



Dependence of Mesomorphism on meta Substituted Lateral Groups

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ABSTRACT

Thermotropic LC substances of chalconyl derivatives consisting of two phenyl rings, one chalconyl central bridge and two flexible {-OR and -OC₇H₁₅(n)} terminal (para) / lateral (meta) functional groups i.e. RO-C₆H₄-CH=CH-CO-C₆H₄-OC₇H₁₅(n) (meta) have been synthesized and studied for the effect of molecular structure on thermotropic mesomorphism. The thermometric behaviours of novel homologue substances and their textures were determined by an optical polarizing microscopy (POM) equipped with a heating stage. Textures of a nematic phases are threaded or schlieren. The textures of monotropic smectic phase are directly judged from the heating top as smectic-A. Analytical, thermal and spectral data supports and confirms the molecular structures of homologues. Transition curves as depicted in a phase diagram behaves in normal manner. Odd-even effect for N-I transition curve (very short) is observed. Total (C₁ to C₁₈) thirteen homologues are synthesized. Mesomorphism commences from C₇ homologue. C₇ to C₈ homologues are enantiotropic nematic and C₁₀ to C₁₈ homologues are monotropic nematic plus smectogenic. Thermal stability of smectic phase is about fraction of 1.0 °C or 1.0 °C and that of nematic phase is 66.0 °C with total mesophase length minimum to maximum 7.0 °C to 15 °C. Group efficiency order for mesophases is derived on the basis of thermal stabilities from the comparative study of thermometric data determined from structurally analogous series. Hence present novel series behaves in normal manner with very short mesophase lengths, low thermal stabilities and low melting type and predominantly nematogenic and partly smectogenic.

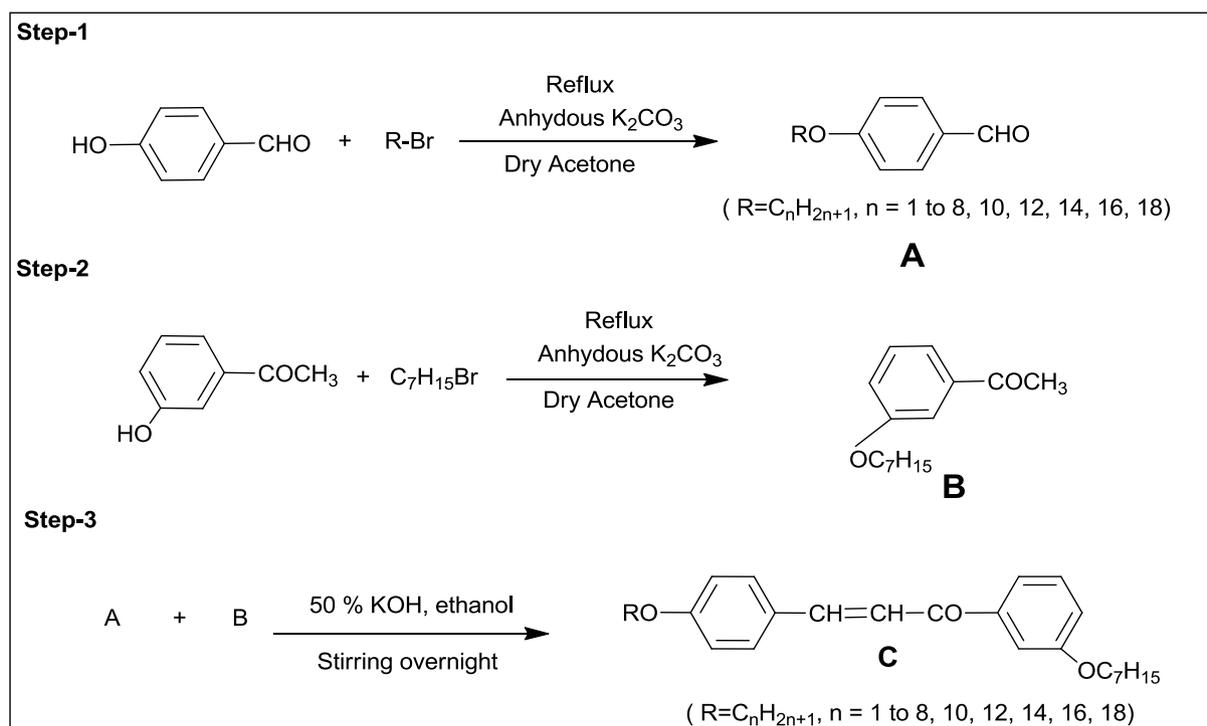
Keywords: Smectic; Nematic; Mesomorphism; Liquid Crystals; monotropy

1. INTRODUCTION

Thermotropic Liquid Crystal (LC) property [1] with bioactivity property is exhibited by chalconyl derivatives, which may be exploited in the benefit of mankind in the manufacture of LC devices and the pharmaceutical preparations [2-8]. Present work is restricted aim and object upto synthesis, characterization, results and discussion on the basis of thermometric data and thermal behaviours of novel series consisting of two phenyl rings linked through –CH=CH-CO- group and its mesomorphism is controlled by flexibility of molecules. The object in views of the study is to understand and establish the effect of molecular structure on LC property with reference to molecular flexibility through lateral groups of present and analogous series [9-12]. Number of homologous series have been reported till the date [13-19] and their thermotropy is discussed on the basis of molecular rigidity and stability [20-23].

2. EXPERIMENTAL

2. 1. Synthesis



Scheme 1. Synthetic route to the series.

Alkylation of 4-hydroxy benzaldehyde to give 4-n-alkoxy benzaldehyde is carried out by reported method [24] and 3-n-alkoxy acetophenone is obtained by alkylation of 3-hydroxy acetophenone by reported method [25] Thus, the chalconyl homologue derivatives (C) were prepared by usual establish method [26] Homologues were filtered, washed with ethanol solution dried and purified till constant transition temperatures obtained using an optical

polarising microscope equipped with a heating stage. Alkyl halides, EtOH, KOH, 3-Hydroxy acetophenone, 4-Hydroxy benzaldehyde etc., required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below as Scheme 1.

2. 2. Characterization

Selected members of the novel homologous series were characterized by Elemental Analysis, infrared spectroscopy, ¹H NMR spectra. IR spectra were recorded by Perkin-Elmer spectrum GX,¹H NMR spectra were recorded on Bruker using CDCl₃ as solvent. Microanalysis was performed on a Perkin-Elmer PE2400 CHN analyzer. Transition temperature and LC properties (Textures) were determined using an optical polarizing microscope equipped with a heating stage. Textures of nematic phase of representative homologues determined by miscibility method. Thermodynamic quantity enthalpy (ΔH) and entropy (ΔS) are qualitatively discussed instead of DSC scan.

2. 3. Analytical Data

Table 1. Elemental Analysis for Decyloxy, tetradecyloxy, Hexadecyloxy and Octadecyloxy derivatives.

Sr. No.	Molecular formula	% Elements found		% Elements Theoretical	
		C	H	C	H
1	C ₃₂ H ₄₆ O ₃	80.33	9.62	80.30	9.58
2	C ₃₆ H ₅₄ O ₃	80.89	10.11	80.86	10.09
3	C ₃₈ H ₅₈ O ₃	81.18	10.32	81.10	10.30
4	C ₄₀ H ₆₂ O ₃	81.39	10.50	81.32	10.47

IR Spectra in cm⁻¹ for Heptyloxy&Octadecyloxy Derivatives:

Heptyloxy: 2919 (C-H str. of alkane), 2848 (C-H str. of -(CH₂)_n group of -OC₇H₁₅ group), 1600-1672 (C=O str. of carbonyl group of chalconyl group), 1660 (C=C str. of alkene), 1587 (C=C str. of aromatic ring), 1067, (C-H bending of alkene), 1172 (C-O str. of ether linkage), 1259 (C-O str. of carbonyl group), 778 Polymethylene (-CH₂-) of -OC₇H₁₅, 821 (-C-H- def. m di-substituted-Para), IR data confirms the molecular structure.

Octadecyloxy: 2918 (C-H str. of alkane), 2848 (C-H str. of -(CH₂)_n group of -OC₁₈H₃₇ group), 1595-1687 (C=O str. of carbonyl group of chalconyl group), 1662 (C=C str. of alkene), 1596 (C=C str. of aromatic ring), 1070, (C-H bending of alkene), 1170 (C-O str. of ether linkage), 1269 (C-O str. of carbonyl group), 786 Polymethylene (-CH₂-) of -OC₁₈H₃₇, 823 (-C-H- def. m di-substituted-Para), IR data confirms the molecular structure.

¹HNMR spectra in CDCl₃ in δ ppm for Hexyloxy & Tetradecyloxy Derivative:

Hexyloxy: 0.87 (t, -CH₃ of polymethylene -C₆H₁₃ and -C₇H₁₅), 1.80 (p, CH₃-CH₂-CH₂-CH₂-CH₂- of -OC₆H₁₃ and -OC₇H₁₅), 1.29 (m, -CH₂-CH₂-CH₂- of -OC₆H₁₃ and -OC₇H₁₅), 1.48 (q, -CH₂-CH₃), 4.04 (t, -OCH₂-CH₂-), 7.59 (d, -CH=CH-), 7.41, 7.26 & 7.79 (meta substituted phenyl ring), 7.57 & 7.62 (phenyl ring with alkoxy chain). NMR data confirms the molecular structure.

Tetradecyloxy: 0.88 (t, -CH₃ of -C₁₄H₂₉ and -C₇H₁₅), 1.78 (CH₃-CH₂-CH₂-CH₂-CH₂-CH₂- of -OC₁₄H₂₉ and -OC₇H₁₅), 1.32 (polymethylene -CH₂-CH₂-CH₂- of -OC₁₄H₂₉ and -OC₇H₁₅), 1.46 (q, -CH₂-CH₃), 4.07 (t, -OCH₂-CH₂-), 7.57 (d, -CH=CH-), 7.43, 7.28 & 7.83 (meta substituted phenyl ring), 7.55 & 7.60 (phenyl ring with alkoxy chain). NMR data confirms the molecular structure.

Table 2. Texture of Nematic Phase of C, C₁₀, C₁₄, C₁₆ by miscibility method.

Sr. No.	Homologue	Texture
1	C ₇	Threaded
2	C ₁₂	Schlieren
3	C ₁₆	Schlieren
4	C ₁₈	Schlieren

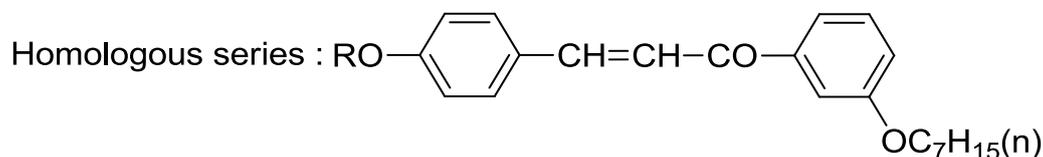


Table 3. Transition Temperature of Homologous series.

Sr. no	R = n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	C1	-	-	87.0
2	C2	-	-	81.0
3	C3	-	-	78.0
4	C4	-	-	70.0
5	C5	-	-	65.0

6	C6	-	-	68.0
7	C7	-	53.0	63.0
8	C8	-	56.0	69.0
9	C10	(57.0)	(64.0)	72.0
10	C12	(54.0)	(60.0)	69.0
11	C14	(51.0)	(58.0)	66.0
12	C16	(60.0)	(67.0)	73.0
13	C18	(58.0)	(70.0)	77.0

() indicates monotropy

3. RESULT AND DISCUSSIONS

Novel series of chalcones synthesized by condensing two nonmesomorphic components viz. 4-n-Alkoxy benzaldehyde and 3-Heptyloxy Acetophenone (m.p.- 32 °C, yield- 77.34%), yielded thermotropicmesogenic homologue derivatives. Mesomorphism commences from C₇ homologue. C₁ to C₆ homologues are nonmesogenic, C₇ and C₈ homologues are enantiotropicallynematogenic, C₁₀ to C₁₈ homologues are monotropicallynematogenic plus smectogenic.

Transition temperatures of homologues C₁ to C₁₈ were plotted against the number of carbon atoms present in n-Alkyl chain 'R' of -OR to understand the phase behaviours of series by joining like or related points to construct a phase diagram as depicted in Figure 1. A, Cr-N/I transition curve adopted zigzag path of rising and falling manner and behaves in normal manner. A, N-I/ I-N transition curve initially descended upto C₁₄ homologue and then ascended from C₁₆ to C₁₈ homologue with exhibition of very narrow and short odd-even effect upto C₉ homologue. An, I-Sm transition curve rises from C₁₀ to C₁₆ and descended after passing through maxima at C₁₆, till the last homologue C₁₈ with absence of odd-even effect. Thus, all the transition curves behaved in normal manner. Odd-even effect diminishes from and beyond C₉ homologue at the merging of curves for odd and even number of homologues.

The sequential order of mesophase appearance for monotropy and enantiotropy is reverted as compared to normal order which normally observed for other homologous series. The variations in mesogenicbehaviours or properties from homologue to homologue in the same series is observed throughout a novel series with increasing number of carbon atom in n-Alkyl chain 'R', keeping rest of the molecule part unchanged. Exhibition of mesomorphism either in monotropic or enantiotropic manner by the homologues of present novel series synthesized from two nonmesomorphs is attributed to the increase in molecular length, molecular polarity and polarizability, molecular rigidity and flexibility, permanent dipole moment across the long molecular axis, suitable magnitudes of dispersion forces and dipole dipoleinteractions which under exposed thermal vibrations leads to facilitating molecular

arrangement required to induce smectic and/or nematic phase reversibly or irreversibly above or below to isotropic temperature from C₇ homologue under floating condition.

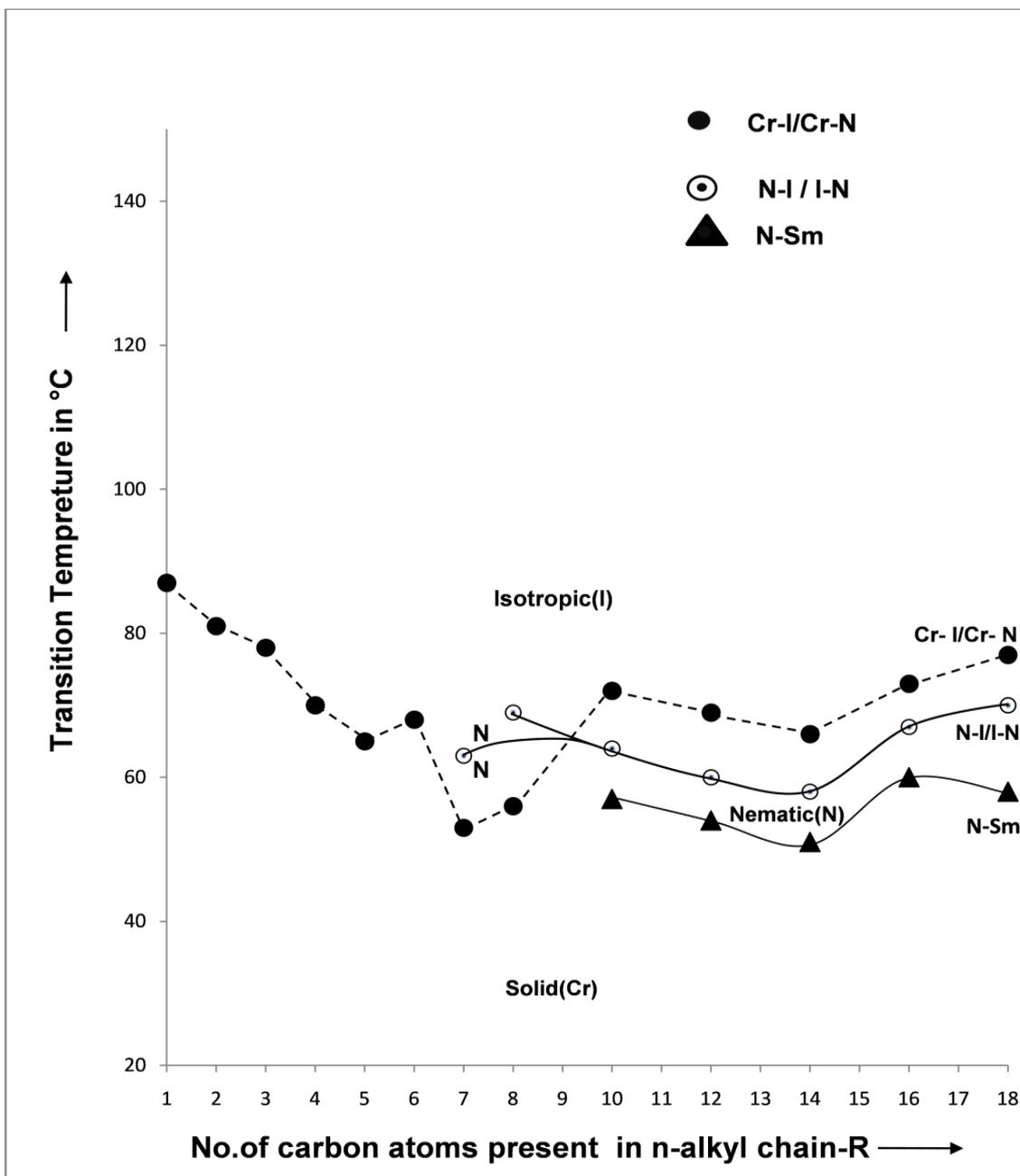
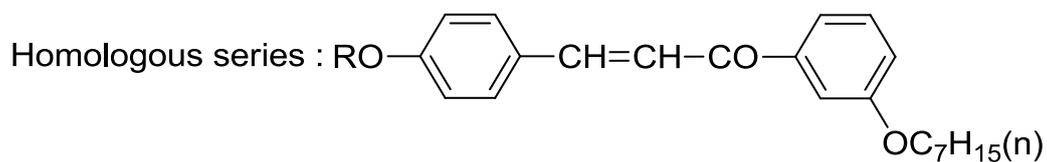


Figure 1. Phase behaviour of series.

The lowering of transition temperatures of homologues is attributed to the predominance of intermolecular distances due to widening of molecule which causes reduction in cohesive forces in competition with cohesive forces generated by polarizability occurrence by laterally meta substituted $-OC_7H_{15}(n)$ flexible group from C_7 and C_{10} homologue as nematic and smectic respectively. The odd-even effect observed for N-I transition curve is due to sequentially added methylene unit or units. The nonmesomorphic behaviours of C_1 to C_6 homologues is due to the low magnitudes of dispersion forces and low magnitudes of dipole-dipole interactions leading to high crystallising tendency and inducing unsuitable magnitudes of anisotropic forces of end to end and lateral attractions. Diminishing of odd-even effect for higher homologues beyond C_9 homologue of longer n-alkyl chain 'R' of $-OR$ and $-OC_7H_{15}(n)$ lateral flexible groups is attributed to coiling, bending, flexing and coupling with the major axes of core structure of a molecule. Therefore reversal of monotropy and enantiotropy in a present novel series may be due to the unexpected and uncertainty arising from unpredictable status of the n-alkyl chain 'R' of $-OR$ and $-OC_7H_{15}(n)$ of meta substituted $-OC_7H_{15}$ lateral group. The variations in mesogenic properties and the degree of mesomorphism from homologue to homologue in the same series or from series to series for the same homologue is attributed to the changing magnitudes of molecular rigidity and flexibility due to varied molecular polarity and polarizability and other related parameters concerning suitable magnitudes of intermolecular cohesions and closeness. The mesogenic properties of presently investigated homologous Series-1 are compared with structurally similar series X [27] and Y [28] as under in Figure 2.

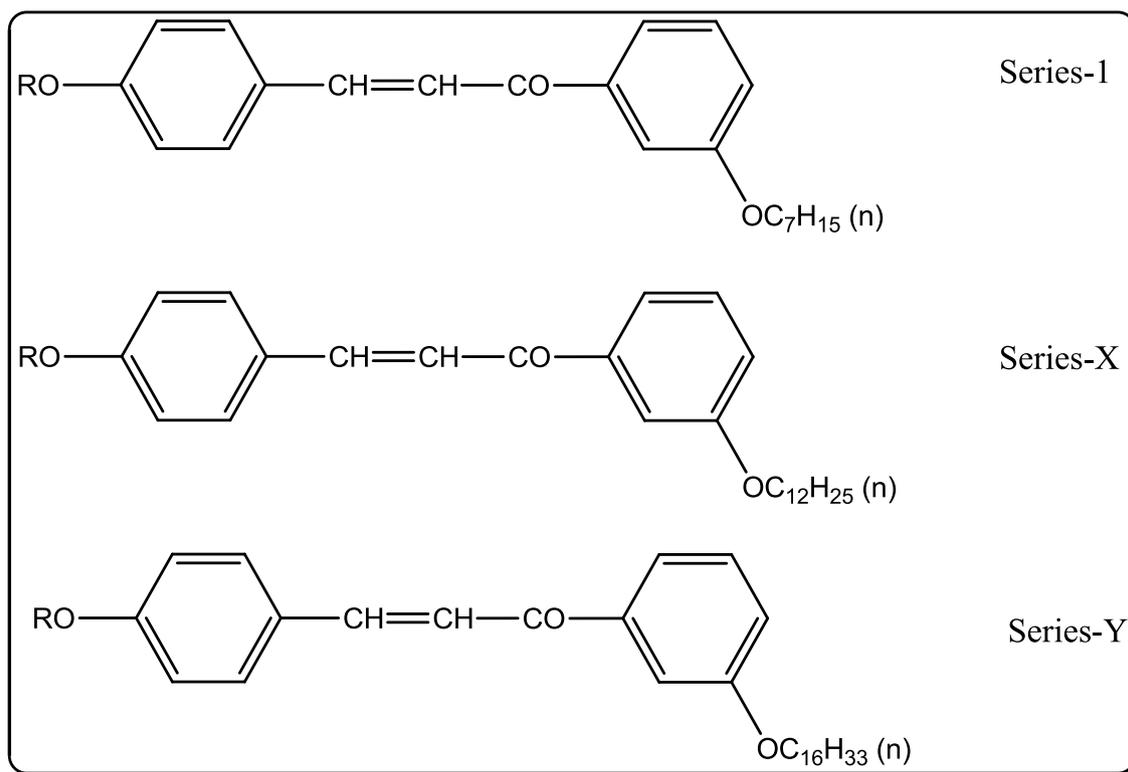


Figure 2. Structurally analogous series.

Homologous Series-1 and the structurally analogous similar Series X and Y chosen for comparison are identical with respect to two phenyl rings bridged through common $-\text{CH}=\text{CH}-\text{CO}-$ chalconyl group and identical geometry which contributes to the total molecular rigidity.

The left n-alkoxy (-OR) terminal group is also commonly present which contributes partly to the total molecular flexibility for the same homologue from series to series. However, the laterally meta substituted $-\text{OC}_7\text{H}_{15}(\text{n})$, $-\text{OC}_{12}\text{H}_{25}(\text{n})$ and $-\text{OC}_{16}\text{H}_{33}(\text{n})$ flexible groups which partly contributes to total molecular flexibility differ for the same homologue from series to series, Therefore the magnitudes of differing features (flexibility due to differing n-alkoxy lateral groups) for the same homologue from series to series and from homologue to homologue in the same series due to changing flexibility of left terminal $-\text{OR}$ group causes variations in mesogenic properties and the degree of mesomorphism.

Following Table 4 represents some thermometric properties in comparative manner.

Table 4. Thermal Stability in °C.

Series →	Series-1 ($-\text{OC}_7\text{H}_{15}(\text{n})$)	Series-X ($-\text{OC}_{12}\text{H}_{25}(\text{n})$)	Series-Y ($-\text{OC}_{16}\text{H}_{33}(\text{n})$)
Sm-I or I-Sm Commencement of Smectic phase	Fraction of 1 °C or 1 °C ($\text{C}_{10} - \text{C}_{18}$) C_{10}	56.0 ($\text{C}_4 - \text{C}_5$) C_4	1.0 or 2.0 (few degrees) ($\text{C}_7 - \text{C}_{18}$) C_7
N-I or I-N Commencement of nematic phase	66.0 ($\text{C}_7 - \text{C}_8$) C_7	70.5 ($\text{C}_2 - \text{C}_5$) C_2	72.6 ($\text{C}_2 - \text{C}_6$) C_2
Total mesophase lengths in °C	07.0 to 15.0 $\text{C}_{10/14/16}$ C_{12}	05.0 to 29.0 $\text{C}_{10/14}$ C_4	05.0 to 21.0 C_{18} C_4

Above Table 4 represents that, homologous series 1, X and Y are:

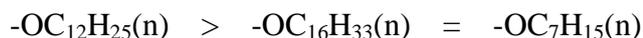
- Smectogenic plus nematogenic either in monotropic or enantiotropic condition.
- Smectic thermal stability for Series-1 and Y are very low of the order of 1 to 2 °C but for Series-X is 56.0.
- The nematic thermal stabilities for Series-1, X and Y are in increasing order ranging between 66.0 to 72.6.
- Smectogenicmesophase commences earliest for Series-X from C_3 homologue and latest for present Series-1 from C_{10} homologue and from C_7 homologue of Series-Y.
- Nematic mesophase commences latest from C_7 homologue for Series-1 and it commences earliest from C_2 homologue for Series-X and Y.
- Lower mesophaselength of Series-1 is longest and of equal magnitudes for Series-X and Y as well as upper mesophaselength increases from Series-1 to Y to X.

The increasing order of nematic thermal stability is attributed to the increasing order of intermolecular cohesions corresponding to increasing number of carbon atoms present from Series-1 (-OC₇H₁₅) to series-X (-OC₁₂H₂₅) to Series-Y (-OC₁₆H₃₃) due to increasing order of polarities and polarizability caused by their lateral groups for the same homologue respectively. But, the smectic thermal stability is variable due to the type of packing based on molecular geometrical status of the shape leading to molecular planarity. The molecules of Series-X is more coplanar as compared to Series-1 and Y. Therefore, based on molecular noncoplanarity the mesophase commences early or late. The facilitating of mesophase lengths varies with the changing molecular flexibility of changing dispersion forces and the dipole-dipole interactions related to lateral group for the same homologue from series to series. Thus, thermal resistivity, enthalpy value (ΔH) and the extent of molecular planarity and changing polarizability for the same homologue from series to series causes variations in mesogenic properties.

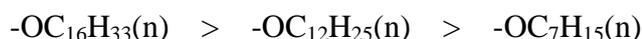
4. CONCLUSIONS

- A novel chalconyl homologous series is predominantly nematogenic and partly smectogenic with low transition temperatures ranging between 51 to 63 °C, 66.0 nematic thermal stability and shorter mesophase length (07 to 15 °C).
- Group efficiency order derived on the basis of (i) thermal stability (ii) early commencement of mesophase and (iii) mesophase length for smectic and nematic are as under.

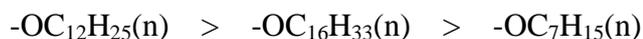
(i) Smectic



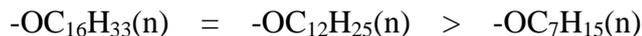
Nematic



(ii) Smectic



Nematic



(iii) Sm + N



- Reversal of sequential order of monotropy and enantiotropy in a chalconyl group containing series of two phenyl rings is observed as compared to other homologous series.
- Mesomorphism is very sensitive and susceptible to a molecular structure.
- Mesomorphism is depended on suitable magnitudes of molecular rigidity and flexibility.
- Present investigation may be useful for LC devices, Their pharmaceutical or biological activity may be exploited for pharmaceutical preparation and agricultural production to reduce the consumption of insecticides and pesticide as they are antibacterial and antifungal.
- Present study supports and raises credibility to the conclusions drawn earlier.

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