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A Study of Mesomorphism Properties and their Relation to the Molecular Structure of Novel chalcone Derivatives

Balvani V. N.^a and Chauhan M. L.

^{*}Chemistry Dept.; Sheth P. T. Arts & Science College, Godhra – 389 001, Gujarat University, Gujarat, India
^aPacific Academy Of Higher Education And Research University, Udaipur.

ABSTRACT:

A novel chalconyl homologous series of liquid crystalline derivatives $RO-C_6H_4-COO-C_6H_4-CO-CH=CH-C_6H_4-OC_4H_9$ (n) (para) have been synthesized and studied with view to correlate the liquid crystal (LC) behavioral properties and the molecular structure of a substance. Present novel series consisted of thirteen homologue members (C_1 to C_{18}) whose, only nematogenic mesomorphism commences from C_5 homologue and continued up to C_{18} homologue in enantiotropic manner with absence of smectogenic character. Transition temperatures and textures of nematic phase were determined using an optical polarizing microscopy equipped with a heating stage (POM). Transition curve Cr-N/I behaved in normal manner. Textures of the nematic phase are threaded or schlieren. Analytical and spectral data supported molecular structures of homologues. Thermal stability for nematic is $118.22\text{ }^\circ\text{C}$ and the degree of mesomorphism vary from $10.0\text{ }^\circ\text{C}$ to $36.0\text{ }^\circ\text{C}$ at the C_{18} and C_6 homologue respectively. It is a middle ordered melting type series, whose relative group efficiency order for nematic derived.

Keywords: Mesomorphism, Mesophase, Mesogen, Smectic, Nematic, Enantiotropy.

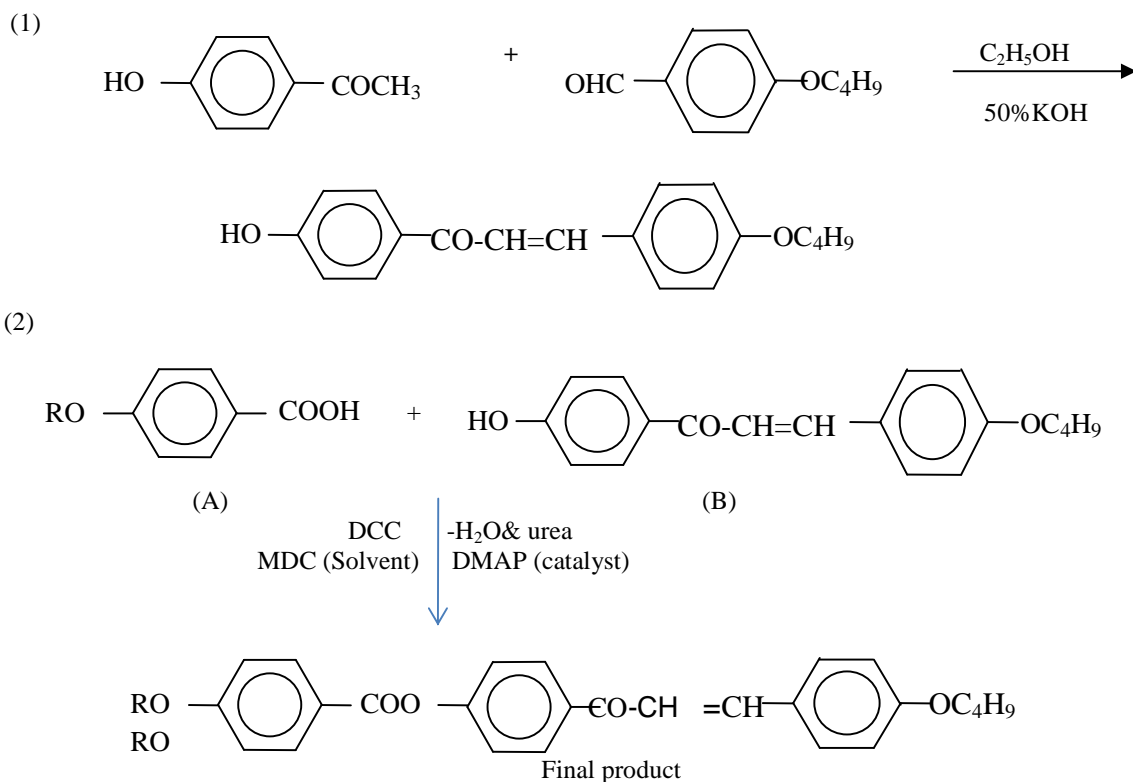
INTRODUCTION

Tropically thermo liquid crystalline (LC) [1] novel homologues of chalconyl derivatives are important from the point of view of their applicability [2-6] in the manufacture of LC devices to be operated at desired or room temperature and their bioactivities to be exploited as anticancer, antimalarial, antibacterial etc in the benefit of mankind. Therefore present investigation was planned to synthesize novel chalconyl ester derivatives which can be useful to all scientific and technological research investigators working on LC state with different aims, objects and views with different angle. The present aim of investigation is fixed with a view to understand and establish the effect of molecular structure [7-10] on properties of thermotropic LC substances, which includes even a minor change in molecular structure can bring about major change in LC behaviour as a consequence of changing molecular rigidity and/or flexibility [11-15]. Numbers of chalconyl ester or azo ester or simple t have been reported till the date [16-p20]. The synthesis of novel homologue series of proposed investigation after their due characterization will be compared with other structurally similar analogous series and then group efficiency order will be derived with respect to thermal stability, early commencement of mesophase and the degree of mesomorphism.

MATERIALS AND METHODS

Experimental : (Synthesis)

- 4-n-alkoxy benzoic acids (A) were prepared by the modified method of Dave and Vora (1970) [21] using suitable alkylating agent (R-X)
- n-alkoxy Benzoic acids were condensed with α -4 Hydroxy benzoyl β -4' t-utylloxy phenyl ethylene [22] (B) by usual established method
- Components (A) and (B) were condensed [23] to give final products. Synthetic route to the series is mentioned below as **scheme-1**. Final products were individually decompose, filtered, washed, dried and purified till the constant transition temperatures obtained.



Where, R= C_nH_{2n+1} , n = 1, 2, 3, 4, 5, 6, 8, 10, 12, 14, 16.

Scheme-1: Synthetic route to the series-1

The chemicals 4- hydroxyl Benzoic acid , alkyl halides, 4- Hydroxy acetophenone, 4- tetrayloxy benzaldehyde, potassium Hydroxide, hydrochloric acid etc. required for synthesis were used as received except solvents which were dried and distilled prior to use.

Characterization:

Some selected members of the titled novel series were characterized by elemental analysis, ¹HNMR spectra and IR spectra,. Microanalysis for C,H,N, elements was performed on Perkin Elmer PE 2400 analyzer (Table-1).¹HNMR spectra were obtained on Bruker spectrometer using CDCl₃ as solvent. IR spectra wererecorded on a Perkin- Elmer spectrum GX. Transition temperatures and liquid crystal properties were investigated using an optical polarizing microscope equipped with a heating stage. Textures of mesophases were characterized by miscibility method.

3. ANALYTICAL DATA

Table -1 Elemental analysis for methyloxy, ethyloxy and propyloxy derivatives

Sr. No.	Molecular Formula	Elements % Found		Elements % Calculated	
		C	H	C	H
1.	C ₂₇ H ₂₆ O ₅	75.01	5.95	75.34	6.04
2.	C ₂₈ H ₂₈ O ₅	75.30	6.10	75.67	6.30
3.	C ₂₉ H ₃₀ O ₅	76.09	6.41	75.98	6.55

H¹NMR: in ppm. For Hexyloxy homologue.

Ethylenes: (200 MHz) δ (CDCl₃) (ppm) 0.9 (-CH₃-CH₂ of -C₈H₁₇), 1.4 (long-CH₂- chain), 3.8 -OCH₂ of (-OCH₂ of -C₄H₉), 4.64 and 4.50 - CH=CH-, 7.09 & 6.92, (p-sub. benzene rings) 7.80 & 8.02 (two p-sub. benzene rings)

H¹NMR: in ppm. For Decyloxy homologue.

Ethylenes: (200 MHz) δ (CDCl₃) (ppm) 1.29 - CH₃, 3.95 - O CH₂, 4.11 - O CH₂ of -OCH₂-CH₂-CH₃, 4.50 and 4.62 - CH=CH-, 7.09, 6.92, 8.02, and 8.10 -p-sub .phenyl, (two p sub benzene), 7.34 and 8.12 - p-sub phenyl two p-sub benzene,

IR in Cm⁻¹, For Hexyloxy homologue

Ethylene's: (vmax/cm⁻¹): 2900, 2850, (-C-H, aliphatic), 1740, 1160 (ester group), 1720 (>C=O group), 1600 (-C=C-, aromatic), 1050.1, 1255 (ether group), 850.7 (p- sub. Benzene ring), 1600, 1590, 1450 (Aromatic ring).

For Decyloxy homologue

Ethylene's: (vmax/cm⁻¹): 2930, 2860, 1337.1, (-C-H, aliphatic), 1744, 1164.4 (ester group), 1720 (>C=O group), 1590.3 (-C=C-, aromatic), 1053.4, 1150 (ether group), 846.7 (p- sub. Benzene ring), 1610, 1486, 1450 (Aromatic ring)

Textures by miscibility method

C4 ----- threaded nematic

C8 ----- threaded nematic

C16----- schlieren nematic

Table - 2: Transition Temperatures in °C

Comp. No.	n-alkyl (C _n H _{2n+1}) group	Smectic	Nematic	Isotropic
1	C1	-	-	128
2	C2	-	-	120
3	C3	-	-	125
4	C4	-	-	116
5	C5	-	76	109
6	C6	-	83	119
7	C7	-	92	120
8	C8	-	98	123
9	C10	-	104	130
10	C12	-	100	125
11	C14	-	96	118
12	C16	-	98	112
13	C18	-	98	108

RESULTS AND DISCUSSION

α - 4 - Hydroxy benzoyl β - 4' - butyloxy Phenyl ethylene (m.p. 82.0 °C) is a nonmesomorphic component, which on condensation with n-alkoxy Benzoic acids yielded novel chalconyl derivatives. C₁ to C₄ homologues are nonmesomorphic (NLC), Whereas, rest of the derivatives are (C₅ to C₁₈) enantiotropically nematogenic without exhibition of smectogenic character. Transition temperatures were plotted against the number of carbon atoms present in n-alkyl chain of left n-alkoxy group. Transition curves Cr-I/N and N-I were obtained on linking, like or related points, which showed phase behaviors of series. Cr-I/N transition curve adopted zigzag path of rising and falling with overall descending tendency. Odd-even effect is observed for N-I transition curve. N-I transition curve

for even numbered methylene unit occupied higher position than odd numbers of series. N-I transition curves showing odd-even effect merges into each other at C₈ homologue and then prolonged as a single transition curve for higher homologues of longer n-alkyl chain R or -OR group from and beyond C₈ homologue. Thus, Cr-I/N transition curves behaved on normal manner. N-I transition curve is extrapolated in left for C₃ and C₄ homologues to determine and their latent transition temperature [L.T.T.]; but they are unrealizable due to their crystallizing tendency. Analytical and spectral data conformed the molecular structure of respective homologue. Thermal stability for nematic is 188.22°C and mesomorphic phase length range from 10.0 to 36.0 °C at the C₁₈ and C₆ homologue respectively. Thus, thermometric properties vary from homologue to homologue in present series with changing flexibility due to number of methylene unit or units of left n-alkoxy terminally situated end group keeping rest of molecular part unchanged through the same series. Thus, series of present investigation is partly matogenic and of low melting type and relatively short ranged liquid crystallinity as well as low thermal stability. The exhibition or in exhibition of mesomorphic property by a substance depends upon its suitable or unsuitable magnitudes of anisotropic forces of intermolecular end to end and/or lateral forces as a consequence of favorable or unfavorable molecular rigidity and flexibility. The molecular rigidity remains unaltered throughout the series from homologue to homologue in the same series; but, its molecular flexibility alters from homologue to homologue in the same series due to changing number of methylene unit or units present in n-alkyl chain 'R' bonded to first phenyl ring through oxygen atom. The combined effect of molecular rigidity and flexibility of suitable magnitude induces mesomorphism in a substance to disalign the molecules and resist exposed thermal vibrations on molecules under microscopic examination under floating condition on the surface. The in exhibition or failure of exhibition by C₁ to C₄ homologues is attributed their inability to resist exposed thermal vibrations due to unsuitable magnitudes of intermolecular end to end or/and lateral attractions which abruptly breaks crystal lattices and smoothly transform crystalline state to isotropic state without passing through LC state, due to low dispersion forces and low magnitudes of dipole-dipole and electronic interactions between instantaneous dipole produced by spontaneous oscillations of electron clouds of the molecules leading to high crystallizing tendency. Thus, molecules of non mesomorphs randomly oriented in all possible directions with high order of disorder or uncontrolled movement. Such molecules do not acquire monotropic LC state on cooling the isotropic mass. Thus, any sort of mesomorphism either smectic or nematic is absent for C₁ to C₄ homologues. The exhibition of enantiotropic nematic mesophase formation commencing from C₅ homologue to C₁₈ homologue is attributed to disalignment of molecules at an angle ninety or less than ninety degree which resisted exposed thermal vibrations by suitable magnitudes of end to end attractions, acquiring statistically parallel orientational order of molecular arrangement under floating condition during microscopic examination for definite range of temperature according to molecular permanent dipole moment, Aromaticity, molecular rigidity, flexibility, polarity and polarizability etc.

However, all the mesogenic or nematogenic (C₅ to C₁₈) homologues fails to exhibit smectogenic character due to absence of lamellar packing of molecules in their preoccupied crystal lattices, which eliminated the possibility of acquiring sliding layered molecular arrangement in floating condition to show smectogenic texture under microscopic (POM) observation, either monotonically or enantiotropically for even a single novel homologue. The odd-even effect is observed due to sequentially added methylene unit from C₅ or C₈ homologue. The disappearance of odd-even effect due to merging of N-I transition curves from and beyond C₈ or C₉ homologue for higher homologues (C₁₀ to C₁₈) of longer n-alkyl chain is attributed to the coiling, bending or flexing or coupling of n-alkyl chain of left and right end groups with the principal axis of core structure. Changing trends in mesomorphic properties like thermal stability, commencement of mesophase, mesophase length etc. depended upon molecular length which sequentially undergo varied, with changing permanent dipole moment across the long molecular axis, dispersion forces, thermodynamic quantity enthalpy (ΔH), extent of noncoplanarity which related to changing molecular structure which causes the change in the magnitudes of combined effect of molecular rigidity and flexibility. The molecular rigidity due to phenyl rings and central bridges linking them which remain unaltered through out the same series from homologue to homologue, but the molecular flexibility due to difference in polarity of two end groups of present series undergo varied.

Therefore, the magnitudes of their combined effect (rigidity + flexibility) which changes from homologue to homologue in the same series. Thus, thermometric resistivity and suitable magnitudes of intermolecular cohesion energy; consequently very mesomorphic tendency of a molecule causing variation. The variations in mesomorphic properties of a present novel series are compared with the structurally similar other known homologous series as shown below in **figure-2**.

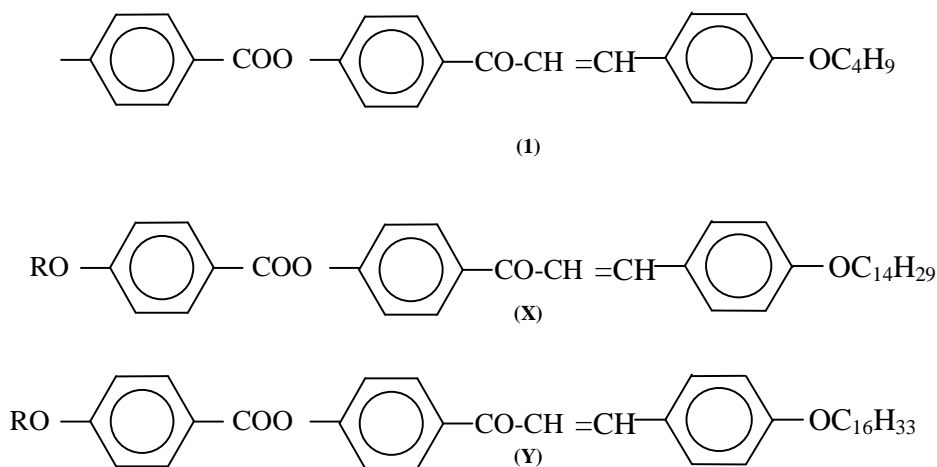


Figure:2 Structurally similar series

Homologous series 1, X and Y are identical with respect to three phenyl rings, central bridges linking phenyl ring, left n- alkoxy terminal end groups same homologue contributing total molecular rigidity and partly to molecular for flexibility. But, they differ with respect to right terminal tails groups at third phenyl ring with Pera substitution. Thus, combine effect of molecular rigidity plus flexibility vary for the same homologue from series to series and from homologue to homologue in the same series. Homologous series 1,X and Y are identical in all above respect except right handed tail end groups, $-OC_4H_9$, $-OC_{14}H_{29}$ and $-OC_{16}H_{33}$ for the same homologue from series -1, X and -Y. Thus, mesomorphic properties are differed due to differing features the series 1,X,Y. Following table-3 represents some thermometric behaviors of presently investigated novel chalconyl homologous series-1 and series-X [24] and Y [25] chosen for comparative study.

Table-3: Relative thermal stabilities in °C

Series	1	X	Y
smectic-isotropic or smectic-nematic Commencement of Smectic phase	-	-	-
Nematic-Isotropic Commencement of Nematic phase	118.22 C° (C ₅ - C ₁₈) C ₅	123.0 (C ₇ - C ₁₈) C ₇	113.0 - 14.0 (C ₆ - C ₁₈) C ₆
Total upper and lower mesophase length range in 0C Ci to Cj	10.0 to 36.0 C ₁₈ C ₆	13.0 to 34.0 C ₇ C ₈ C ₁₀ C ₁₂	10.0 to 26.0 C ₈ C ₁₀

From above table-3 it is clear that

- Homologous series 1, X and Y under comparative study are nematogenic with absence of smectogenic property.
- The mesogenic property commences from C₅, C₇, and C₆ homologue in series 1,X,Y respectively.
- Thermal stability depresses from series X to series 1 to series Y.
- Thermal resistivity is poor and upper mesophase length decreases from series 1 to X to Y.

The intermolecular suitable magnitudes of anisotropic end to end forces as a consequence of favourable molecular rigidity and flexibility induces nematogenic mesophase due to the appropriate permanent dipole moment, dipole-dipole interactions dispersion forces etc. fittest magnitudes facilitate and to induce nematogenic character only, but are insufficient to maintain focal conic networking molecular arrangement in rigid crystal and subsequent sliding layered molecular arrangement in floating condition under exposed thermal vibrations. Thus, smectogenic character fails to facilitate in all the series-1,X and Y under comparative study. The extent of molecular noncoplanarity for all

the series 1,X and Y are equally effective but it slightly differs for the difference of tails terminal. The observed difference for thermal stabilities is attributed to the unusual and unexpected molecular status of n-alkyl chain of both ended n-alkoxy terminals, degree of mesomorphism and transition temperatures of homologues. Thus, thermal stabilities and upper and lower mesophase lengths ranges of series 1,X and Y are not much differed in magnitudes.

Homologous Series :

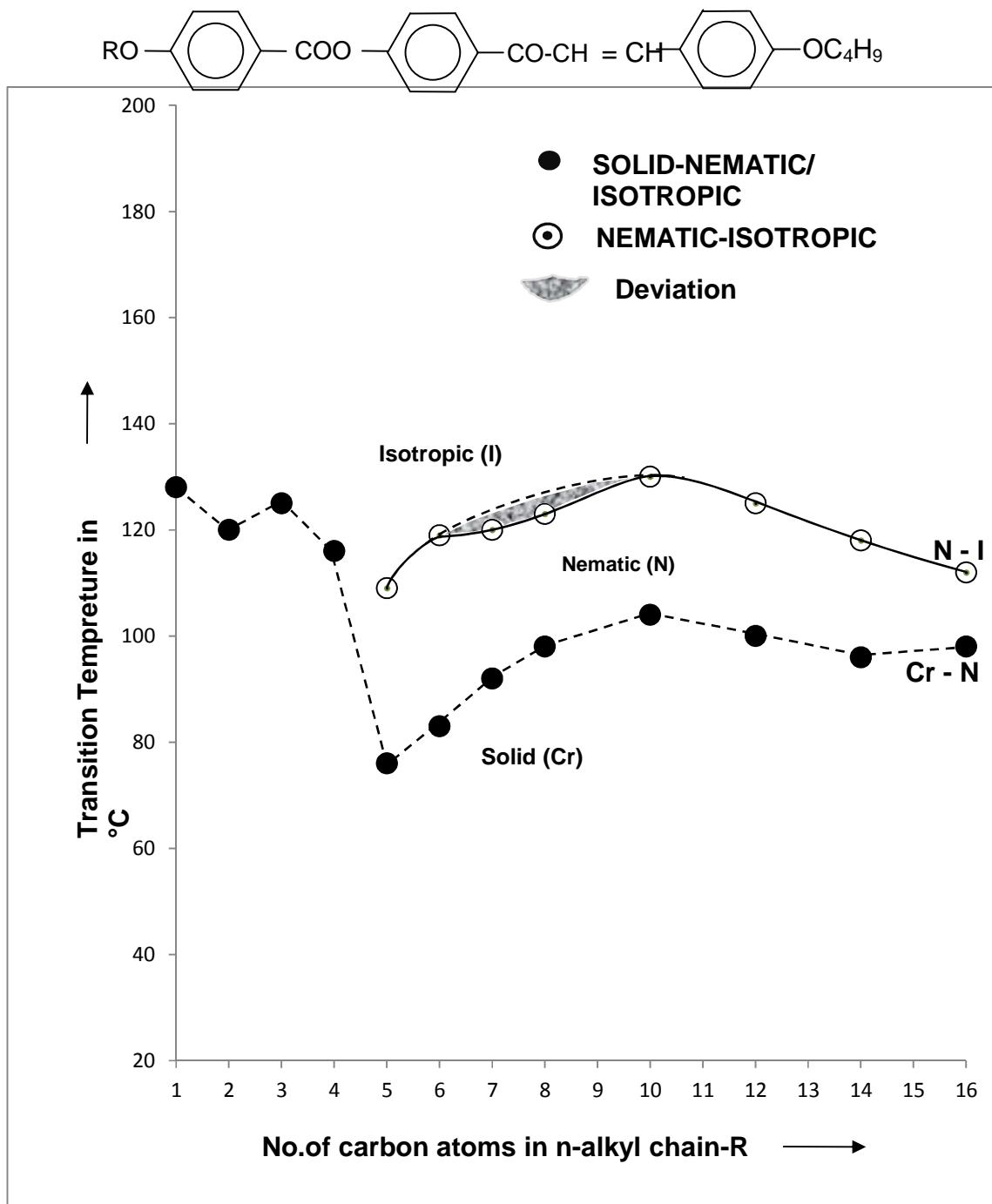


Figure :1 Phase Behavior of Series

CONCLUSION

Presently investigated chalconyl ester series is partly nematogenic whose degree of mesomorphism is shorter and of middle order melting type without exhibition of smectogenic property. The group efficiency order derived on the basis of (i) thermal stability (ii) early commencement of mesophase and (iii) higher degree mesomorphism are as under.

(i) **Smectic** Series-1 = Series-X = Series-Y

Nematic Series-X > Series-1 > Series-Y.

(ii) **Nematic** Series-1 = Series-Y > Series-X

(iii) **Nematic upper mesophase length** Series-1 > Series-X > Series-Y

- Upper mesophase lengths decreases as tail ended n- alkyl chain is lengthened.
- Difference of group polarities at the two terminal end groups decides the mesogenic behaviour of individual homologue in the same homologous series.
- Molecular rigidity and flexibility operates a phenomena of mesomorphism.
- Mesomorphism is very sensitive and susceptible to molecular structure.
- Mesogenic homologues of present study are useful for the study of binary systems for the manufacture of LC devices to be operated between 55°C and 130°C
- Chalconyl derivatives are bioactive molecules, which can be further studied for their bioactivity for the pharmaceutical and medicinal formulation.
- Present study supports and raises the credibility to the conclusions drawn earlier.

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