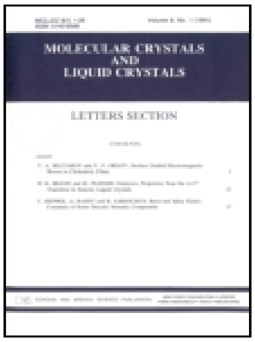

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Mesomorphism dependence on central bridges and the efficiency order of the tail group

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ABSTRACT

A novel homologous series: RO-C_6H_4–CH=CH–COO–C_6H_4–CH=N-C_6H_3 $(CH_3)_2$ of ortho-meta Schiff's bases has been synthesized and studied with a view to understanding and establishing the effects of molecular structure on mesomorphic properties and to provide a source of novel liquid crystalline (LC) materials. The series consists of 13 homologues (C_1 to C_8, C_{10}, C_{12}, C_{14}, C_{16} & C_{18}). C_1 and C_3 homologues are nonmesomorphic, C_2 and C_4monotropicnematic, C_6 and C_7monotropicsmectic in addition to enantiotropicnematic, C_5 is only enantiotropicnematic, C_8, C_{10}, C_{12} are enantiotropically smectogenic plus nematogenic and C_{14}, C_{16}, C_{18} homologues are enantiotropically smectic only. Textures and transition temperatures were determined using an optical polarizing microscope equipped with a heating stage. Analytical and spectral data confirm the molecular structures. Average smectic and nematic thermal stabilities are 100.16°C and 110.83°C, respectively. Mesomorphic properties of present novel series are compared with structurally similar homologous series.

KEYWORDS
Schiff's base; Mesomorphic; Mesogen; Liquid Crystal; Smectic; Nematic

Introduction

Liquid crystal (LC) materials [1] are useful for many researchers in various fields of applications [2–6] either thermotropically or/and lyotropically. The present investigation is planned with a view to generating novel homologous thermotropic liquid crystal materials of Schiff's bases with laterally substituted 2,5-dimethyl tail group in the absence of para substitution, in order to study and evaluate mesomorphic behavior as a function of changing molecular structure [7–10] as a consequence of changing molecular rigidity and flexibility [11–15]. The mesogenic behavior of the novel thermotropic LCs are compared with other structurally similar homologous series and the group efficiency order is derived on the bases of thermal stability, early commencement of mesophase and mesophase ranges. Several homologous series and other LC materials [16–20] have been reported to date, but the proposed novel series will consist of three phenyl rings and two central bridges, –CH=CH–COO– and –CH=N- with flexible *n*-alkoxy (-OR) and laterally substituted 2,5-dimethyl group at the first and last phenyl rings respectively. Mesogenic properties or behaviors of present novel series will be interpreted on the bases of molecular rigidity and flexibility.

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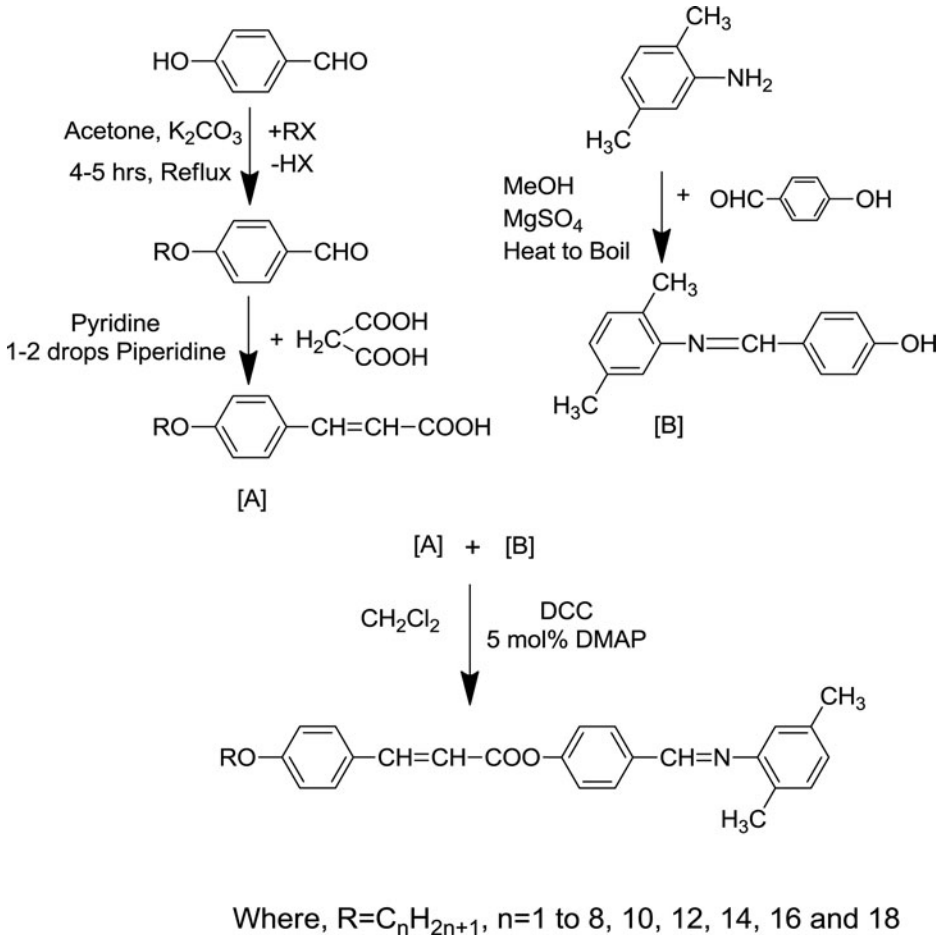

Scheme 1. Synthetic route to the novel series.

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 [21]. 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) [22]. [{(2,5-dimethyl phenyl) imino} methyl] phenol (B) was prepared by an established method [23] M.P.177–179°C, Yield—76.5%. Coupling of compound A and B is done by Steglich esterification to yield 4-(4′-*n*-Alkoxycinnamoyloxy) benzal 2″,5″-dimethyl aniline [24].

The synthetic route to the novel homologous series of Schiff's base cinnamoyl ester derivatives is under mentioned in scheme-1.

Characterization

Some of members of a novel series as the representative member of a series were characterized by elemental analysis (Table 1), Infrared spectroscopy, ^{1}HNMR spectra and mass

Table 1. Elemental analysis for (1)Propyloxy(2)Octyloxy(3)Dodecyloxy derivatives.

		Elements %Found			Elements %Calculated		
Sr.No.	Molecular formula	C	H	O	C	H	O
1	$C_{27}H_{27}NO_3$	78.49	6.55	11.57	78.42	6.58	11.61
2	$C_{30}H_{33}NO_3$	79.15	7.27	10.51	79.09	7.30	10.54
3	$C_{36}H_{45}NO_3$	80.18	8.36	8.85	80.11	8.40	8.89

spectroscopy. Microanalysis was performed on EuroEA Elemental Analyzer. IR spectra were recorded on Shimadzu FTIR Model-IRAffinity-1S (MIRacle 10), ^{1}HNMR 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

Spectral data

^{1}HNMR in ppm for ethyloxy derivative

1.17–1.21 (d,3H,$-CH_3$ of $-OC_2H_5$ group), 3.99–4.04 (m,2H,$CH_3\text{-}\underline{CH_2}\text{-}O$), 7.46–7.48 (d,1H, $-C\underline{H}=CH-COO-$), 6.41–6.45 (d,1H, $-CH=C\underline{H}-COO-$), 8.27 (s,1H, $-C\underline{H}=N-$), 2.23–2.27 (s, 6H, two $-CH_3$ groups attached to benzene), 6.84–6.88 & 7.87–7.90 (4H, phenyl ring containing ethoxy chain), 7.46–7.48 & 7.76–7.80 (4H, middle phenyl ring), 7.02–7.80 (3H, phenyl ring containing two methyl ring). The NMR data are reliable with the molecular structure.

^{1}HNMR in ppm for pentyloxy derivative

0.85–0.88 (t,3H,$-CH_3$ of $-OC_5H_{11}$ group), 1.29–1.32 (m,2H,$CH_3\text{-}\underline{CH_2}-(CH_2)_3-O-$) 1.37–1.39 (p,2H,$-\underline{CH_2}-CH_2-CH_2-O-$), 1.70–1.75 (p,2H,$-\underline{CH_2}-CH_2-O-$), 3.91–3.94 (t,2H,$-CH_2-O-$), 7.45–7.47 (d,1H, $-C\underline{H}=CH-COO-$), 6.40–6.44 (d,1H, $-CH=C\underline{H}-COO-$), 8.27 (s,1H, $-C\underline{H}=N-$), 2.23–2.27 (s, 6H, two $-CH_3$ groups attached to benzene), 7.02–7.04 & 7.75–7.78 (4H, phenyl ring containing ethoxy chain), 7.45–7.47 & 7.75–7.79 (4H, middle phenyl ring), 6.88–7.89 (3H, phenyl ring containing two methyl ring). The NMR data are reliable with the molecular structure.

IR in cm^{-1} for butyloxy derivative

3020 (C–H str. of alkene disubstituted), 2924 & 2866 (C–H str. of $(-CH_2\text{-})_n$ group of $-OC_4H_9$), 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 octyloxy derivative

3037 (C–H str. of alkene disubstituted), 2920 & 2850 (C–H str. of $(-CH_2\text{-})_n$ group of $-OC_8H_{17}$), 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.

Table 2. Transition temperatures in °C.

Compound No.	n-alkyl chain C_nH_{2n+1} (n)	Sm	N	Isotropic
1	1	—	—	139.0
2	2	—	(125.0)	136.0
3	3	—	—	125.0
4	4	—	(112.0)	118.0
5	5	—	108.0	114.0
6	6	(71.0)	97.0	113.0
7	7	(74.0)	86.0	110.0
8	8	81.0	88.0	109.0
9	10	73.0	99.0	112.0
10	12	66.0	103.0	107.0
11	14	80.0	–	104.0
12	16	84.0	—	108.0
13	18	95.0	—	99.0

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

Mass spectra of methyloxy derivative

m/z (rel.int%): 385 $(M)^+$,224,180,161,133,103,77

Mass spectra of heptyloxy derivative

m/z (rel.int%): 469$(M)^+$,343,260,245,224,181,147,119,91,65

Result and discussion

Novel Schiff's base cinnamoyl ester derived from trans *n*-alkoxycinnamic acid and [{(2,5-dimethyl phenyl) imino} methyl] phenol is either monotropically or enantiotropically nematogenic or/and smectogenic in character, except C_1 and C_3 homologue which fails to exhibit mesomorphism. Transition temperatures as determined by polarizing microscopy (Table 2) are plotted against the number of carbon atoms present in *n*-alkyl chain of left n-alkoxy end group (Fig. 1), a phase diagram is obtained which consisted of Cr-I/M, Sm-N/I, N-I or vice versa transition curves, showing phase behaviors of series by linking like or related points. N-I and Sm-N/I transition curves exhibited odd-even effect. The Sm-N/I transition curve for odd members occupy lower positions as compared to even members of a series clearly whereas reverse is the case for N-I transition curve. N-I transition curve is extrapolated [25–28] to nonmesomorphic C_3 homologue from C_5 homologue to determine and predict its monotropicnematic transition temperature (122°C) which is actually not realizable. Transition curves for odd-even effect observed for smectic and nematic merges into each other at C_{11} and C_6 homologue respectively. Then, both curves propagated as a single curve for higher homologue of longer *n*-alkyl chain from and beyond merging into each other. Cr-M/I or vice versa transition curves follows a zigzag path of rising and falling with overall descending tendency. Sm-N/I transition curve initially raises, passes through maxima at the C_{16} homologue and then descended in usual established manner. Similarly N-I transition curve overall descended as series is ascended. Thus, all the transition curves of a phase diagram behaved in normal manner. The mesogenic properties undergo variations from homologue to homologue in the same novel series depending upon member of carbon atoms present in *n*-alkyl chain (-OR) of left terminal end group.

Increasing length of a molecule by $HO\text{-}C_6H_4{-}CH{=}N\text{-}C_6H_3(CH_3)_2$, increases molecular length to breath ratio, rigidity, flexibility, permanent dipole moment across the long molecular axis, molecular polarity and polarizability, intermolecular dispersion and cohesion forces including closeness etc., which causes favorable and suitable magnitudes of anisotropic

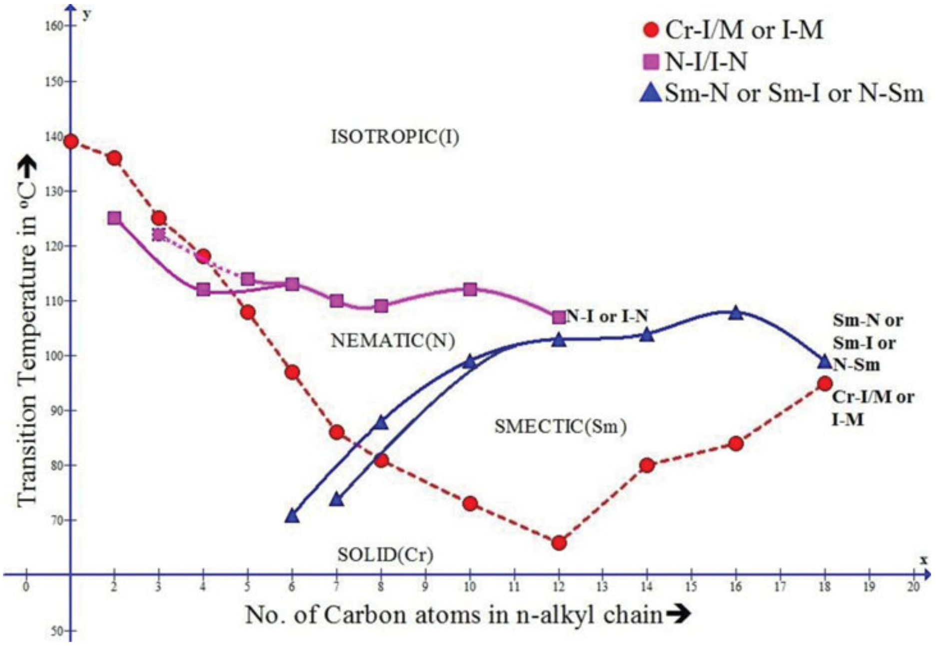

Figure 1. Phase Behavior of Series.

forces of cohesion and closeness, which includes smectic or/and nematicmesophase either monotropic or enantiotropic condition to stabilize suitable mesophase or mesophases within definite ranges of temperature for homologues other than C_1 and C_3. The molecules of C_1 and C_2 are, because of their low magnitudes of dispersion forces and low value of dipole-dipole interactions are unable to resist exposed thermal vibrations. Hence, their (C_1 and C_3) crystal lattices are abruptly breaking and transform into isotropic liquid without passing through liquid crystalline state sharply at their malting point due to their high crystallizing tendency. Rest of the homologues other than C_1 and C_3 are floating on the surface under exposed thermal vibrations maintain molecular arrangement as required by formation of smectic or/and nematic phase. The exhibition of odd-even effect is attributed to the number of odd and even number of methylene unit or units present in *n*-alkyl chain of left *n*-alkoxy (-OR) group. The disappearance of odd–even effect from and beyond merging of curves for odd and even numbered homologues is attributed to the unexpected status of longer *n*-alkyl chains by coiling or bending or flexing or coupling with the major axis of a core structure of molecules, to prolong as a single transition curve. The extrapolated N-I transition curve to C_3, suggests the monotropic transition temperature 122.0°C. However, it is not realizable due to its high crystallizing tendency. The mesogenic behaviors of presently investigated novel series-1 are compared with the structurally similar known series-X [29] as shown in Fig. 2.

Homologous series of present investigation-1 and a series chosen for comparison are identical with respect to (i) three phenyl rings and a left n-alkoxy terminal end group for the same homologue and (ii) identical with respect to two functional groups $-CH_3$ or $-Cl$; because the mesogenic group efficiency of $-CH_3$ and $-Cl$ are almost equal or equivalent i.e. $-CH_3{=}{-}Cl$. The differing features of series-1 and X are the effect due to both central bridges which contributes to the total molecular rigidity keeping almost identical molecular flexibility due to equivalent group polarities of $-CH_3 \approx -Cl$. Thus, the liquid crystal (LC) properties and the degree of mesomorphism as depended upon thermodynamic quantity enthalpy (ΔH) of molecular structure which differs and depend upon changing magnitudes of intermolecular

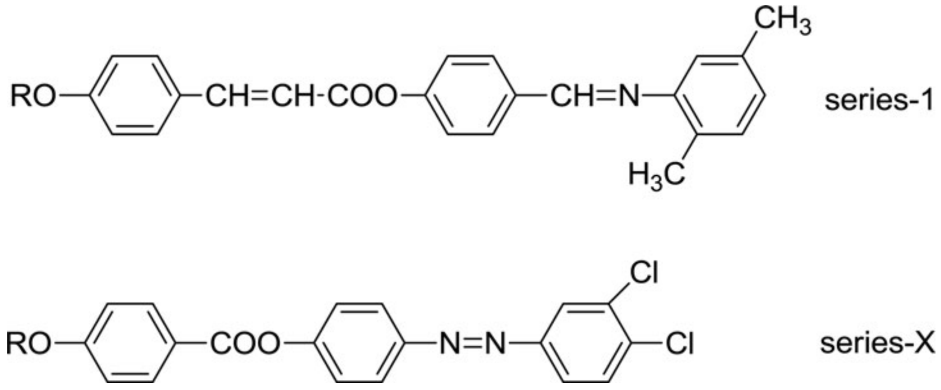

Figure 2. Structurally similar series.

dispersion forces as a consequence of changing a part of molecular rigidity due to changing the both central bridges; viz, −CH=CH−COO− or −COO− and −CH=N− or −N=N− in case of series-1 and X respectively for the same homologue from series to series and from homologue to homologue in the same series. Table 3 represents some changing features in terms of thermometric LC properties for series-1 and X, under comparative study.

Table 3 indicates that,

- Series-1 and X are smectogenic in addition to nematogenic.
- Smectic thermal stability of both homologous series under comparison is nearly equivalent with difference of about only six units.
- Nematic thermal stability of present series-1 is lower than a series-X under comparison.
- Smectogenic character commences from C_6 member of a series-1 as well as series-X.
- Nematogenicmesophase formation commences form C_2 or C_1 homologue for series-1 and X, respectively.
- Melting and transition temperatures of present novel series-1 are relatively lower than a series-X.
- Total upper and lower mesophase length ranges for present novel series-1 are relatively lower than a series-X.
- Odd–even effect in the transition curves of a phase diagram is observed for both series.

The exhibition of smectogenic property identically from C_6 homologue is attributed to the similar magnitudes of combined effects of molecular rigidity and flexibility as occurred by commencement of lamellar packing of molecules in crystal lattices which facilitate sliding layered molecular arrangement in floating condition monotropically for series-1 and enantiotropically for series-X under exposed thermal vibrations to include smectogenic character. Moreover the extent of molecular noncoplanarity form and beyond C_6 homologue of both

Table 3. Relative thermal stabilities in °C.

Series →	1	X
Smectic-Isotropic or Smectic–NematicCommencement of smecticmesophase	100.16(C_8–C_{18})C_6	106.0(C_6–C_{16})C_6
Nematic-IsotropicCommencement of nematic phase	110.83(C_5–C_{10})C_2	157.01(C_1–C_{16})C_1
Total mesophase length range (Sm+N)	4.0 (C_{18})to 41.0 (C_{12})	22.0(C_4)to 88.0 (C_1)

the series under comparative study which causes similar effect towards commencement of smectic phase. Looking to the values of smectic thermal stability of series-1 and X which are nearer to each other (100.16°C and 106.0°C) also very well support to equivalence of mesogenic group efficiency of $-CH_3$ and $-Cl$. Observed difference of about six units is attributed to the positional difference of two $-CH_3$ (ortho & meta) group and two $-Cl$ (meta & para) in series-1 and X, respectively. Two lateral $-CH_3$ group raises molecular polarizability while one of $-Cl$ lateral group (meta) induces polarizability and other $-Cl$ group (meta) induces polarizability and other $-Cl$ group (para) induces end to end attractions relatively more than a series-1. Thus, intermolecular end to end attractions of series-X, exceeds the intermolecular lateral attractions through polarizability factor; which maintained and facilitated statically parallel orientational order of molecules in floated condition more under the exposed thermal vibrations. Therefore facilitation of nematic phase, though, commences from nearer (second and first) homologues, but their thermal stabilities differ with wide range of about 56 units. As regards to the upper and lower values of total mesophase length range and thermal stability for nematic which are higher for series-X than a present series-1; should be expected higher for a series-1 as compared to series-X by apparent look of molecular structure because, $-CH{=}CH-COO-$ central group is relatively longer and stronger than identical $-COO-$ central bridge of series-X. However, contribution to molecular rigidity of $-CH{=}CH-COO-$ plus $-CH{=}N-$ central bridge due to absence of para substituted terminal tail group $-CH_3$ of series-1 can reduce the end to end attractions as compared to $-COO-$ plus $-N{=}N-$ central bridges of series-X; which offers presence of para substituted $-Cl$ tail group and strangles end to end intermolecular attractions and cohesions to float on the surface with statistically parallel orientational order for higher range of transition temperature, depending upon thermodynamical quantity enthalpy change, based on respective molecular structure for the same homologue from series to series and from homologue to homologue in the same series.

Conclusions

- Novel Schiff's base homologous series of LC family is predominantly nematogenic and partly smectogenic whose mesophase length is relatively low and transition temperature vary between 66.0°C and 139.0°C and of low thermal stability.
- Mesogenic properties are dependent of the effects due to central bridges.
- $-CH_3$ and $-Cl$ group are equipolar but 2,5 dimethyl and 3,4 dichloro groups are not equipolar and equipolarizable due to their positional difference, affecting end to end attractions and molecular flexibility.
- Phenomena of mesomorphism are very sensitive and susceptible to molecular structure.
- Smectogenic and nematogenic homologues of below 80°C may be useful for the devices to be operated with the study of binary systems.
- The present investigation has supported and raised the credibility of conclusion drawn earlier.

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