in living organisms. To advance research in this field, the development and exploitation of novel LC substances are essential. This investigation aims to understand and establish the effects of molecular structure on LC properties by synthesizing a novel homologous series of thermotropic LCs. This series will serve as a source of novel LC materials for researchers with diverse objectives and approaches, aiding in the development of relationships between mesomorphism and novel molecular structures [11-14]. Several homologous series have been reported to date [15 - 20]. The novel series in this study will consist of three phenyl rings bonded through $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{N}=\text{N}-$ central bridges, with lateral-substituted ($-\text{OCH}_3$) group and terminal $-\text{Br}$ group and varying $-\text{OR}$ groups. The effect of the flexible terminal group, in conjunction with changes in the n-alkyl chain, will be studied using polarizing optical microscopy (POM) and characterized through spectral and analytical data. This characterization will examine how changing molecular flexibility, with or without constant molecular rigidity, influences the properties of these novel compounds[21-24]. The mesomorphic behaviors of the novel series will be evaluated and compared with structurally similar series.

2. MATERIALS AND METHODS

The chemicals and solvents used in the synthesis, including 4-hydroxy-3-methoxy benzaldehyde, n-alkyl bromides (R-Br), K_2CO_3 , malonic acid, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), p-bromo Aniline, m-cresol, NaOH, pyridine, piperidine, were procured from Spectrochem, Merck, and Sigma-Aldrich. All reagents and solvents were used without further purification. The purity of the synthesized compounds was confirmed by Thin-Layer Chromatography (TLC) using 0.2 mm pre-coated silica gel G60 F254 plates (Merck). Visualization was achieved under UV light at wavelengths of 256 nm and 366 nm. To represent the novel series, a selection of members was subjected to elemental analysis using the EuroEA Elemental Analyzer. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 spectrometer. Proton nuclear magnetic resonance (^1H NMR) and carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were obtained using a Bruker spectrometer with DMSO- d_6 as the solvent. Mass spectra were recorded using a Shimadzu GC-MS Model No. QP-2010.

2.1. Preparation of 4-n-Alkoxy 3-methoxy Cinnamic Acid [A]

4-n-Alkoxy 3-methoxy cinnamic acid (A) was synthesized by the Verley-Doebner modification of the fundamental Knoevenagel condensation. In a 25-mL, round-bottom flask, 4-n-alkoxy 3-methoxy benzaldehyde (0.1 mol) and malonic acid (0.2 mol) were dissolved in pyridine (25 mL) and a few drops of piperidine. The mixture was heated to reflux for 2 hours under appropriate ventilation in a fume hood[25]. After the reflux period, the resulting solution was carefully poured into an aqueous solution of 2M HCl and then allowed to cool to room temperature. The solid precipitate formed was collected by filtration, washed with water, and subsequently subjected to recrystallization from methanol until a pure single spot product was obtained. The resulting 4-n-alkoxy 3-methoxy cinnamic acids were found to be trans isomers[26].

2.2. Synthesis of 4-Hydroxy-2-methyl phenyl azo-4'-bromo benzene [B]

4-Bromo aniline (1 equivalent) was measured and weighed in a 500 mL beaker. The compound was then combined with a mixture of hydrochloric acid (HCl) and water. Magnetic stirring was employed in an ice bath until the solid completely dissolved. In a separate container, an appropriate quantity of sodium nitrite (NaNO_2) was dissolved in water and slowly added to the reaction mixture with caution. The resulting mixture was stirred for a duration of 1 hour. Simultaneously, m-cresol (1 equivalent) and sodium hydroxide (NaOH) were dissolved in an appropriate volume of water. After cooling, the two solutions were gradually and carefully mixed together. The resulting mixture was stirred for more than 1 hour until the completion of the reaction, leading to the formation of a yellow-colored precipitate[27]. To isolate the desired product, the mixture was filtered using vacuum filtration. The crude product obtained was further purified by recrystallization in ethanol. The overall yield of the reaction was determined to be 72.4%

2.3. Synthesis of 4-(4'-n-Alkoxy-3'-methoxy cinnamoyloxy)2-methyl phenyl azo 4''-bromo benzene

In a 250 mL single-neck round-bottom flask (RBF), 1 equivalent of 4-n-alkoxy-3-methoxy cinnamic acid [A] was dissolved in an appropriate dichloromethylene solvent. Dicyclohexylcarbodiimide (DCC) (1.2 equivalents) and a pinch of 4-dimethylaminopyridine (DMAP) were added to the reaction mixture. The resulting mixture was stirred for 1 hour at room temperature. Then, 1 equivalent of 4-hydroxy-2-methyl phenyl azo 4'-bromo benzene [B] was added, and the solution was stirred for 24 hours at room temperature. [28] The progress of the reaction was monitored by thin-layer chromatography (TLC). After the completion of the reaction the solution was filtered using vacuum filtration to remove any precipitated dicyclohexylurea (DCU). The solvent was evaporated using a rotary evaporator. The crude product was then recrystallized in ethanol. The synthesis route of homologues series of azo vinyl ester derivatives is under mentioned in figure 1.

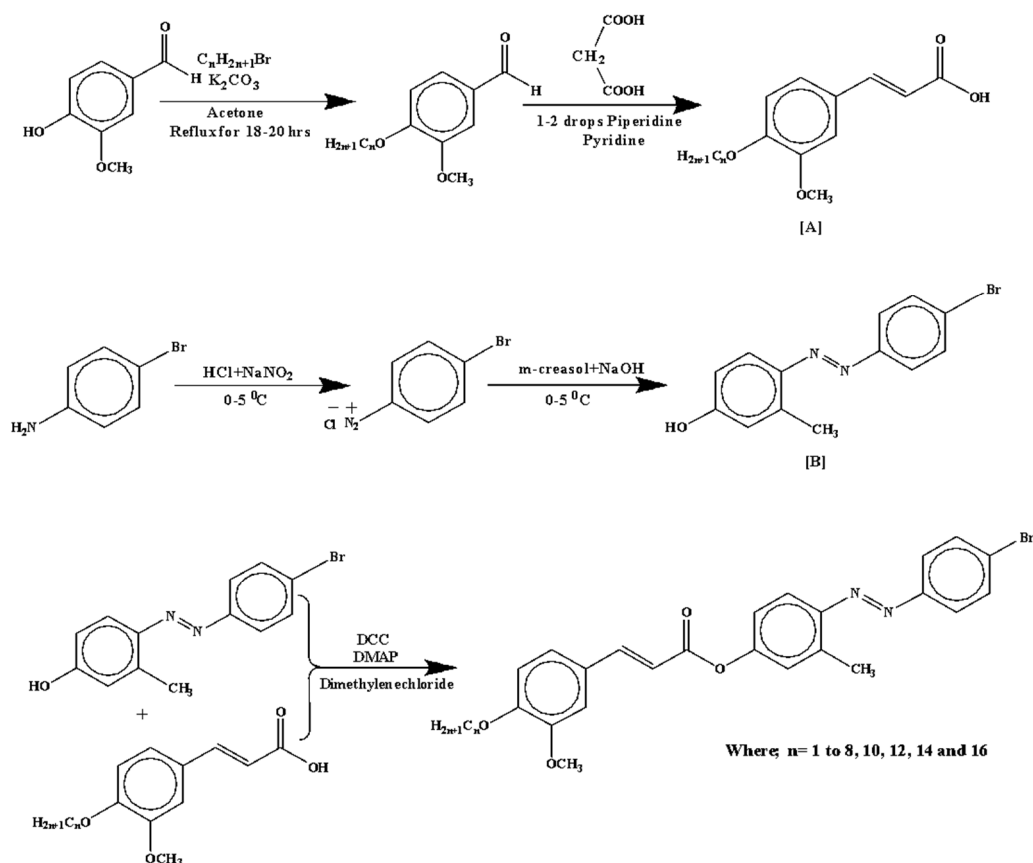


Figure 1. Synthetic Route of Novel Series

3. CHARACTERIZATION

The homologues of the series were characterized using a variety of analytical techniques. Elemental analysis was performed to determine the elemental composition of the samples (Table-1) Infrared (IR) spectra were recorded to identify the functional groups present in the samples. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained to provide detailed information about the molecular structure of the samples. Mass spectra were recorded to identify the molecular weight and fragmentation patterns of the samples. The thermal behavior of the samples was studied using a Differential Scanning Calorimeter (DSC) to determine the melting and boiling points, glass transition temperature, and other thermal properties of the samples. The mesomorphic properties of the samples were observed using a polarized optical microscopy to visualize the different phases of the samples and to determine their optical properties. The results of the analytical techniques were used to characterize the members of the series and to gain a better understanding of their chemical and physical properties. This information will be useful for future studies of the series and for the development of new applications for these compounds.

4. ANALYTICAL DATA

4.1. Elemental analysis

Table 1. Elemental Analysis for (1) Ethyloxy, (2) Octyloxy, (3) Dodecyloxy derivatives

Sr. No.	Molecular Formula	Elements % Found			Elements % Calculated		
		C	H	O	C	H	O
1	$\text{C}_{25}\text{H}_{23}\text{BrN}_2\text{O}_4$	60.55	4.70	12.83	60.60	4.64	12.92
2	$\text{C}_{31}\text{H}_{35}\text{BrN}_2\text{O}_4$	64.20	6.10	11.00	64.24	6.04	11.05
3	$\text{C}_{35}\text{H}_{43}\text{BrN}_2\text{O}_4$	66.07	6.82	10.01	66.14	6.77	10.07

4.2. Spectral data

- ^1H NMR (CDCl_3) of Butyloxy derivative

0.89-0.96 (t, 3H, $-\text{CH}_3$ of $-\text{OC}_4\text{H}_9$ group), 3.80-3.86 (s, 3H, $-\text{CH}_3$ of $-\text{O}-\text{CH}_3$ group), 1.35-1.75 (m, 4H, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{O}-$), 3.85-4.12 (t, 2H, $-\text{O}-\text{CH}_2$), 6.24-6.42 (d, 1H, $-\text{COO}-\text{CH}=\text{CH}-$), 7.46-7.52 (d, 1H, $-\text{COO}-\text{CH}=\text{CH}-$), 2.30-2.35 (s, 3H, $-\text{CH}_3$ of Ph- CH_3 group) 7.75-7.98 (d, 4H, phenyl ring with -Br group), 7.24-7.85 (3H, middle phenyl ring), 7.00-7.08 & 7.20-7.30 (3H, phenyl ring with alkoxy chain). The ^1H NMR information corresponds faithfully to the molecular arrangement.

- **¹H NMR (CDCl₃) of Hexyloxy derivative**

0.88-0.92 (t, 3H, -CH₃ of -OC₆H₁₃ group), 3.82-3.87 (s, 3H, -CH₃ of -O-CH₃ group), 1.35-1.78 (m, 6H, CH₃-CH₂-CH₂-CH₂-CH₂-O-), 3.90-4.14 (t, 2H, -O-CH₂-), 6.28-6.40 (d, 1H, -COO-CH=CH-), 7.45-7.50 (d, 1H, -COO-CH=CH-), 2.32-2.36 (s, 3H, -CH₃ of middle Ph-CH₃ group), 7.78-7.98 (m, 4H, phenyl ring with -Br group), 7.24-7.84 (m, 3H, middle phenyl ring), 7.00-7.08 & 7.20-7.30 (m, 3H, phenyl ring with alkoxy chain). The ¹H NMR information corresponds faithfully to the molecular arrangement.

- **¹³C NMR (CDCl₃) in ppm for Decyloxy derivative**

14.1 (-CH₃), 22.7-31.9 (CH₃-(CH₂)₄), 69.0 (-OCH₂), 56.1 (Ph-OCH₃) 147.9 (-CH=CH-COO-), 115.5 (-CH=CH-COO-), 164.3 (-CH=CH-COO-), 17.8 (middle Ph-CH₃), 111-158 (Ar-C). The ¹³C NMR data is reliable with the molecular structure.

- **¹³C NMR (CDCl₃) in ppm for Hexyloxy derivative**

14.2 (-CH₃), 22.5-32 (CH₃-(CH₂)₆), 69.5(-OCH₂), 56.1 (-OCH₃) 147.8 (-CH=CH-COO-), 115.5 (-CH=CH-COO-), 164.3 (-CH=CH-COO-), 17.7 (middle Ph-CH₃), 110-159 (Ar-C). The ¹³C NMR data is reliable with the molecular structure.

- **Mass spectra of Octyloxy derivative**

m/z: 579.9 (M)⁺, 288.3 (base peak), The mass spectra and data is reliable with the molecular structure.

- **Mass spectra of Decyloxy derivative:**

m/z: 607.8 (M)⁺, 317.0 (100%, base peak), The mass spectra and data is reliable with the molecular structure.

- **IR (KBr) in cm⁻¹ for Ethoxy derivative:**

3030-2978 (C-H str. of alkene disubstituted), 1728.28 (C=O str. of carbonyl carbon of ester group), 1589.40, 1620 (C=C str. of alkene), 1606, 1514 & 1471 (C=C str. of aromatic ring), 1325 & 1290 (C-H bending of alkene disubstituted), 1226.77 (C-O str. of ether linkage), 1134.18 (C-O str. of ester group), 997, 966 & 833 (C-H bending of alkene), 516.94 (C-Br str.). The IR data is reliable with the molecular structure.

- **IR (KBr) in cm⁻¹ for Butyloxy derivative:**

3020-3150 (C-H stretching of alkene disubstituted), 2978 & 2860 (C-H str. of -(CH₂)_n group of -OC₄H₉), 1736 (C=O str. of carbonyl carbon of ester group), 1627.97 (C=C str. of alkene), 1597, 1512 & 1465 (C=C str. of aromatic ring), 1303 & 1226 (C-H bending of alkene disubstituted), 1265.35 (C-O str. of ether linkage), 1126 (C-O str. of ester group), 1026 & 972.16 (C-H bending of alkene), 833.28 (C-Cl str.). The IR data is reliable with the molecular structure.

5. RESULT AND DISCUSSION

Novel azo vinyl ester derived from 4-n-alkoxyl-3-methoxy cinnamic acid and 4-hydroxy-2-methyl phenyl azo-4'-bromo benzene is either monotropically or enantiotropically nematogenic or smectogenic in character. Transition temperatures as determined by optical polarising microscopy (Table 2) are plotted against the number of carbon atoms present in n-alkyl chain of left n-alkoxy and group (Fig-2), a phase diagram is obtained which consisted of Cr→I/M, Sm→N/I, N →I or I→ N transition curves, showing phase behaviours of series by linking like or related points. The Cr→I/M transition curve continuously falls up to C₁₀ homologue, except C₄ homologues and rises in zigzag manner at the C₁₀ to C₁₆ homologues. N →I or I→N transition curve rises up to C₄ homologue and then smoothly descends up to C₁₂ homologues. Sm→N or Sm→I transition curve commenced from C₈ homologue and behaved in a normal, established manner. Thus, all the transition curve of a phase diagram behaved in normal manner.

The mesomorphic properties under go variations from homologue to homologue in the same novel series, depending upon member of carbon atoms present in n-alkyl chain (-OR) or left terminal end group.

Table 2. Phase transition temperature of series in⁰C

Compound No.	Flexible Chain	No. of C in chain	Sm	N	Isotropic
1	Methyl	1	-	(171.0)	207.5
2	Ethyl	2	-	(179.2)	193.6
3	Propyl	3	-	(185.1)	187.4
4	Butyl	4	-	(188.2)	192.4
5	Pentyl	5	-	(160.5)	166.5
6	Hexyl	6	-	(144.8)	152.5
7	Heptyl	7	-	106.4	127.5
8	Octyl	8	86.6	116.4	120.5
9	Decyl	10	70.4	105.4	109.9
10	Dodecyl	12	-	98.3	103.2
11	Tetradecyl	14	65.6	-	82.4
12	Hexadecyl	16	96.5	-	100.9

Sm= Smectic, N= Nematic, (I) indicate monotropic

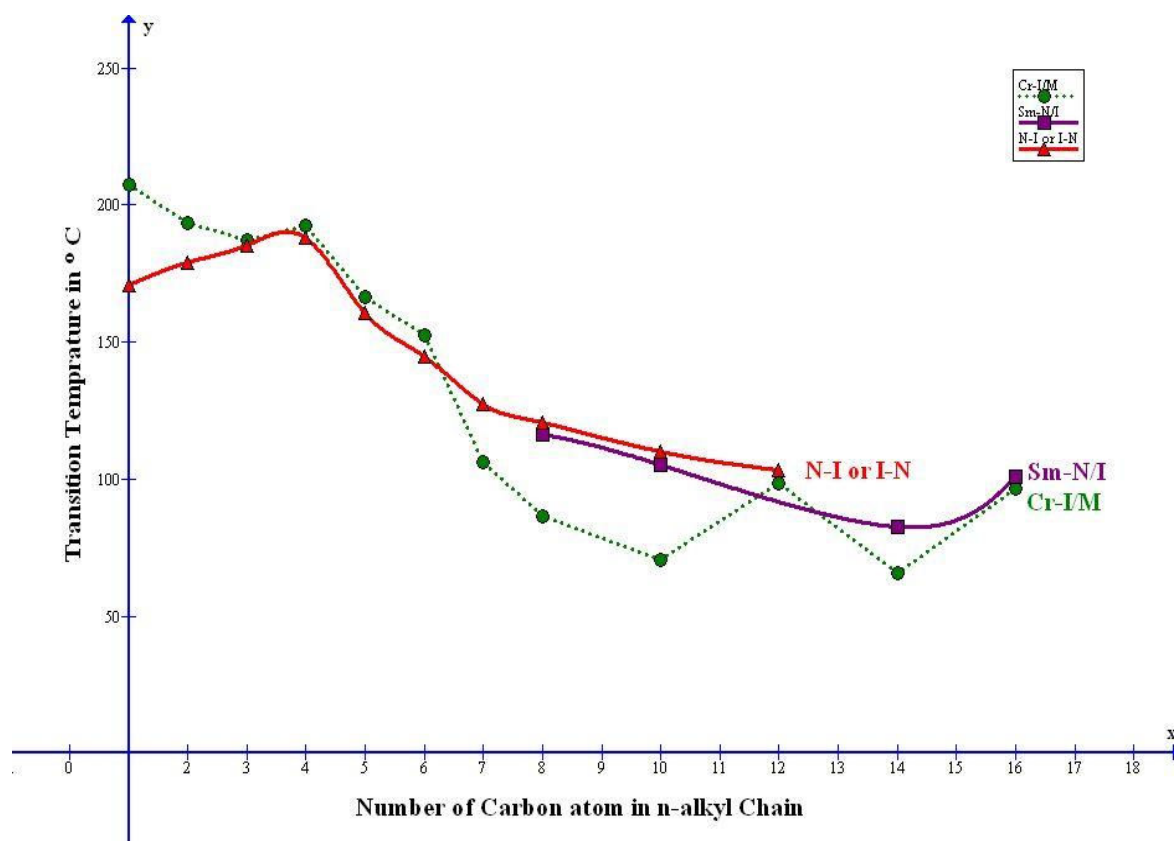


Figure 2. Phase behaviour of series

The mesophase formation by C_8, C_{10}, C_{14} & C_{16} homologues is attributed to the disalignment of molecules, perpendicular or at an angle less than ninety degree to the floating surface, depending upon thermal resistivity causes by suitable magnitudes of intermolecular dipole-dipole interaction and dispersion forces, which induces by favourable end to end attractions or/and lateral attractions of suitable magnitudes as a consequences of their molecular rigidity and flexibility, which maintains mainly sliding layered molecular arrangement for all the mesogenic homologues as well as maintain statistically parallel orientational order of molecular under floated condition for C_1 to C_{12} homologues. Thus, C_8, C_{10}, C_{14} & C_{16} mesogenic homologues showed smectogenic character, whereas C_1 to C_{12} homologues shows nematogenic mesophase formation of different textures and different range of temperatures. All molecules of each mesogenic homologues individually randomly orient in all possible directions from and beyond isotropic temperature, which on cooling the same from and below isotropic temperature reappears smectic or/and nematic mesophase formation in reversible manner for a temperature range which was appeared on heating. C_7 to C_{16} homologues are enantiotropically mesogenic. Some mesogenic behaviour and properties of presently investigated novel series 1 are compared with structurally similar series X [29] as mentioned below in fig-3.

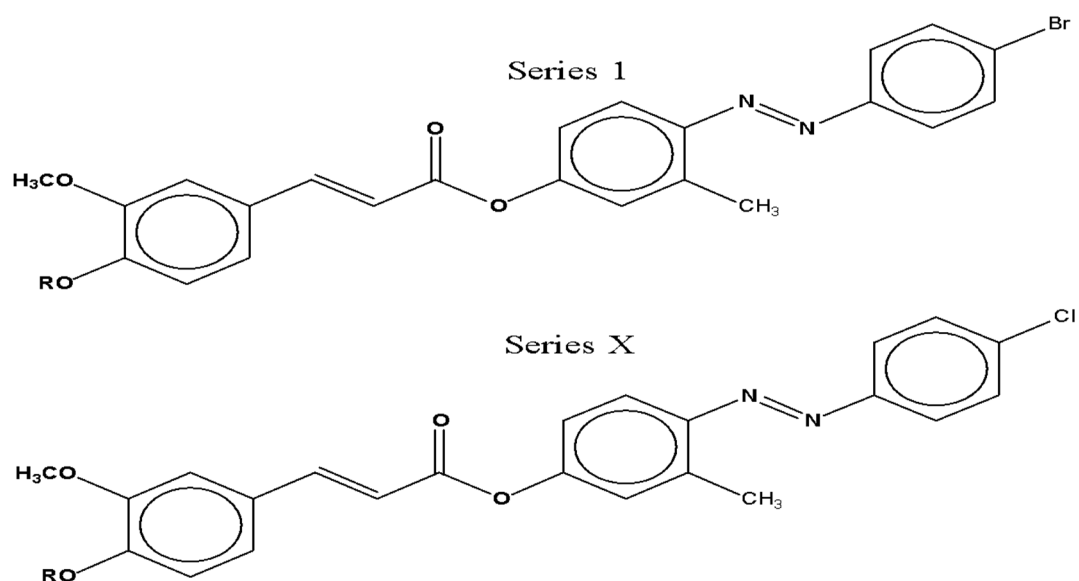


Figure 3. Comparisons of Series 1 and Series X

Homologous series 1 and X are identical with respect to three phenyl ring two central bridges, meta - OCH₃ and ortho -CH₃ lateral groups, and the left n-alkoxy (-OR) terminal end group for the same homologue from series to series. But they differ with respect to polar group -Br and -Cl substituted at the para position respectively of series 1 and series X. Thus, molecular rigidity of series 1 and X remains unaltered, but molecular flexibility alters for the same homologue from series to series. Thus, the mesogenic properties and the degree of mesomorphism as depending on the suitable magnitudes of combine effect of molecular rigidity and flexibility, which varies with molecular structure for the same homologue from series to series and from homologue to homologue in the same series. Table 3 represents some thermometric property of presently investigated novel series 1 and series X selected for comparative study.

Table 3. Commencement and Average Transition Temperature of Series 1& Series X

Series	Series 1	Series X
Smectic-Nematic	101.2 ⁰ C (C ₈ -C ₁₆)	124.2 ⁰ C (C ₂ & C ₁₄ -C ₁₆)
Commencement of smectic phase	C ₈	C ₂
Nematic-Isotropic	115.2 ⁰ C (C ₇ -C ₁₂)	139.4 ⁰ C (C ₁ -C ₁₆)
Commencement of nematic phase	C ₁	C ₁
Total mesophase length in ⁰ C (Sm+N)	4.4 ⁰ C to 39.5 ⁰ C C ₁₆ C ₁₀	3.8 ⁰ C to 64.3 ⁰ C C ₁ C ₂

Table 3, indicates that

- Series-1 and Series-X exhibit both smectogenic and nematogenic properties.
- Smectic properties commence from C₈ and C₂ homologues for Series 1 and Series X respectively.
- Nematic properties for Series 1 & Series X commence from C₁ homologue.
- The thermal stability of the smectic phase decreasing order from series X to Series 1
- The nematic thermal stability of series X is more than series 1.
- The total mesophase length is highest for series X, and lowest for Series 1.

The para-substituted –Br group in Series 1 increases intermolecular distances, lowering transition temperatures and thus reducing thermal stability. In contrast, the para-substituted –Cl tail group in Series X maintains molecular linearity, enhancing intermolecular cohesion and closeness. Consequently, transition temperatures and resistance to thermal vibrations are higher in Series X for the same homologue. Therefore, Series X has greater thermal stability and longer mesophase length ranges compared to Series 1. The commencement of the smectic phase depends on the extent of molecular non-coplanarity, which varies with the positional differences of functional groups with different polarities and polarizability for the same homologue across series. Intermolecular dispersion and dipole-dipole interactions of residual forces beyond the upper transition of the smectic phase induce nematic mesophase formation. This nematic mesophase formation occurs from the very first member (C₁) to the C₁₂ in Series 1 and for all members of Series X, but with different degrees of mesomorphism. Thus, the thermometric properties of mesomorphic (liquid crystalline) substances depend on the magnitudes of favorable molecular rigidity and flexibility. Even minor differences in molecular structure, either within the same homologue across different series or from homologue to homologue within the same series, significantly impact these properties.

6. CONCLUSIONS

Ester homologous series of azodye central bridge is partly smectogenic and predominantly nematogenic and middle order melting type with considerable mesophase lengths.

- The group efficiency order based on (i) thermal stabilities, (ii) commencement of mesophase, and (iii) the total upper and lower degree of mesophase length range for smectic and nematic phases is as follows:
 1. Thermal stabilities:
 - Smectic: Series X > Series 1
 - Nematic: Series X > Series 1
 2. Commencement of mesophase:
 - Smectic: Series X > Series 1
 - Nematic: Series 1 = Series X
 3. Total mesophase length range (Smectic + Nematic):
 - Series X > Series 1
- Suitable magnitudes of the combined effect of molecular rigidity and flexibility can induce mesomorphism.
- The phenomenon of mesomorphism is highly sensitive and susceptible to molecular structure due to the resultant molecular rigidity and flexibility.

- This study is valuable for researchers working on the liquid crystalline state as a source of liquid crystalline material.
- The study supports and enhances the credibility of previously drawn conclusions.

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