Mesomorphism dependence on molecular flexibility Involving Lateral -OCH$_3$ Group and Vinyl Carboxylate Central Linkage

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Abstract

In the present investigation, a newly synthesized ester homologous series of mesogenic compounds having a vinyl carboxylate group as central linkage with two phenyl rings and a laterally substituted methoxy group as well as -CH=CH-COOC$_6$H$_{13}$ terminal end group were synthesized. Eleven homologues were synthesized. Among these eleven homologues first seven derivatives C$_1$ to C$_7$ of the investigated series are nonmesomorphic by nature. Rest of the homologs are smectic by nature, among these C$_8$, C$_{10}$ and C$_{12}$ and C$_{14}$ homologues show monotropicaly smectic phase Thus, presently investigated series is predominately smectogenic by nature without exhibiting nematic mesophase. Transition temperatures and textures of synthesized compounds were observed through an optical polarizing microscope equipped with a heating stage. The textures of smectogenic mesophase are focal conic fan-shaped. Some representative members were characterized by IR, ^{1}HNMR, mass spectroscopy and elemental analysis. Transition temperatures of homologues are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group. Isotropic-smectic / smectic-isotropic transition curve behaves in a normal ascending manner. Thermal stability and other mesogenic characteristics are compared with other structurally similar homologous series. The mesogenic phase length ranges between 5^0 C and 17^0 C and is of middle-order melting type.

Keywords: *Liquid crystals, Mesomorphism, Smectogenic, Thermotropic, DSC*

I. INTRODUCTION

Thermotropic liquid crystal [1] dual character as fluid and optically active studied by chemists, physicists, biologists, engineers, pharmacists etc. with a different aim, object and with a view as the different angle. Optical devices and temperature/humidity sensors are important applications in the field of liquid crystal (LC) instrumentation [2-6]. The addition of new mesogens or aromatic rings, as well as different terminal substituents such a compact group or alkoxy/alkyl chains, will impact the molecular geometry, flexibility and offer wide thermal stability ranges of the designed materials [7]. Further slight changes in the molecular architecture can lead to considerable changes in the mesomorphic behaviour and play an important role in the mesomorphic properties, types of mesophase and stability of the observed mesophase [8-17]. Achievement of the proper characteristics for new device applications requires structure-activity relationship tools to design suitable materials [18-21].

In recent times, numerous mesomorphic compounds have been reported to contain substituents with varying polarities at both ends of their molecular axis. These substituents have been observed to either enhance or inhibit the mesomorphic properties of the compound. From the typical terminal substituents, one may mention -OCH$_3$, -CH$_3$, -F, -Cl, -Br and -NO$_2$ as polar groups possessing dipole moments that support mesomorphic properties; the increased dipole moment improves the stability of lattice and consequently increases its melting temperatures. If in the rigid core of LC molecule introduce the lateral substituent to make molecule broad and its important play in the mesomorphic behavior. This will modify the arrangement and molecular polarizability, consequently affecting the strength of anisotropic attractive forces. Goodby et al. [35, 36] have reported that the type and mesophase stability are influenced by free volume that is affected by molecular architecture and its deformation.

The researcher generated numerous homologous series, incorporating various linking groups and diverse terminal and lateral substituents.. Most synthesized mesomorphic homologous series contain central linking group –COO- or –CH=CH-COO- and -N=N- bridge to rigid phenyl core ring bearing with different terminal and lateral groups. However, they succeed to prepare liquid crystalline molecules varying linking groups as well as other terminal and lateral groups with respect to the changed molecular structure which is important to show mesomorphism and also change molecule properties i.e physical and chemical properties.

II.   MATERIALS AND METHODS

4-hydroxy 3-methoxy cinnamic acid, n-alkyl bromides (R-Br), KOH, 4-hydroxy cinnamic acid, n-hexanol, Methanol, HCl, Ethanol, Acetic acid, n-hexane, con. H_2SO_4, Sodium bicarbonate, $MgSO_4$, dichloromethane (CH2Cl2), DMAP (4-Dimethylaminopyridine), Dicyclohexyl Carbodiimide (DCC), and other reagents etc. required for the synthesis were purchased from Spectrochem, Merck, and Sigma-Aldrich. All reagents and solvents were used as received.

Selected homologues of the synthesized series were characterized by elemental analysis (Table-1). Infrared spectroscopy, ^{1}H NMR spectra, mass spectroscopy, and transition temperatures were confirmed by The Differential Scanning Calorimeter (DSC).

III. EXPERIMENTAL

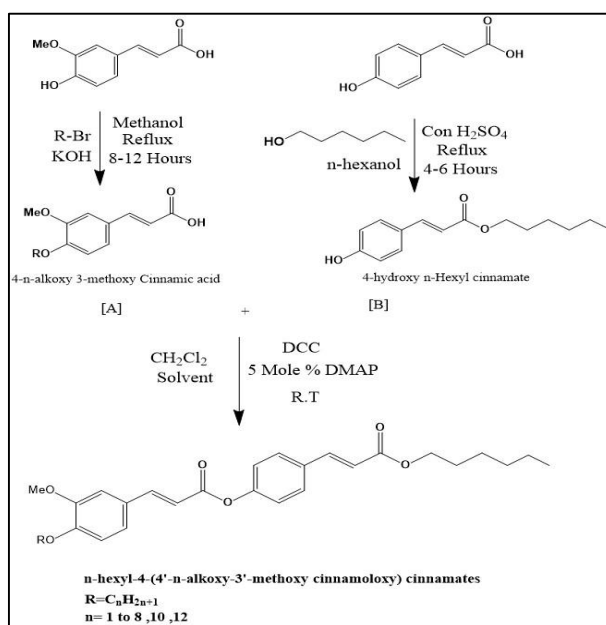### 3.1   Synthesis of 4-n-alkoxy 3-methoxy Cinnamic acid [A]

As shown in the Reaction Scheme-1. 4-n-alkoxy 3-methoxy cinnamic acid [A] prepared by Dave and Vora's modification method [37], a mixture of 4-hydroxy 3-methoxy cinnamic acid (4.85 g, 0.025 mol), alkyl bromide (0.03 mol), potassium hydroxide (3.2 g, 0.062 mol), and ethanol (50 ml) were refluxed in RBF for 4-5 hours. After cooling, the mixture was poured into a stirred mixture of concentrated hydrochloric acid (25 ml) and ice-cold water (25 ml). The product was then filtered. The compounds were washed with hot water, dried, and recrystallized using ethanol to obtain a constant melting point. The purity of the compounds was checked by TLC and the Melting point. [38]

3.2   Synthesis of 4-hydroxy n-hexyl cinnamate [B]

An Equimolar proportion of 4-hydroxy cinnamic acid and absolute n-hexyl alcohol was mixed in a 250 ml single neck round bottom flask in the presence of two drops of H2SO4, and the reaction mixture was refluxed for 4-5 hours. The reaction mixture was then decomposed in ice-cold water and allowed to settle. A Crude product, 4-hydroxy n-hexayl cinnamate, was obtained. The product was filtered, washed, dried, and purified by crystallization to yield 61.68% and M.P. 160 [0] C. [39, 40]

3.3   Synthesis of n-hexyl-4-(4'-n-alkoxy-m'-methoxy cinnamoyloxy) cinnamates. [A+B]

Homologues of the titled homologous series were prepared using the Steglich esterification method to yield n-hexyl-4-(4'-n-alkoxy-m'-methoxy cinnamoyloxy) cinnamates. The synthesized compounds (A) and (B) were condensed using N, N'-dicyclohexyl carbodiimide (DCC), 4-dimethyl amino pyridine (DMAP), and dichloromethane (DCM) as the solvent, and the reaction was performed at room temperature. The product was then filtered, washed with water and $NaHCO_3$, dried, and recrystallized in glacial acetic acid until a constant melting point was obtained. The purity of the compounds was checked by TLC and characterized by elemental analysis and spectral data. [41-43]

Scheme 1: Synthesis of n-hexyl-4-(4'-n-alkoxy-3'-methoxy cinnamoyloxy) cinnamates.

3.4 Analytical data

3.4.1 ^{1}H NMR in δppm of Decyloxy derivative (C$_5$)

^{1}H NMR (400 MHz, DMSO) δ 7.86 – 7.76 (m, 3H), 7.68 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.32 (dd, J = 8.5, 2.0 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.6 Hz, 2H), 3.83 (s, 3H), 1.79 – 1.58 (m, 4H), 1.46 – 1.31 (m, 4H), 1.34 (s, 3H), 1.34 – 1.23 (m, 3H), 0.89 (dt, J = 8.4, 6.9 Hz, 6H).

^{1}H NMR in δppm of Tetradecyloxy derivative (C$_7$)

^{1}H NMR (400 MHz, DMSO) δ 7.85 – 7.76 (m, 3H), 7.68 (d, J = 16.0 Hz, 1H), 7.46 (s, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.3 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 6.65 (d, J = 16.0 Hz, 1H), 4.15 (t, J = 6.6 Hz, 2H), 4.00 (d, J = 6.7 Hz, 2H), 3.83 (s, 3H), 1.77 – 1.59 (m, 4H), 1.38 (d, J = 14.1 Hz, 3H), 1.30 (d, J = 11.0 Hz, 11H), 0.87 (d, J = 7.1 Hz, 6H).

^{1}H NMR in δppm of Tetradecyloxy derivative (C$_{10}$)

^{1}H NMR (400 MHz, DMSO) δ 7.86 – 7.76 (m, 3H), 7.68 (d, J = 16.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.32 (dd, J = 8.5, 2.0 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.01 (d, J = 8.4 Hz, 1H), 6.81 (d, J = 15.9 Hz, 1H), 6.65 (d, J = 16.1 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 4.00 (t, J = 6.5 Hz, 2H), 3.83 (s, 3H), 1.78 – 1.59 (m, 4H), 1.39 (d, J = 6.3 Hz, 2H), 1.39 – 1.23 (m, 20H), 0.92 – 0.82 (m, 6H).

3.4.2 FTIR Spectrum in Cm^{-1} of Decyloxy derivative (C$_8$)

FTIR (ATR, υ$_{max}$, cm^{-1}): 682.41 (poly methylene of -C$_8$H$_{18}$ and -CH$_3$), 841.20 (p-sub. Benzene ring), 2949.62 & 2930.33 (CH$_2$ Str.), 1717.16, 1627.82 & 1277.42 (-COO & -CO), 1511.20 & 1422.63 (aromatic -HC=CH-), 1161.77 (-CO of alkoxy), 923.03 (-CH=CH-), 3003.95 (CH of aromatic Str), 802 (p-substitution aromatic ring)

FTIR Spectrum in Cm^{-1} of Tetradecyloxy derivative (C$_{14}$)

FTIR (ATR, υ$_{max}$, cm^{-1}): 682.41 (poly methylene of -C$_{14}$H$_{30}$ and -CH$_3$), 841.20 (p-sub. Benzene ring), 2949.62 & 2930.33 (CH$_2$ Str.), 1717.16, 1627.82 & 1277.42 (-COO & -CO), 1511.20 & 1422.63 (aromatic -HC=CH-), 1161.77 (-CO of alkoxy), 923.03 (-CH=CH-), 3003.95 (CH of aromatic Str), 802 (p-substitution aromatic ring)

3.4.3 Mass Spectra of Decyloxy derivative (C$_7$)

m/z (int of %) 536 (M$^+$), 317 (100% base peak ester linkage break)

Mass Spectra of Tetradecyloxy derivative (C$_{12}$)

m/z (int of %) 592 (M$^+$), 373 (100% base peak ester linkage break)

Table 1: Elemental analysis of (1) Hexyloxy (2) Octyloxy (3) Tetradecyloxy derivatives.

Sr. No.	R=n-alkyl chain	Molecular formula	Element % found			Element % calculated		
			C	**H**	**O**	**C**	**H**	**O**
1	C$_6$	C$_{29}$H$_{36}$O$_6$	72.48	7.55	19.97	72.60	7.50	19.90
2	C$_8$	C$_{31}$H$_{40}$O$_6$	73.20	7.93	18.87	73.50	7.90	18.60
3	C$_{14}$	C$_{37}$H$_{52}$O$_6$	74.97	8.84	16.19	74.91	8.88	16.21

IV. RESULT AND DISCUSSION

Here, the synthesized homologous series "n-hexyl-4-(4'-n-alkoxy-3'-methoxy cinnamoloxy) cinnamates" is discussed in a brief, comparative study, and some important conclusions were drawn.

Eleven homologues were synthesized by coupling (E)-4-n-alkoxy 3-methoxy Cinnamic acid with the non-mesogenic compound 4-hydroxy n-hexyl cinnamate. And the reaction scheme of the synthesized series was shown in scheme-1 and a detailed experimental procedure was described in the experimental procedure. The homologues were confirmed by different analytical data, such as ^{1}H NMR, IR, and Mass spectrometry. The synthesized homologs of C_1 to C_7 are not mesomorphic because the magnitudes of anisotropic forces of intermolecular end-to-end and/or lateral attractions occurred as a consequence of unsuitable molecular rigidity and flexibility which induces the inability to resist exposed thermal vibrations to cause mesomorphism, and hence possess a high crystallizing tendency, but from the homolog of C_8 onward, mesomorphism commences in a monotropic manner as smectic type and continues until the C_{14} homolog of series, And generate a lamellar packing of molecular with a layered structure. Thus, only smectogenic mesophase formation is observed within a definite temperature range. Nematic type of mesophase is not exhibited by any of the series showing mesogenic character. Mesomorphic properties vary from homolog to homolog in synthesised present series because of the change of number in methylene units present at left side of n-alkoxy chain. which changes molecular length, polarizability and polarity, length-to-breadth ratio etc. which causes variation in molecular rigidity and flexibility for emerging suitable or unsuitable magnitudes of anisotropic forces of intermolecular attraction to induce mesomorphism [42]. Transition temperatures of homologues (Table 2) are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy terminal end group in Figure 2. Careful observation of the phase diagram indicate that the solid-isotropic or solid-smectic transition curve show a falling tendency as series is ascended to pentyl derivative of the series without following zig-zag path of rising and falling up to heptyl derivative of series from hexyl and then transition curve rises from Hexyl to octyl and from then on, the curve is falls to the last homologous of the series. The Crystallin-Isotropic and Smectic-isotropic transition curves behaved in a normal manner. The average Thermal stability of smectic is 82.5 ^{0} C, and the mesomorphic phase length ranges from 5 ^{0} C to 17 ^{0} C in tetradecyl and octyl homologue respectively. Transition and melting temperatures are relatively low. Thus, the series is of low melting type with a low range of smectogenic character and without exhibiting nematogenic character.

The showing of monotropically smectogenic mesomorphism higher homologues from C_8 to C_{14} monotropic manneris due to suitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions as a result of favourable monotropic magnitudes of molecular rigidity and flexibility, dispersion forces and dipole-dipole as well as electronic interactions. Therefore, the molecules of C_1 to G_7 homologues do not exhibit enantiotropically or monotropically smectogenic character. Conversely, the molecules of higher homologues C_8 to C_{14} of longer n-alkyl chain 'R' of -OR end group firstly transformed into the isotropic state due to uncooperative accommodations of longer –OR group. Then, on cooling the same sample below that isotropic temperature, the same molecules of isotropic mass, settle themselves in statically parallel orientational order and then in an arrangement of sliding layered molecular arranged in an unalterable manner; to cause monotropic smectic phase. Compounds of the series accredited to weak of gradual intermolecular forces and resulting in lowering of transition temperature ongoing from lower to higher homologues with increasing additions of methylene($-CH_2$) unit or units. The reversal of consecutive order for enantiotropic and monotropic mesomorphism may be due to the presence of only and only **–CH=CH-COO-** central bridge and as well as laterally situated **-OCH₃ polar** groups. The absence of mesomorphism of C_1 to C_7 homologous their high crystallizing affinity arising from incompatible magnitudes of anisotropic forces of intermolecular end to end attractions as a concern of unfavorable molecular rigidity and flexibility, which induces an inability to repel exposed thermal vibrations.
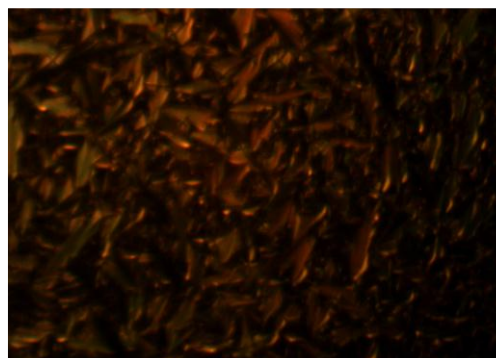
4.1 Mesomorphic Behavior.

The mesomorphic properties of synthesized compounds were recorded in a polarizing optical microscope (POM) equipped with a Mettler FP82HT heating plate. The sample was prepared as follows, ~1 mg compound was sandwiched in between a glass plate and coverslip with the help of heating up to its mesomorphic/isotropic temperature; The prepared slip with a thin section of the compound was observed under POM using heating and cooling rate for the transition temperature is 10 C min^{-1}. According to measurements of phase transition temperature (^{0} C) are tabulated in Table 2, and the mesophase texture observed by POM is shown in Figure 1.

Table 2: Transition temperature in ^{0} C on heating rate

Compound No.	R=n-alkyl group: C_nH_{2n+1}	Commencement temperature of Smectic phase during heating	Isotropic
1	C_1	-	112^0
2	C_2	-	104^0
3	C_3	-	108^0
4	C_4	-	92^0
5	C_5	-	81^0
6	C_6	-	85^0
7	C_7	-	89^0
8	C_8	$(75)^0$	92^0
9	C_{10}	$(72)^0$	77^0
10	C_{12}	$(70)^0$	78^0
11	C_{14}	$(68)^0$	83^0

(a)

(b)

Figure 3: Mesophase texture observed by POM (a) Smectic A shape phase of compound C_{10} at 75^0 C; (b) Smectic A phase of compound C_{14} at 68^0 C during the Cooling cycle.
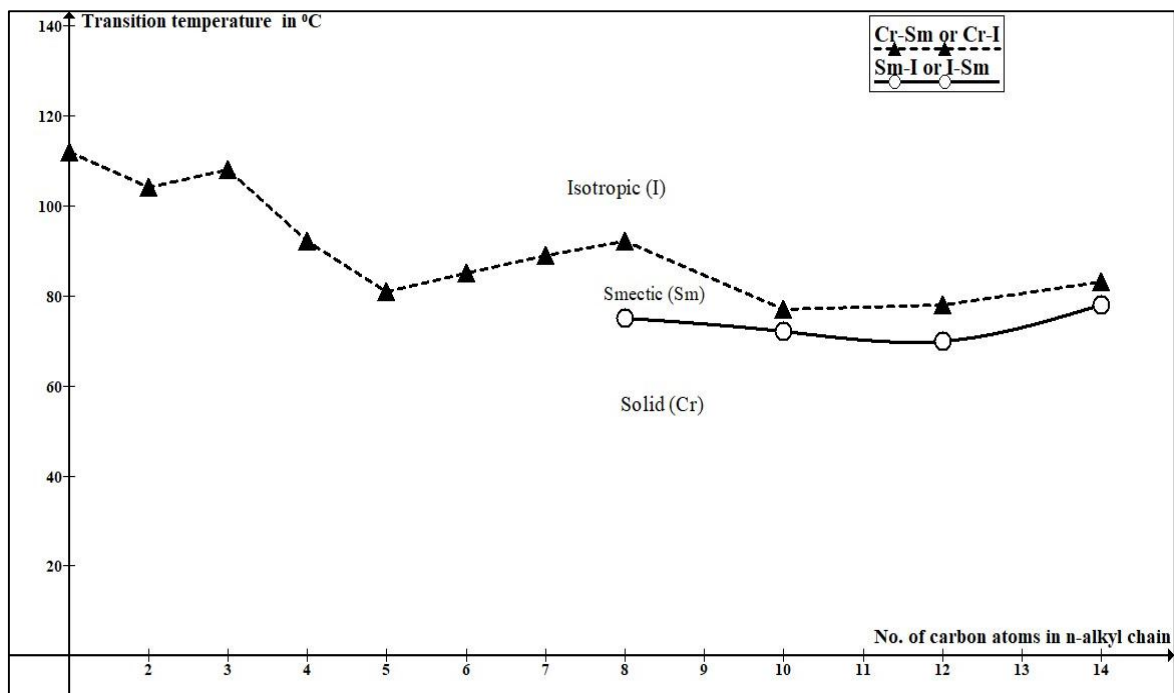
Figure 3: Phase behavior of homologues series.

4.2 DSC Analysis

DSC is used for the measurement of changes in physical properties by the influence of temperature and detection of the change in the physical properties of the compound at a particular temperature. The Mesogens (C_8 and C_{12} of series-1) Were screened using the DSC Method. To confirm the phase transition temperature of the synthesized ester-based homologues, analysis was performed on both heating and cooling cycles at a rate of 10 ^{0} C /min. The two specific thermograms are presented in Figure 3 and 4; their phase lengths are listed in Table 3, and Figures 3 and 4 show the DSC spectra of the octyloxy and dodecyloxy derivatives, respectively.

From Figures 5, we observed that the presence of one sharp endothermic peaks in higher alkyl chain substituted compounds indicates the presence of solid-isotropic phases. The octyloxy derivative containing compound C_8 had one endothermic peak, the compounds melt, without their liquid crystal mesophase behavior persists through the isotropic point. Additionally, at temperatures above 92 ^{0} C, an isotropic phase change was noticeable. And the system's enthalpy was found to be 78.65 J/g, which is similar to a transition state in the endothermic phase. During the cooling or exothermic cycles, these two-phase transition curves were also observed in reverse order. The material displayed isotropic behavior throughout the cooling process at 92 ^{0} C, whereas the smectic transition commenced below this temperature range at 75 °C. This large difference indicates that the chemical has a considerable smectic phase preference during the exothermic cycle. During this cycle, the isotropic behavior collapses. This indicates that the LC mesophase and a transition with an enthalpy change, starting at -6.77 J/g, occurs. The molecule reverted to its crystalline form at temperatures below 60 °C.
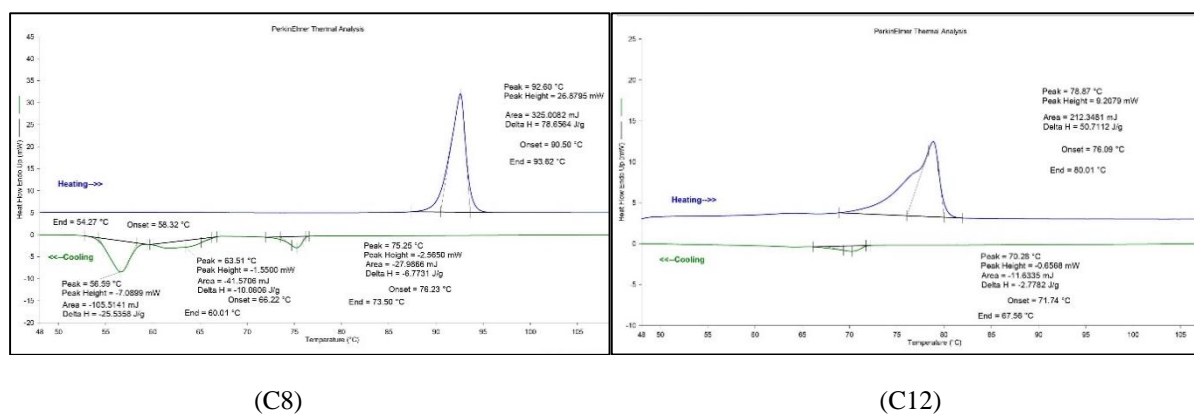

(C8)   (C12)

Figure 5: Representative DSC thermograms of the C_8 and C_{12} derivative during the heating and cooling cycles (10 ^{0} C /min).

The dodecyloxy containing compound C_{12} had only one endothermic peak observed at 78 °C for the isotropic phase. The enthalpy of the system was found to be 50.71 J/g and did not provide any phase length during the heating cycle. Under cooling conditions, the compound displayed mesophase behavior at 70.28 °C and returned to the crystalline state below 50 ⁰ C. The enthalpy change in this cycle is from -2.77 J/g. These transition temperatures and POM transition temperatures are satisfactorily correlated. DSC analysis supported the monotropic and enantiotropic mesophase behavior of the synthesized ester-based homologues.

Table 3: Transition enthalpy and entropy changes of C_8 and C_{12} homologues.

Homologue	Transition	Peak Temp. in⁰ C	ΔH/ Jg⁻¹	ΔS/ Jg⁻¹K⁻¹	Phase length
C_8	I-Sm	75.25	6.77	0.0194	Sm-18.37
C_{12}	I-Sm	70.28	2.77	0.0080	Sm-9.73

4.3 Comparative study of Series A with Series X and Series Y

The mesomorphic properties of the investigated series-A were compared with two structurally similar known homologous series-X [40] and series-Y [44], as shown in Figure 5.
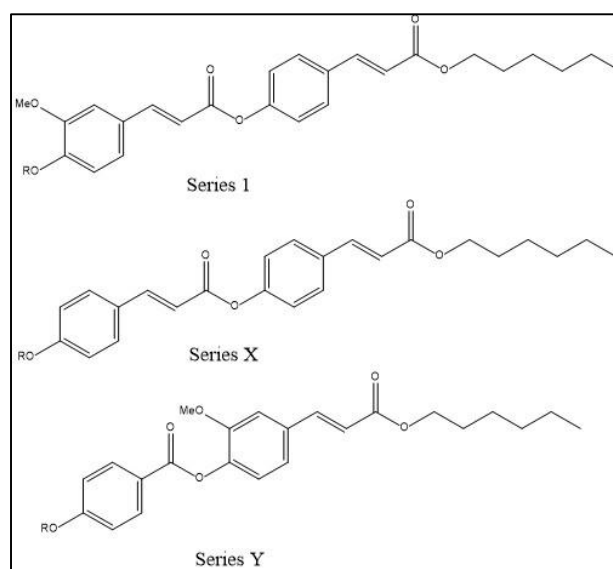

Figure 5: Structurally similar series

The Homologous series of the present investigation (series-A) and known homologous series-X and series-Y were chosen for comparison and were identical for the two phenyl rings. The central bridge was the same in series-X: –CH=CH-COO-. And in Series-Y The central bridge is -COO-. Homologous series-A differed significantly from series-X because of the laterally substituted -OCH₃ polar group. Series-Y differs from the unsaturated double bond is absent in the terminal central ester linkage, and -OCH₃ polar group is present in central benzene ring, while an unsaturated double bond is present in the ester group at the terminal position -CH=CH-COOC₆H₁₃ (n) in series-X and series-Y. These two major changes alter the polarity and polarizability of the structures. Thus, variations in the mesomorphic properties and degree of mesomorphism vary according to variations in the molecular structure. The intermolecular forces of attraction arising from polarity, polarizability, length-to-breadth ratio, Pai electron density, varying structural arrangement of the butyl end group, and its special steric effect cause variation in the magnitude of intermolecular forces of attraction among series A, X, and Y for the different homologues of the same series and same homologue from series to series. In Table 4. The structural similarities and differences between the series under comparison are shown in tabular form.

Table 4: A structural overview of the homologues series-A, series-X and series-Y.

Homologues Series	Noticeable change in molecular substitution and polarity and polarizability		
Series-A	Laterally substituted -OCH$_3$ group present at the left-hand benzene ring	Central bridge is -CH=CH-COO-	Terminal substituted function groups are n-alkoxy and -CH=CH-COOC$_6$H$_{13}$ (n)
Series-X	Laterally substituted -OCH$_3$ group is absent at left-hand benzene ring	Central bridge is -CH=CH-COO-	Terminal substituted function groups are n-alkoxy and -CH=CH-COOC$_6$H$_{13}$ (n)
Series-Y	Laterally substituted -OCH$_3$ group present at the central benzene ring	Central bridge is -COO-	Terminal substituted function groups are n-alkoxy and -CH=CH-COOC$_6$H$_{13}$ (n)

Table 4 provides a structural overview of the homologues series-A, series-X, and series-Y to investigate and compare "the position of the laterally bulky and polar methoxy -OCH3 group and change in the terminal substituted function group" on the types of mesomorphism and thermal stabilities of these compounds.

Table 5: Relative thermal stability in ^{0} C.

Series:	Series-A	Series-X	Series-Y
Smectic-isotropic or Smectic-nematic	82.5 ^{0} C (C$_8$ to C$_{14}$)	153.2 (C$_7$ to C$_{11}$)	111.1^0 C (C$_4$ toC$_{16}$)
Commencement of smectic phase	C$_8$	C$_7$	C$_4$
Nematic-Isotropic or Isotropic-Nematic	-	170.9 ^{0} C (C$_3$ to C$_{12}$)	-
Commencement of nematic phase	-	C$_3$	-
Mesophase length (Sm+N) in ^{0} C	5 ^{0} C to 17 ^{0} C	10 ^{0} C to 34 ^{0} C	8 ^{0} C to 33 ^{0} C

Table 5 reveals the following comparative facts.

- Homologous Series-A and Series-Y were smectogenic, whereas Series-X was smectogenic as well as nematogenic mesophase formation.
- Smectogenic property in series-A commences from octyloxy homologue, while in series-Y it commences from butyloxy homologue and in series-X it commences from heptyloxy homologues.
- Nematic mesophase only appeared in Series-X and the commencement of nematogenic properties are from the propyloxy Homologue.
- The mesomorphic phase length range of Series A lies in a comparatively short temperature range (5^0 C to 17^0 C), whereas the mesomorphic phase length ranges of Series X and Series Y were (10^0 C to 34^0 C) and (8^0 C to 33^0 C) respectively.
- Smectic thermal stability increases from series-A to Series-Y,
- Nematic thermal stability is zero for series-A and Series-Y, and up to 170.9 ^{0} C for series-X.

- In series-A and Series-Y, changing the laterally substituted -OCH$_3$ group present on the left hand lowers the transition temperature as compared to series-X. And removed nematogenic mesomorphic properties.
- Series-X possesses middle-order melting temperatures, whereas series-A and series-Y exhibit lower transition temperatures.

V. CONCLUSION

➤ Homologous series of the present investigation with two phenyl rings, the-OCH$_3$ lateral group at the left-side phenyl ring, -CH=CH-COO- as the Central bridge, and–CH=CH-COO-C$_6$H$_{13}$(n) terminal end group is smectogenic without exhibiting nematic properties, whose smectic property commences from the C$_8$ homolog, and intermolecular cohesive forces are more conducive to molecular width instead of molecular polarizability.

➤ The group efficiency order derived for smectic and nematic mesophase formation based on (i) thermal stability, (ii) commencement of mesophase, and (iii) total mesophase temperature length range are as follows.
(i-a) Nematic thermal stability: Series-X > Series-A = Series-Y
(i-b) Smectic thermal stability: Series-Y> Series-A > Series-X
(ii-a) Early commencement of Smectic mesophase: Series-Y>Series-X> Series-A
(ii-b) Early commencement of Nematic mesophase: Series-X> Series-A=Series-Y
(iii)Total Mesophase length range (Sm + N): Series-X > Series-Y > Series-A

➤ The present investigation supports earlier views that the large size of the laterally substituted -OCH$_3$ group hinders parallel arrangements of molecules that reduce end-to-end intermolecular attraction, and that the dipole moment associated with this group should operate at an angle across the long molecular axis and could enhance smectic properties.

➤ The present novel homolog series possesses Sm-I transition temperatures ranging from 68 to 75 °C. Such mesomorphs are useful for studying binary systems for devices that can operate at room temperature.

➤ The sequentially added methylene unit at the left side of the n-alkoxy terminal end group affects the change in mesomorphic characteristics of the homolog to the homolog in the same synthesis series containing the same central bridge and terminal group.

➤ The degree of mesomorphism depends on the molecular structure and the rigidity of the molecules.

➤ The present investigation supports earlier views that the central bridge has less of an effect on mesogenic properties than the terminal end group.

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