

Study of the Effect of Chalconyl Central Bridge on Mesomorphism

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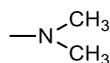
ABSTRACT. A novel homologous series of chalconyl ester derivatives of thermotropic type of liquid crystals (LC) variety have been synthesized with its general molecular formula $RO-C_6H_4-CH=CH-COO-C_6H_4-CO-CH=CH-C_6H_4-N(CH_3)_2$ (Para). Present investigation is planned with a view to understand and establish the relation between molecular structure and the mesomorphic behavior of the constituent homologue derivatives as well as to avail novel mesomorphic (LC) substances to the researcher working on multidisciplinary thermotropic LC material with different aims, objects and views at different angles. Novel homologous series consists of twelve homologues C_1 to C_5 homologues are nonliquid crystals (NLC) and the rest of the C_6 to C_{16} are monotropically nematogenic liquid crystals. Transition temperatures and texture of the LC and NLC were determined by an optical polarizing microscopy equipped with heating stage (POM). Textures of nematic phase are threaded or schlieren. Analytical and spectral data confirms the molecular structures of homologues. Thermal stability for monotropy is very low of the magnitudes of few second and of negligible degree of temperature difference. Thermal properties of present novel series are compared with of structurally similar series, data interpreted in terms of molecular rigidity and flexibility to derive group efficiency order.

1. INTRODUCTION

Chalconyl derivatives of aromatic n-alkoxy acids are more important in lyotropic condition due to their Bioactivity [1,2,3,4,5]. However, attempt is made to test their thermotropic liquid crystalline (LC) [6] nature through an optical polarizing microscopy equipped with a heating stage (POM). Thus, present study is aimed to understand and establish the effect of molecular structure [7,8,9,10,11] on liquid crystal property with special reference to chalconyl central bridges; by synthesis of a homologous series involving chalconyl group as one of the central bridges. Moreover, the targeted aim is extended to provide novel LC material to scientists and technologists working on the multidisciplinary unique LC state. Present investigation is planned to synthesized a novel homologous series which will consist of three phenyl rings bonded through $-CH=CH-COO-$ and $-CO-CH=CH-$ central bridges and two tail groups $-OR$ (left) and (right) contributing to molecular flexibility. Thermometric behaviors of novel homologues will be studied and will be characterized through analytical and spectral data. Evaluated thermometric data will be interpreted and discussed in terms of molecular rigidity and flexibility [12,13,14,15]. Then it's some LC properties will be compared with structurally similar series to derive group efficiency order etc. number of ester or chalconyl ester derivatives have been reported till the date [16,17,18,19,20,21].

2. EXPERIMENTAL

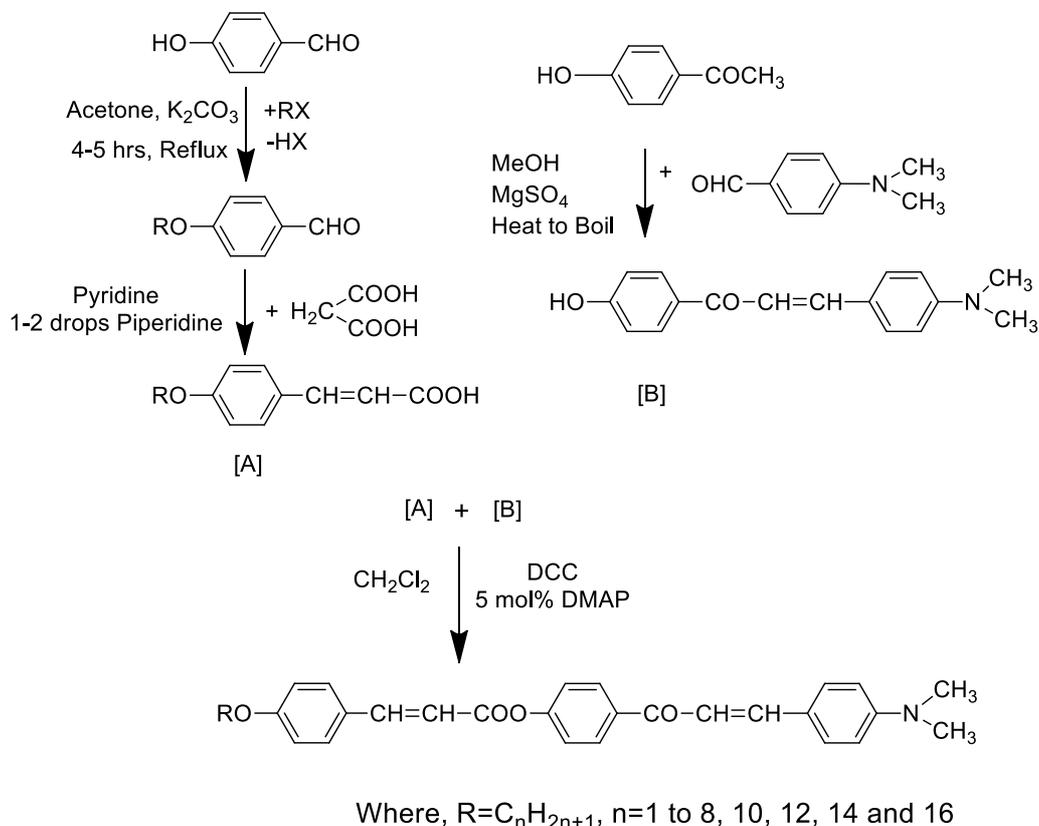
Synthesis:



4-n-Alkoxybenzaldehydes were synthesized by refluxing 4-hydroxybenzaldehyde (1 equiv.) with corresponding n-alkyl bromides (1 equiv.) in the presence of potassium carbonate (1 equiv.) and acetone as a solvent [22]. The resulting 4-n-alkoxybenzaldehydes were reacted with malonic acid (1.2 equiv.) in the presence of 1-2 drops piperidine as catalyst and pyridine as solvent to yield corresponding trans 4-n-alkoxy cinnamic acids (A) [23]. α -4-hydroxy benzoyl β -4'-N,N dimethyl

phenyl ethylene (B) was prepared by an established method [24] M.P.152-154 °C Yield- 63.9%. Coupling of compound A and compound B is done by steglich esterification to yield α -[4(4'-n-alkoxy cinnamoyloxy) benzoyl]- β -(4''-N, N dimethyl) ethylene [25].

The synthetic route to the novel homologous series of ethylene derivatives is under mentioned in scheme-1.



Scheme-1: Synthetic route to the novel series

Characterization:

Some of members of a novel series as the representative member of a series were characterized by elemental analysis (Table-1), Infrared spectroscopy, 1H NMR spectra and mass spectroscopy. Microanalysis was performed on EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR Model -IRAffinity-1S (MIRacle 10), 1H NMR spectra were recorded on Bruker spectrometer using $CDCl_3$ as a solvent and mass spectra were recorded on Shimadzu GC-MS Model No.QP-2010. The liquid crystal behavior and the type of textures were determined by miscibility method on microscopic observations.

Analytical data:

Table-1: Elemental analysis for (1) Ethyloxy (2) Butyloxy (3) Decyloxy derivatives

Sr.No.	Molecular formula	Elements %Found			Elements %Calculated		
		C	H	O	C	H	O
1	$C_{28}H_{27}NO_4$	76.22	6.13	14.46	76.17	6.16	14.49
2	$C_{30}H_{31}NO_4$	76.79	6.67	13.67	76.73	6.65	13.63
3	$C_{36}H_{43}NO_4$	78.15	7.86	11.59	78.09	7.83	11.56

Spectral Data:**¹H NMR in ppm for Methoxyloxy Derivative**

3.78 (s,3H,-CH₃ of -OCH₃ group), 2.96 (s,6H, -CH₃ of -N(CH₃)₂ group), 7.46-7.48 (d,1H, -CH=CH-COO-), 6.40-6.44 (d,1H, -CH=CH-COO-), 7.18-7.24 (d,1H, -CO-CH=CH-), 7.46-7.48 (d,1H, -CO-CH=CH-), 6.85-6.87 & 7.71-7.79 (4H, phenyl ring containing methoxy group), 7.46-7.48 & 7.98-8.00 (4H, middle phenyl ring), 6.60-6.62 & 7.72-7.78 (4H, phenyl ring containing -N(CH₃)₂ group). The NMR data are reliable with the molecular structure.

¹H NMR in ppm for Pentyloxy Derivative

0.85-0.88 (t,3H,-CH₃ of -OC₅H₁₁ group), 1.36-1.39 (m,2H,CH₃-CH₂-(CH₂)₃-O-) 1.39-1.42 (p,2H,-CH₂-CH₂-CH₂-O-), 1.83-1.86 (p,2H,-CH₂-CH₂-O-), 4.00-4.03 (t,2H,-CH₂-O-), 7.28-7.33 (d,1H, -CH=CH-COO-), 6.50-6.53 (d,1H, -CH=CH-COO-), 6.94-6.96 (d,1H, -CO-CH=CH-), 7.54-7.58 (d,1H, -CO-CH=CH-), 6.85-6.87 & 7.81-7.85 (4H, phenyl ring containing methoxy group), 7.46-7.48 & 8.08-8.10 (4H, middle phenyl ring), 6.70-6.22 & 7.72-7.78 (4H, phenyl ring containing -N(CH₃)₂ group). The NMR data are reliable with the molecular structure.

IR in cm⁻¹ for Propyloxy Derivative

3020 (C-H str. of alkene disubstituted), 2924 & 2866 (C-H str. of (-CH₂)_n group of -OC₃H₇), 1726 (C=O str. of carbonyl carbon of ester group), 1629 (C=C str. of alkene), 1598 & 1508 (C=C str. of aromatic ring), 1309 & 1265 (C-H bending of alkene), 1203 (C-O str. of ether linkage), 1132 (C-O str. of ester group), 999,970 & 931 (C-H bending of alkene). The IR data are consistent with the molecular structure.

IR in cm⁻¹ for Heptyloxy Derivative

3037 (C-H str. of alkene disubstituted), 2920 & 2850 (C-H str. of (-CH₂)_n group of -OC₇H₁₅), 1720 (C=O str. of carbonyl carbon of ester group), 1629 (C=C str. of alkene), 1600,1571 & 1506 (C=C str. of aromatic ring), 1394 & 1319 (C-H bending of alkene), 1246 (C-O str. of ether linkage), 1118 (C-O str. of ester group), 991, 968 & 923 (C-H bending of alkene). The IR data are consistent with the molecular structure.

Mass spectra of Hexyloxy Derivative

m/z (rel.int%): 497 (M)⁺, 267, 238, 231, 175, 147, 119, 91

Mass spectra of Octyloxy Derivative

m/z (rel.int%): 525(M)⁺, 441, 267, 259, 238, 231, 175, 147, 119, 91

3. RESULTS AND DISCUSSION

Trans n-alkoxy cinnamic acids on linking with α-4-hydroxy benzoyl β-4'-N,N-dimethyl phenyl ethylene yielded chalconyl ester derivatives of thermotropic monotropic liquid crystals (LC) of novel substances. Homologous series consisted of twelve homologues (C₁ to C₁₆). LC Property commences from C₆ homologue as monotropic nematic i.e. C₆ to C₁₆ homologues are monotropic nematic and the rest of the homologues (C₁ to C₅) are nonliquid crystalline (NLC) in character. Transition temperatures and the textures of nematic phase were determined by an optical polarizing microscopy equipped with a heating stage (POM). Analytical and the spectral data supported structures of molecules. Transition temperature (Table-2) of novel homologues were plotted versus the number of carbon atoms present in n-alkyl chain bonded to first phenyl ring through oxygen atom (-OR) and a phase diagram (Figure-1) showing phase behaviors of series is obtained by linking like or related transition point. A Cr-I transition curve follows a zigzag path of rising and falling with overall falling tendency and behaved in normal manner. An I-N transition curve descended from C₆ homologue and continues to descend up to C₁₆ homologue and behaved in normal expected manner. I-N transition curve for even members occupied higher position than the odd member's transition curve. Both curve for odd and even homologues (I-N) are merging into each other at the C₁₀ homologue and then further prolonged as a single I-N transition curve from and beyond C₁₀ homologue. I-N transition curve for odd and even members is extrapolated [26, 27, 28, 29] to C₅ and C₄ homologues respectively, keeping in view of the trend of a respective transition curve to determine and predict their probable latent transition temperatures (LTT) for nematic 141°C and 149°C respectively. Transition temperatures, structure and thermometric properties vary

from homologue to homologue in the present same series. Thermal stability of nematic is very low with negligible range of mesomorphism and upper middle ordered meeting type series.

Table-2 Transition temperatures in °C

Compound No.	n-alkyl chain C_nH_{2n+1} (n)	Sm	N	Isotropic
1	1	-	-	222.0
2	2	-	-	194.0
3	3	-	-	180.0
4	4	-	-	191.0
5	5	-	-	186.0
6	6	-	(149.0)	165.0
7	7	-	(140.0)	157.0
8	8	-	(147.0)	162.0
9	10	-	(135.0)	152.0
10	12	-	(121.0)	136.0
11	14	-	(118.0)	133.0
12	16	-	(115.0)	127.0

Sm=Smectic, N=Nematic, () indicate monotropy

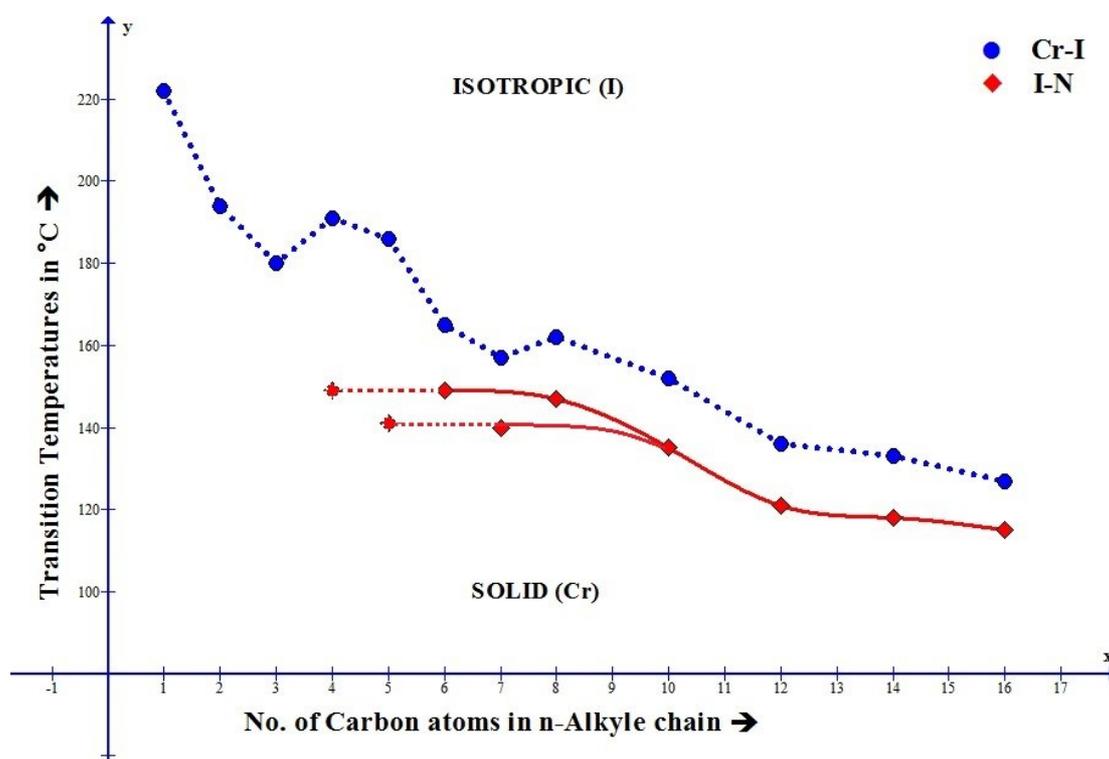


Figure-1: Phase Behavior of Series

The dimerization of trans cinnamic acid disappear on esterification process by breaking of hydrogen bonding between two molecules. The nonmesogenic (NLC) behaviors of C_1 to C_5 homologues are attributed to abrupt breaking of crystal lattices under the influence of exposed thermal vibrations due to low intermolecular dispersion forces and low dipole-dipole interactions which induces inability to resist or bear thermal environmental situation leading to high crystallizing tendency. Thus molecules of C_1 to C_5 and C_6 to C_{16} homologues are sharply melted directly to isotropic state without passing through an intermediate state of matter between crystalline solid and isotropic liquid, called as LC state or mesogenic state or anisotropic state or mesogenic stete etc. The molecules of all the homologues C_1 to C_{16} are randomly oriented in all

possible direction with high order of disorder or high entropy ($\Delta S = \Delta H/T$). However, the molecules of C_6 to C_{16} on cooling the same isotropic mass carefully, from and below isotropic temperature of respective mesogenic homologues acquire statistically parallel orientational molecular order in irreversible manner, showing a monotropic nematic mesophase formation for few seconds or a fraction of a second or for negligible difference of temperature range. But C_1 to C_5 failed to show monotropic mesophase formation in an irreversible manner like C_6 to C_{16} homologues. Thus, suitable magnitudes of anisotropic forces of end to end attractions as a consequence of favorable molecular rigidity and flexibility effectively induce disalignment of molecules at an angle perpendicular or less than ninety degree to the plane of surface which resisted exposed thermal vibrations to exhibit a molecular arrangement in floating condition, causing showing up of nematic phase. Absence of lamellar packing of molecules hinders formation of layered structure of molecules which eliminates the possibility of sliding layered molecular floating on the surface and hence absence of smectic property is observed. The odd-even effect is observed due to sequential addition of n-alkyl chain on left n-alkoxy terminal end group. Odd-even effect diminishes as series is ascended and it ceases at the C_{10} homologue. Then both I-N transition curves merges into each other and prolonged as a single curve because longer n-alkyl chain (C_{10} to C_{16}) may coil, bend or flex or couple to lie with the core structure of the molecule inducing uncertainty in the status of n-alkyl chain. The extrapolation of I-N transition curve predicted 149°C and 141°C transition temperatures for C_4 and C_5 homologues respectively, but actually they are not realizable due to high crystallizing tendency of respective homologues instead of showing monotropic nematic phase. However, extrapolation of I-N transition curves intensified and highlighted odd-even effect very clearly. The changing trend in mesogenic behaviors or properties from homologue to homologue in the same series is attributed to the added $-\text{CH}_2-$ unit or units to the n-alkyl chain of left n-alkoxy ($-\text{OR}$) terminal which alters the molecular length, size, permanent dipole moment across the molecules, intermolecular dispersion forces depending upon magnitudes of end to end cohesion and closeness, molecular polarity and polarizability etc., which contributes to the molecular rigidity and flexibility related to the molecular structure and its geometrical shape and size. Some LC properties of present novel series are compared with structurally similar homologous series as mentioned below in figure-2.

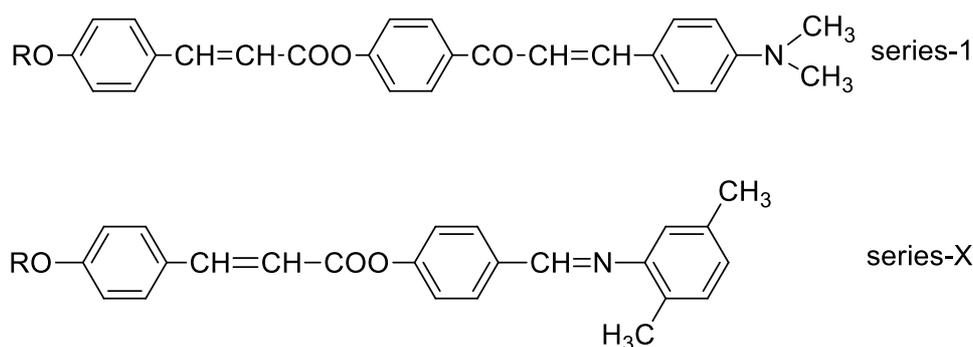


Figure-2: Structurally similar series.

Homologous series-1 of present investigation and a homologous series-X [30] selected for comparative study are identical with respect to three phenyl rings and a central bridge $-\text{CH}=\text{CH}-\text{COO}-$ linking first and middle phenyl ring which partly contributes to the total molecular rigidity and the left n-alkoxy terminal end group $-\text{OR}$ is identically similar for the same homologue from series to series which partly contributes to total molecular flexibility. However, they differ with respect to central bridges $-\text{CO}-\text{CH}=\text{CH}-$ and $-\text{CH}=\text{N}-$ linking middle and third phenyl rings, including tail end group $-\text{N}(\text{CH}_3)_2$ and 2, 5- di methyl group in which two methyl groups are bonded directly to Nitrogen atom in present novel series-1 and two methyl groups bonded to nitrogen atom through third phenyl ring in case of series-X. Such differing features of molecular and party to the molecular structure which contributes partly to molecular rigidity and partly to the molecular flexibility, for the same homologue from series to series. Differing features of molecular structures of series-1 and X causes variations in mesomorphic properties and mesomorphic

behaviors including degree of mesomorphism as a consequence of effective magnitudes of combined effect of molecular rigidity and flexibility for the same homologue from series to series and from homologue to homologue in the same series. Following table-3 represents some thermometric properties for the series-1 and X chosen for comparative study.

Table-3 Relative thermal stabilities in °C

Series →	1	X
Smectic-Isotropic or Smectic-Nematic	-	100.16 (C ₈ -C ₁₈)
Commencement of smectic mesophase	-	C ₆
Nematic-Isotropic	-	110.83 (C ₅ -C ₁₀)
Commencement of nematic phase	C ₆	C ₂
Total mesophase length range (Sm+N)	Very short range	41.0 (C ₁₂) to 4.0 (C ₁₈)

Table-3 indicates that,

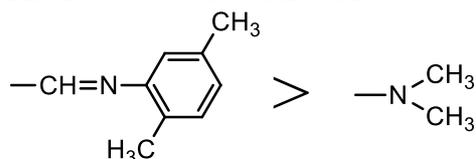
- Though the series-1 and X derived from trans cinnamic acid but series-1 of present investigation is monotropically nematogenic whereas series-X is monotropically and enantiotropically nematogenic and smectogenic.
- Nematogenic mesophase formation commences from C₆ homologue in series-1, whereas it commences from C₂ homologues in series-X.
- Smectogenic property is totally absent in case of series-1 whereas it appears from C₆ to C₁₈ in case of series-X under comparison.
- Total mesophase length is negligibly shorter for series-1 and it varies from 4.0°C to 41.0°C for series-X.

Homologous series-1 and X are synthesized from trans n-alkoxy cinnamic acid as major component but their thermotropic LC behaviors differs quite from each other due to the difference of their one of the central bridges linking middle phenyl ring and a third (tail) phenyl ring including attachment of two -CH₃ groups directly to nitrogen atom (series-1) and indirectly to nitrogen atom (series-X). The 4-n-alkoxy cinnamic acids and their esters are richer in exhibition of mesomorphism. However, the magnitudes of degree of mesomorphism in presently investigated homologous series reduce to a very great extent. The linking of third phenyl ring through central bridges like -CO-CH=CH- or -N=CH- causes suitable magnitudes of intermolecular end to end and for lateral attractions depending upon terminal tail groups like dimethyl groups bonded directly to nitrogen or indirectly bonded to nitrogen. The magnitudes of molecular rigidity and/or flexibility caused by the presence of conjugated double bond between middle and third phenyl ring which hinders the suitable magnitudes of intermolecular cohesions and closeness to facilitate molecular arrangement required for the formation of either partly or fully smectic and/or nematic phase under floating condition of thermometric environment. The early commencement of mesophase of series-X or comparatively late commencement of mesophase of series-1 is attributed to the difference of magnitudes of the extent of molecular noncoplanarity related to suitable resistivity of a molecule against the exposed thermal vibrations. The absence or presence of smectogenic property is attributed to absence or presence of lamellar packing of molecules in crystal lattices of series-1 or X. Thus, present novel series is less thermotropically mesogenic than series-X and a parental molecule of trans-4-n-alkoxy cinnamic acid, but bioactivity of novel homologues may raise their bioactivity in lyotropic condition for the benefit of mankind.

4. CONCLUSIONS

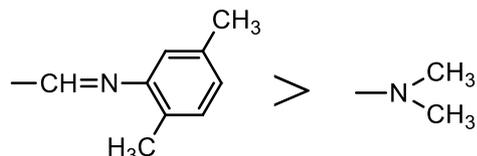
- Suitable magnitudes of anisotropic forces of intermolecular attractions required to induce mesomorphism is reduced if two central bridges, linking three phenyl rings bear conjugated double bonds, especially in the case of chalconyl group $-\text{CO}-\text{CH}=\text{CH}-$ or $-\text{CH}=\text{CH}-\text{CO}-$.
- Suitable magnitudes (not more or less) of molecular rigidity and flexibility can induce mesomorphism.
- Phenomena of mesomorphism are very sensitive and susceptible to molecular structure.
- Group efficiency order derived on the basis of (a) thermal stability (b) early commencement of mesophase and (c) mesophase length range for smectic and nematic are as under :

a) Smectic: $-\text{CH}=\text{N}-$ > $-\text{CO}-\text{CH}=\text{CH}-$

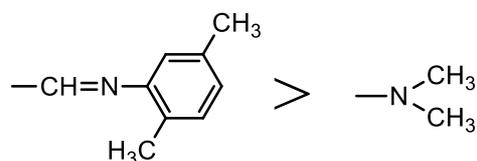


Nematic : $-\text{CH}=\text{N}-$ > $-\text{CO}-\text{CH}=\text{CH}-$

b) Smectic: $-\text{CH}=\text{N}-$ > $-\text{CO}-\text{CH}=\text{CH}-$



Nematic :



c) Mesophase length: $-\text{CH}=\text{N}-$ > $-\text{CO}-\text{CH}=\text{CH}-$

- Present novel chalconyl derivatives may be useful for the study of binary systems and can be more useful for the study of their biological activity in lyotropic condition.
- Present study supports and raises the credibility to the conclusions drawn earlier.

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