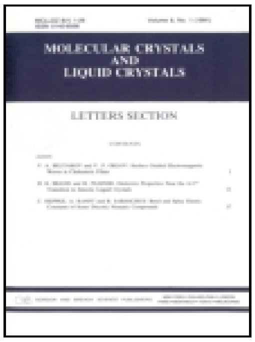

Molecular Crystals and Liquid Crystals

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Study of Molecular Structure, Mesomorphism and Their Relation with Molecular Rigidity-Flexibility

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ABSTRACT
Entirely smectogenic novel chalconyl homologue derivatives of thermotropic liquid crystals (LC) have been synthesized with a view to understanding and establishing the effects of molecular structure on liquid crystal properties and the degree of liquid crystallinity. The homologous series consists of 12 (C_1 to C_{16}) homologues with absence of nematogenic character throughout the present series. The textures of smectic phase are fan shaped or batonnet type of smectic-A or of smectic-C. Phase transition temperatures and thermotropic data were determined by an optical polarizing microscope equipped with a heating stage. The smectic–isotropic (Sm-I) phase transition curve and the Cr-Sm transition curve behave in normal manner in the phase diagram. Analytical and spectral data confirm molecular structures of novel homologues. The average thermal stability for smectic is 139.42°C and the mesogenic phase length ranges from 3.5°C to 79.6°C. Mesogenic properties are compared with the structurally similar known series.

KEYWORD
Liquid crystal; mesogenic; nematogenic; smectic

Introduction

The liquid crystalline (LC) state of a substance [1] has varying applications in either thermotropic LC or lyotropic LC especially for the chalconyl derivatives belonging to homologous series [2–7]. Therefore, the present investigation is planned to study the chalconyl novel homologous series of LC substances with a view to understanding and establishing the relation between LC properties and the molecular structure [8–,11(a)]. The study is aimed to determine the LC state and the range of liquid crystallinity through an optical polarizing microscope equipped with a heating stage and the phase behavior will be discussed and interpreted in terms of molecular rigidity and flexibility [11(b),12–15]. Several homologous series of LCs have been reported previously [16–21]. The proposed investigation involves the synthesis of novel molecules, which consisted of three phenyl rings bridged through -COO- and -CO-CH=CH- groups as well as -OR and -CH_3 flexible terminal end groups.

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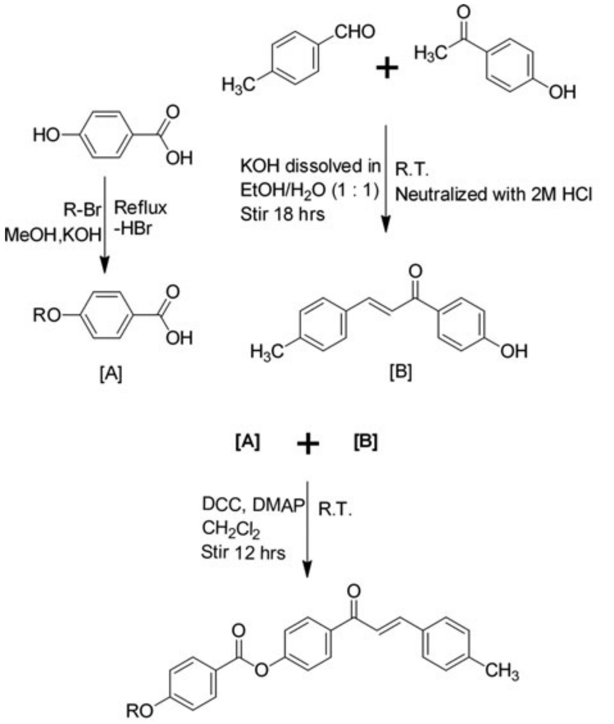

α-4-(4'-n-Alkoxy benzoyloxy) benzoyl β-4"-methyl phenyl ethylenes

Where, R= C_nH_{2n+1} and n = 1 to 8 and 10,12,14,16

Scheme 1. Synthetic route to the novel series.

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating agents (R–X) by the modified method of Dave and Vora [22]. Condensation of 4-methyl benzaldehyde and 4-hydroxy acetophenon for the synthesis of α-4-hydroxy benzoyl β-4′-methyl phenyl ethylene was effected by the usual conventional method [23]. A mixture of 4-n-alkoxy benzoic acids, α-4-hydroxy benzoyl-β-4′-methyl phenyl ethylene, 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP) in dichloromethane was used for the synthesis of α-4-(4′-n-Alkoxy benzoyloxy) benzoyl β-4″-methyl phenyl ethylenes [24]. The synthetic route to the series is shown in Scheme 1. The final chalconyl derivatives were decomposed, filtered, washed, dried and crystallized until constant transition temperatures obtained.

The chemicals 4-hydroxy benzoic acid, 4-hydroxy acetophenon, 4-methyl benzaldehyde, alkyl bromide (R-Br), methanol, KOH, 1,3-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, dichloromethane, ethanol etc. were used as received except solvents, which were dried, purified and distilled prior to use.

Characterization

The molecular structures were identified using various analytical techniques such as elemental analysis. (Table 1), ^{1}H NMR spectra (Figs. 1 and 2), ^{13}C NMR spectra (Figs. 3 and 4), IR spectra (Figs. 5 and 6), and mass spectra (Figs. 7 and 8). Transition temperatures were

Table 1. Elemental analysis for (1) Methoxy (2) Ethyloxy (3) Propyloxy derivatives.

		Elements%Found			Elements%Calculated		
No. of C atoms	M. F.	C	H	O	C	H	O
1	$C_{24}H_{20}O_4$	76.51	5.21	16.12	77.40	5.41	17.18
2	$C_{25}H_{22}O_4$	78.05	4.11	15.16	77.70	5.74	16.56
3	$C_{26}H_{24}O_4$	78.21	5.14	14.91	77.98	6.04	15.98

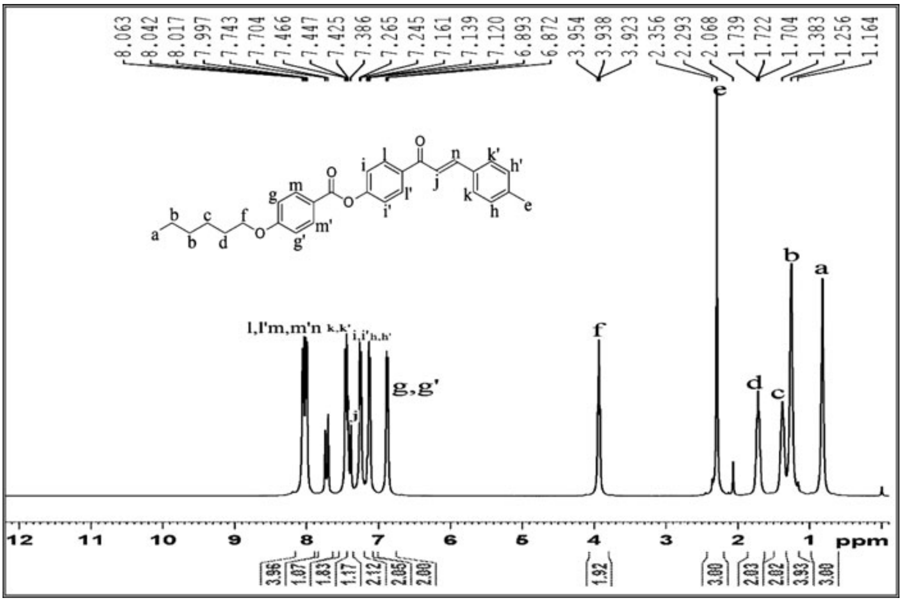

Figure 1. ^{1}H MNR spectrum of hexyloxy derivative.

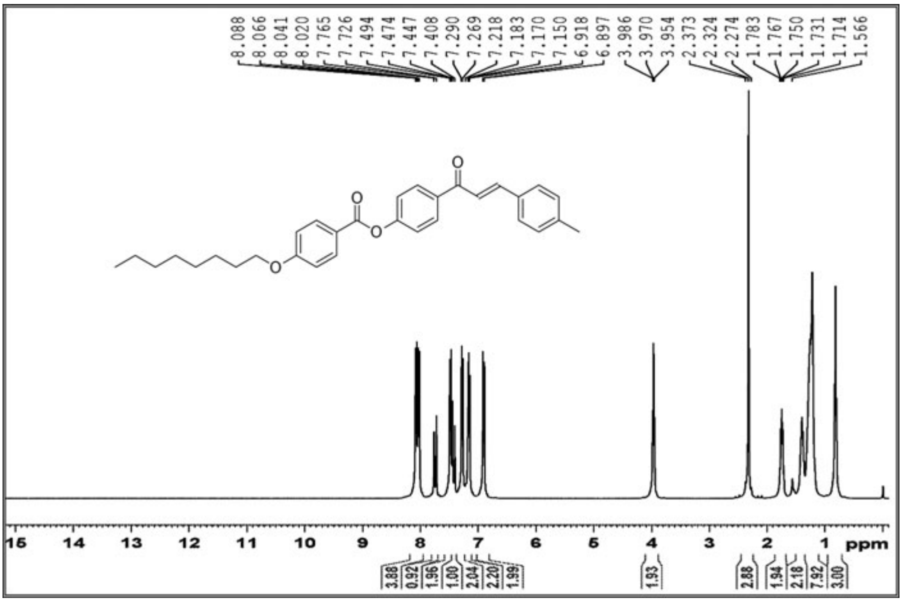

Figure 2. ^{1}H MNR spectrum of octyloxy derivative.

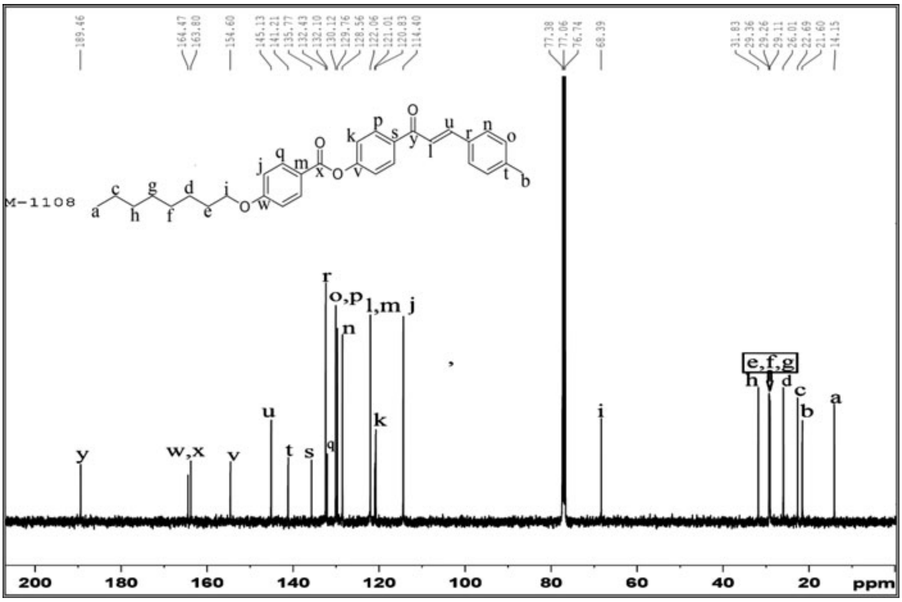

Figure 3. ^{13}C spectrum of octyloxy derivative.

determined using an optical polarizing microscope equipped with a heating stage. Elemental analysis data obtained from the experimental Perkin Elmer PE 2400 CHN Analyzer-Waltham, Massachusetts, U.S.A. system and IR data were recorded on SHIMATZU FTIR-8400 Spectrophotometer- Nishinokyou Kuwabara-cho, Nakagyo- Ku Kyoto, Japan. ^1H NMR

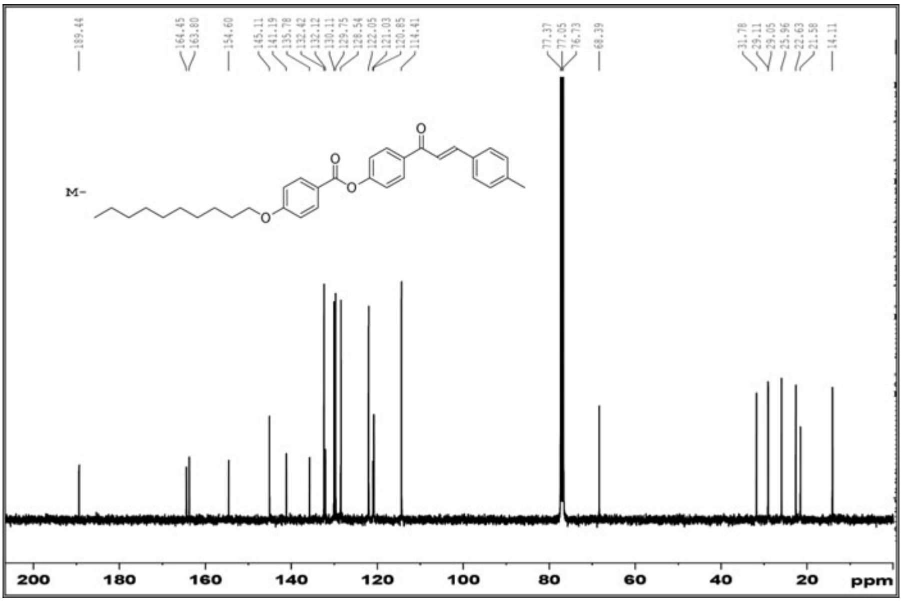

Figure 4. ^{13}C spectrum of decyloxy derivative.

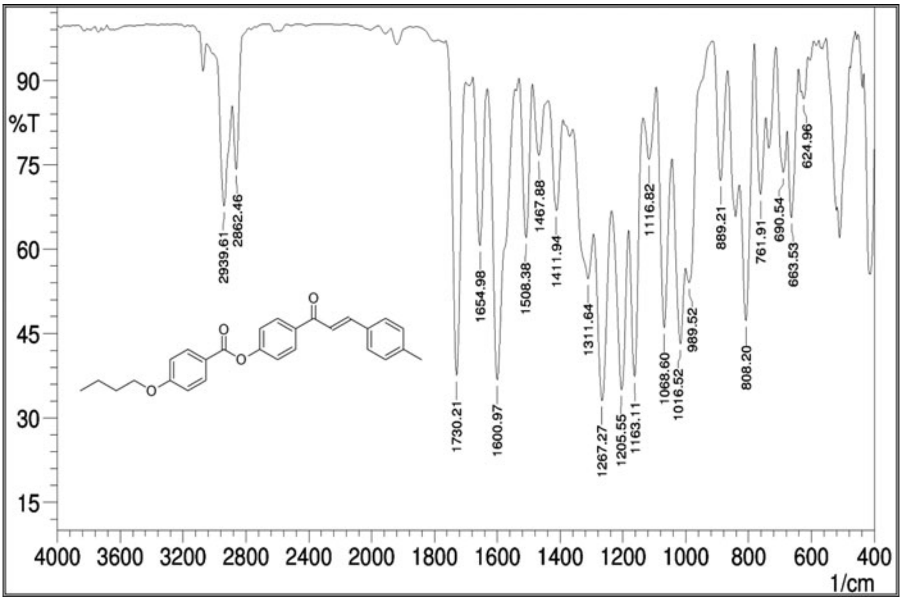

Figure 5. IR spectrum of butyloxy derivative.

spectra were recorded using BRUKER Avance-III (400 MHz) Spectrometer- Billerica, Massachusetts, U.S.A. using $CDCl_3$ as a solvent. The molecular ion peak obtained from the experimental EI-MS data were recorded by the help of Shimadzu GC-MS Model No. QP-2010, Nishinokyou Kuwabara-cho, Nakagyo-Ku, Kyoto, Japan. All analytical data were matched with the synthesized molecule and found to be satisfied. The liquid crystal behavior and the type of textures were determined by a miscibility method on microscopic observations.

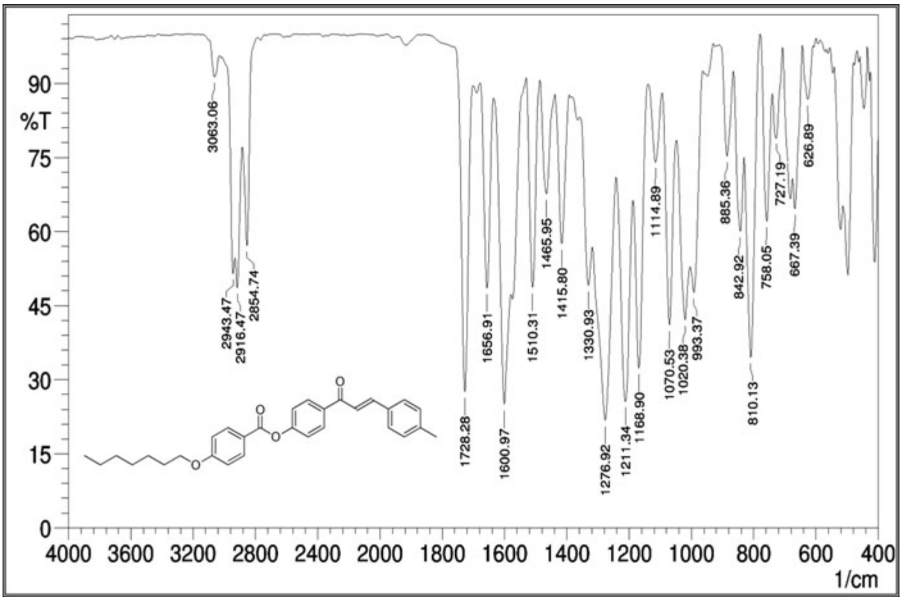

Figure 6. IR spectrum of heptyloxy derivative.

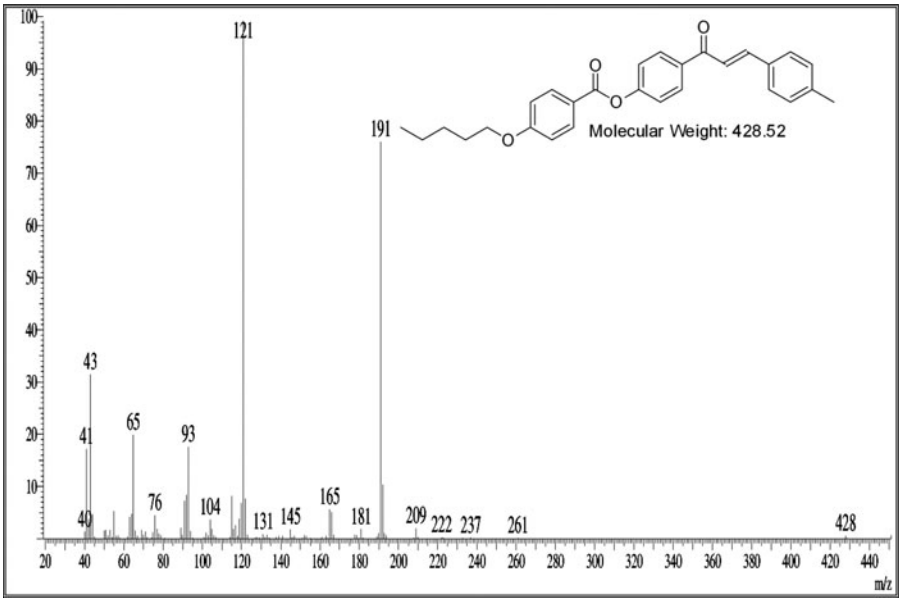

Figure 7. Mass spectrum of pentyloxy derivative.

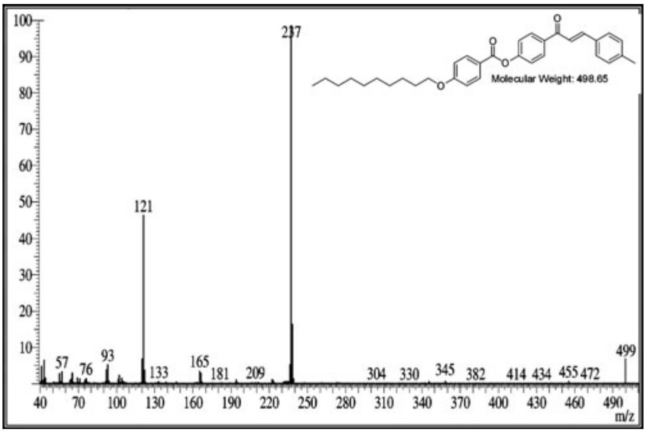

Figure 8. Mass spectrum of decyloxy derivative.

Analytical data

Spectral data

^{1}HNMR in ppm for hexayloxy derivative. 0.81–0.83 (t, 3H,-CH_3 of –OC_6H_{13} group), 1.16–1.25 (m, 4H, polymethylene group of –OC_6H_{13} group), 1.37–1.39 (p, 2H, Ar-O-$(CH_2)_2$-$\mathbf{CH_2}$), 1.70–1.74 (p, 2H, Ar-O-(CH_2)-$\mathbf{CH_2}$), 2.29 (3H, s, Ar-$\mathbf{CH_3}$), 3.92–3.95 (t, 2H, Ar-O-CH_2), 6.87–6.89 (d, 2H, Ar-H), 7.12–7.16 (d, 2H, Ar-H), 7.24–7.26 (d, 2H, Ar-H), 7.38–7.42 (d, 1H, chalcone), 7.44–7.47 (d, 2H, Ar-H), 7.70–8.01 (d, 4H, Ar-H). 8.04–8.06 (d, 1H, chalcone).The NMR data are consistent with the molecular structure.

^{1}HNMR in ppm for octyloxy derivative. 0.81–0.83 (t, 3H,-CH_3 of –OC_8H_{17} group), 1.22–1.26 (m, 8H, polymethylene group of –OC_8H_{17} group), 1.36–1.40 (p, 2H, Ar-O-$(CH_2)_2$-$\mathbf{CH_2}$), 1.71–1.78 (p, 2H, Ar-O-(CH_2)-$\mathbf{CH_2}$), 2.32 (3H, s, Ar-$\mathbf{CH_3}$), 3.95–3.98 (t, 2H, Ar-O-CH_2), 6.89–6.91 (d, 2H, Ar-H), 7.15–7.17 (d, 2H, Ar-H), 7.26–7.29 (d, 2H, Ar-H), 7.40–7.44 (d, 1H, chalcone), 7.47–7.49 (d, 2H, Ar-H), 7.72–8.04 (d, 4H, Ar-H). 8.06–8.08 (d, 1H, chalcone). The NMR data are consistent with the molecular structure.

^{13}CNMR($CDCl_3$) in ppm for octyloxy derivative. 14.15 (CH_3), 21.60 (Ar-CH_3) 22.96–31.93 (CH_2), 68.39 (OCH_2), 121.01 (-CH=CH-C=O) 145.13 (-CH=CH-C=O) 114.40–163.80 (Ar-C), 164.47 (>C=O), 189.46 (>C=O of Chalcone).

^{13}CNMR($CDCl_3$) in ppm for decyloxy derivative. 14.11 (CH_3), 21.58 (Ar-CH_3) 22.63–31.78 (CH_2), 68.39 (OCH_2), 121.03 (-CH=CH-C=O) 145.11 (-CH=CH-C=O) 114.41–163.80 (Ar-C), 164.45 (>C=O), 189.44 (>C=O of Chalcone).

IR in cm^{-1}(KBr) for butyloxy derivative. 3081 (m,=C-H Str. of Phenyl nucleus), 2939 & 2862 (s, C-H aliphatic sym. & asym. str.), 1730 (s, Aromatic C=O Str.), 1654 (C=O Str. of chalcone), 1600 (C=C Str. of vinyl gr. of chalcone & aromatic), 1508 (m, C-C aromatic str.), 1467 (m, C-H bend alkanes), 1267–1068 (C-O-C Str. of alkoxy), 1163 (C-CO-C Str.) 808 (C-H oop. phenyl ring), 761 (C-H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} (KBr) for heptyloxy derivative. 3063 (m,=C-H Str. of Phenyl nucleus), 2916 & 2854 (s, C-H aliphatic sym. & asym. str.), 1728 (s, Aromatic C=O Str.), 1658 (C=O Str. of chalcone), 1600 (C=C Str. of vinyl gr.of chalcone & aromatic), 1510 (m, C-C aromatic str.), 1465 (m, C-H bend alkanes), 1278–1070 (C-O-C Str. of alkoxy), 1168 (C-CO-C Str.) 842 (C-H oop. phenyl ring), 758 (C-H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

Where, s=strong, m=medium.

Mass spectra of pentyloxy derivative. *m/z* (rel.int%): 428 $(M)^+$, 191 (base peak, ester linkage break), 121(p-hydroxy benzoic acid).

Mass spectra of decyloxy derivative. *m/z* (rel.int%): 237$(M)^+$, 237 (base peak, ester linkage break), 121(p-hydroxy benzoic acid).

Texture determination by miscibility method

- Butyloxy homologue: smectic-C
- Octyloxy homologue : smectic-A
- Decyloxy homologue: smectic-C

Results and discussion

4-n-Alkoxy benzoic acids are dimeric, whose dimerization disappears by linking then with α-4-hydroxy benzoyl β-4′-methyl phenyl ethylene (m.p. 172–175°C, yield-74–78%). High order of mesomorphic molecular arrangement stabilizes on linking common chalconyl hydroxyl derivative with changing components of 4-n-alkoxy benzoic acids. All the members of the chalconyl derivatives of novel homologous series are enantiotropically smectogenic with absence of nematogenic property.

Table 2. Transition temperatures in°C of series-1.

		Transition temperature in °C		
Compound no.	R = n-alkyl group	Sm	N	Isotropic
1	Methyl	136.5	–	140.0
2	Ethyl	149.8	–	158.3
3	Propyl	115.2	–	122.1
4	Butyl	106.6	–	186.2
5	Pentyl	157.7	–	184.3
6	Hexyl	115.8	–	166.6
7	Heptyl	107.2	–	114.4
8	Octyl	108.5	–	120.0
9	Decyl	92.8	–	116.1
10	Dodecyl	85.7	–	134.8
11	Tetradecyl	88.2	–	109.8
12	Hexadecyloxy	89.4	–	114.3

Sm- Smectic: N- Nematic.

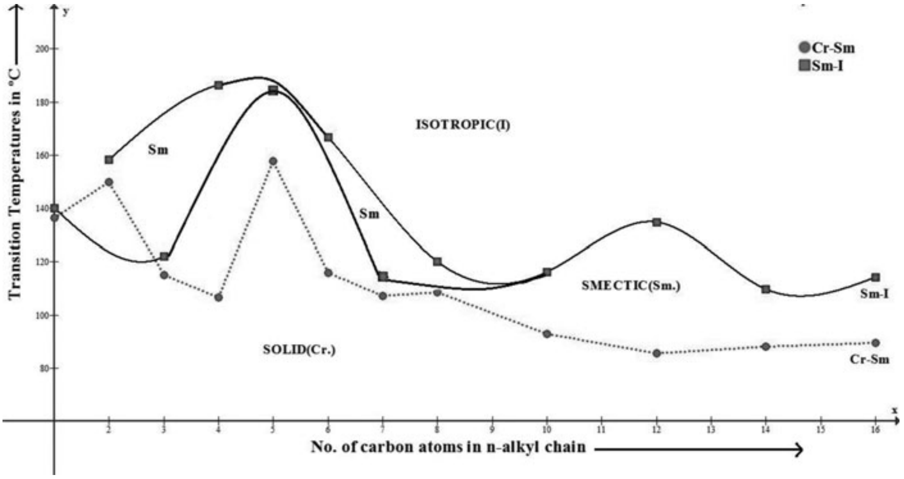

Figure 9. Phase behavior of series.

Transition temperatures (Table 2) are plotted versus the number of carbon atoms present in n-alkyl chain of left n-alkoxy flexible polar end group to understand the phase behaviors of series in its phase diagram (Fig. 9a) by drawing smooth transition curves Cr-Sm and Sm-I, through like or related points. Cr-Sm transition curve adopted zigzag path of rising and falling values as series is ascended with overall descending tendency. The Sm-I transition curve exhibited odd-even effect up to the decyloxy(C_{10}) homologue derivative. A Sm-I transition curve for odd members occupy lower position below a Sm-I transition curve for even numbered homologue derivatives in usual manner. Both transition curves for odd and even members, initially rises and passes through two maxima at pentyl (C_5) and dodecyl (C_{12}) homologue derivatives. Moreover both curves merge into each other at the decyloxy (C_{10}) homologue and then continue as a single transition curve. Thus, Cr-Sm and Sm-I transition curves behaved in normal manner. Thermal stability for smectic is 139.42°C and the smectogenic mesophase length ranges minimum of 3.5°C at the first (C_1) homologue to a maximum of 79.6°C at the butyloxy (C_4) homologue. Thus, present novel series is smectogenic and middle ordered melting type. The mesogenic property from homologue to homologue varies in present series, with changing molecular flexibility by -OR end group.

The exhibition of higher ordered smectogenic character by all the members of the present novel series may be attributed to the linking of chalconyl derivative with n-alkoxy benzoic acids by esterification process, which increases molecular length, aromaticity, rigidity through multiple bond of -CH=CH- unit, permanent dipole moment across the longer molecular axis, dipole-dipole interactions, dispersion forces etc which favors the building of lamellar packing of molecules in preoccupied rigid crystal lattices forming layered arrangement. The inter layered attractions are loosened under the influence of exposed thermal vibrations till thermal frequency exceeds the internal energy (ΔH) or resistivity towards externally exposed thermal energy corresponding to attraction between the sides of two layers; the layers of molecules may start to sides out at Cr-Sm transition temperature and then sliding out of layers continue up to Sm-I transition temperature in floating condition with appearance of smectic mesophase of appropriate texture or textures. On continued heating a sample under microscopic observation from and beyond isotropic temperatures, the molecules are randomly oriented in all possible directions with high order of disorder or high entropy ($\Delta S = \Delta H/T$) and without formation of any less ordered molecular arrangement which can induce nematic phase. On cooling the isotropic mass, the smectogenic mesophase reversibly reappears at the same temperature at which it had cleared on heating. The exhibition of odd-even effect in Sm-I transition curve is attributed to even and odd number of carbon atoms present in n-alkyl chain. The diminishing of odd-even effect in Sm-I transition curve for higher homologues from and beyond decyloxy (C_{10}) homologue is attributed to the coiling or bending or flexing or coupling of n-alkyl chain with the principle axis of a core structure of molecule. The variations in mesomorphic properties from homologue to homologue in the same present novel series is due to the changing number of methylene unit or units added progressively in n-alkyl chain of left terminal end group. Absence of nematogenic character in a series is attributed to the weaker end to end intermolecular adhesion as a consequence of molecular rigidity and flexibility associated with the enthalpy change (ΔH) of the substances concerned.

Some mesomorphic properties of present novel series are compared with structurally similar other known series-X [25] and Y [26] as shown in Figure 10.

Homologous series-1, X and Y resemble to each other with respect to three phenyl rings, central bridge -COO- linking first and middle phenyl rings and left n-alkoxy terminal end group (-OR) for the same homologue from series to series. Homologous series-1 and X resemble to each other with all above resembling features and an added feature is another central bridge -CO-CH=CH- linking middle and third or a last phenyl rings, but differs with respect to tail end groups -CH_3 and -Br. Similar homologous series-1 and Y resemble each other with respect to tail end group -CH_3; but differs with respect to central bridges -CO-CH=CH- and -N = N- linking middle and the last phenyl rings. Thus, the combined effect of molecular rigidity (ΔH) and flexibility vary from homologue to homologue in the same series and for the same homologue from series to series. Thus, changing trend in mesomorphic properties and the degree of mesomorphism depend upon the suitable magnitudes of anisotropic forces of intermolecular end to end lateral attractions as a consequence of molecular rigidity and flexibility. The changing trend in average thermal stability, commencement of mesophase, mesophase lengths etc are recorded in following Table 3 related to series-1, X and Y under comparison.

Table 3 indicate that,

- Homologous series-1 and X of chalconyl derivatives are smectogenic without exhibition of nematic property but azoester series-Y is smectogenic in addition to nematogenic.

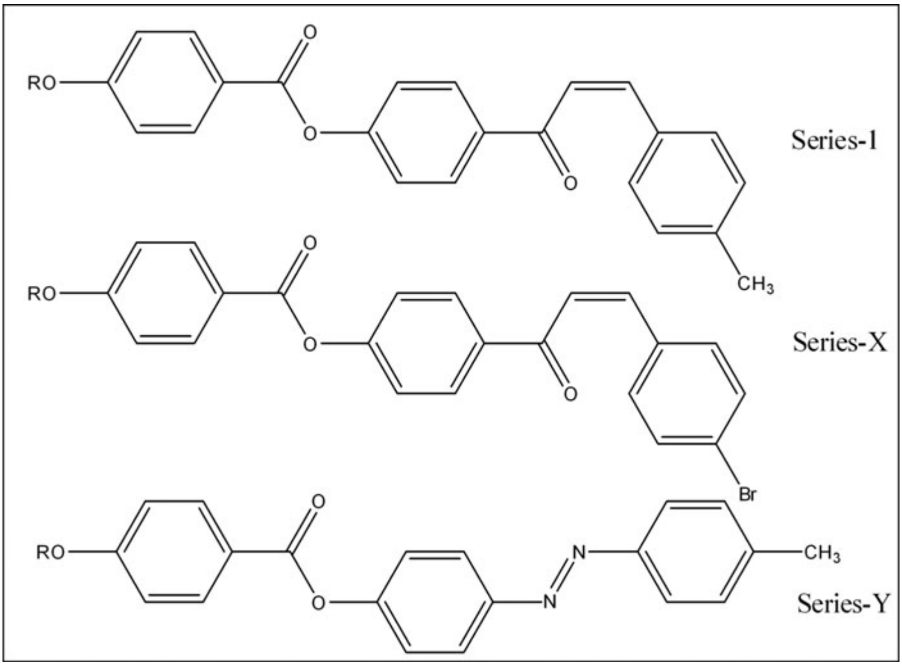

Figure 10. Structurally similar homologous series.

- Smectogenic mesophase commences from very first (C_1) member of the chalconyl ester derivatives of series-1 and X, whereas it commences from decyloxy (C_{10}) homologue of azoester series-Y.
- Nematogenic mesophase does not commence till the last (C_{16}) member of a series-1 and X, but it commences from very first member (C_1) of a series-Y.
- Smectic thermal stability of present series-1 is lower than chalconyl ester series-X, but it is higher than azoester series-Y.
- Nematogenic thermal stability is the highest of series-Y among the series under comparative study.
- Total mesophase length (Sm+N) range of present series is higher than the series-X and Y under comparison.
- Odd–even effect is observed for the transition curves in the phase diagram for the series in which mesophase commences from C_1 homologue.
- The phase diagrams of the series-X and Y chosen for comparative study purpose are shown in Figure 9b and Figure 9c along with phase diagram of present series-1.

Table 3. Average thermal stability in°C..

Series →	[1]	[X]	[Y]
Smectic — Isotropic or Smectic — Nematic	139.42 $[C_1\text{-}C_{16}]$	154.79 $[C_1\text{-}C_{16}]$	106.5 $[C_{10}\text{-}C_{16}]$
Commencement of smectic phase	C_1	C_1	C_{10}
Nematic —isotropic	—	—	242.0
Commencement of nematic phase	—	—	$[C_1\text{-}C_8]$ C_1
Total mesophase length in°C	3.5 to 79.6 C_1 C_4	5.1 to 24.4 C_3 C_{16}	82.0 to 121.0 C_{14} C_4

The exhibition of smectic property by all the series under comparison and the missing of nematic phase by series-1 and X can be attributed to the weakening of the forces holding the planes of layers together in the preoccupied lamellar packing of molecules in their rigid crystals relative to the intermolecular attractions within a given layer under the influence of exposed thermal vibrations at solid-mesomorphic transition temperature and the layers become free to slide and rotate out over one another giving smectic phase fore definite range of temperature in floating condition. However, on heating the smectic phase to a higher temperature at which smectic phase ceases to appear the intermolecular end to end attractive forces of cohesion are weakened for the molecules of series-1 and X to such an extent that, statistically parallel orientational order of molecular arrangement fails to exhibit, and nematic mesophase formation does not appear in the microscopic observation under polarize light and exposed thermal vibrations. However, the homologue molecules of azoester series-Y resists exposed thermal vibrations with sufficient potentiality and maintains statistically parallel orientational molecular order in floating condition beyond another range of temperature after ceasing of smectic phase appearance at Sm-N transition temperature. Thus, the formation of nematic phase is missed by series 1 and X but nematic phase formation in addition to smectic phase appears from C_1 to C_{16} homologues of an azoester series-Y. All homologues of the three homologous series under comparison, transform into isotropic state, by passing through only one or two mesomorphic state. The molecules concerned are randomly oriented in all possible directions from and beyond isotropic temperature with high order of disorder or high entropy ($\Delta S = \Delta H/T$). The mesophase formation reversibly reappears on cooling carefully to the isotropic mass of the samples under study at the same phase transition temperature at which they were appeared for smectic or/and nematic phase formation on heating. The commencement of smectic phase occurs from very first member of the series-1 and X, but it occurs late from C_{10} homologue. Early or late commencement of series depends on the extent of non coplanarity of a molecule. The early commencement of smectic phase related to less non coplanarity at the molecule. The extent of non coplanarity and the lateral attractions due to the common central bridges -COO- and -CO-CH=CH- central bridge being almost equal for the same homologue from series-1 to series-X. the observed difference in thermal stability of 15.37 units is attributed to the polarity and polarizability difference of $-CH_3$ and -Br tail end group of series-1 and X respectively but this difference is less effective for the its contribution to the extent of noncoplanarity of the molecules of same homologue from series-1 to series-X. Therefore, the molecules of series-1 and X are being equicoplaner their smectogenic character commences equally from very first member of the both series. But the uncommon central bridges -CO-CH=CH- (series-1 and X) and -N = N- (series-Y), the -CO-CH=CH- central bridge is longer than -N = N- causes more noncoplanarity due to the twist obtained as the oxygen atom of the -CO-CH=CH- group bump into the non bonded adjacent hydrogen atoms of the phenyl ring which causes considerable strain on the molecule. Consequently the coplanarity of the molecule is reduced to some extent. The central bridge -N = N- is shorter than -CO-CH=CH- which reduces length to breadth ratio affecting intermolecular cohesive forces with common tail group $-CH_3$ of present series-1. Therefore Sm-N thermal stability of series-Y is lowered considerably due to overall decrease in length and polarizability of the molecule. The difference value in thermal stability for smectic is due to the -CH=CH- unit. However, the molecular linearity being maintained through -N = N- unit the commencement of mesophase of less ordered than smectic (i.e. nematic) takes place from very first member whose nematic thermal stability is much higher than its smectic thermal stability due intermolecular closeness and weaker lamellar packing of molecules in crystal lattices; which facilitated smectic phase formation late from C_{10} homologue of lower thermal stability; as compared to series 1 and X. The mesophase length range is a direct result of the resistivity towards exposed thermal vibrations which vary from homologue to homologue in the same series and series to series for the same homologue depending upon favorable molecular rigidity and flexibility to cause mesophase formation. Thus, variation of smectogenic mesophase formation of series-1 and X occurred due to dissimilarity in the flexible tail groups -CH$_3$ and -Br whose molecular flexibility differs due to the difference in C-CH$_3$ and C-Br bond polarity and polarizability keeping rest of the rigid molecular part unchanged for the same homologue. Similarity variations in the mesomorphic behaviors of series-Y from series-1 and X is attributed to the variation in molecular rigidity due to changing central bridges -N = N- and -CO-CH=CH- whose rest of the molecular part including flexible part for the same homologue remain unaltered.

Conclusions

- Novel chalconyl ester derivatives of homologous series is entirely smectogenic with -CH$_3$ and -OR flexible end groups whose mesophase length ranges from 3.5°C to 79.6°C and it is of middle ordered melting type.
- The group efficiency order derived on the basis of (i) thermal stability (ii) early commencement of mesophase and (iii) degree of mesomorphism are as under for smectic and/or nematic phase.

(i) **Nematic**: -N = N- > -CO-CH=CH- = -CO-CH=CH- (with -CH$_3$) (with -CH$_{3)}$ (with -Br)

(1) **Smectic**: -CO-CH=CH- > -CO-CH=CH- > -N = N- (with -Br) (with -CH$_{3)}$ (with -CH$_{3)}$

(ii) **Nematic**: -N = N- > -CO-CH=CH- = -CO-CH=CH- (with -CH$_3$) (with -CH$_{3)}$ (with -Br)

(2) **Smectic**: -CO-CH=CH- = -CO-CH=CH- > -N = N- (with -CH$_{3)}$ (with -Br) (with -CH$_3$)

(iii) **Smectic± Nematic**: -CO-CH=CH- > -N = N- > -CO-CH=CH- (with -CH$_3$) (with -CH$_3$) (with -Br)

- Molecular rigidity and flexibility operate the suitable magnitudes of anisotropic forces of intermolecular cohesion and closeness to induce mesomorphic (LC) state.
- The phenomenon of mesomorphism is sensitive and susceptible to molecular structure.
- Chalconyl derivatives are biologically active molecules whose bioactivity can be exploited as antibacterial, antimalerial, anti cancer, anti-inflammatory etc.
- Binary systems of chalconyl esters can be studied to construct thermotropic articles or display devices.
- The Sm-I transition curve of an entirely smectogenic series passes through two maxima.

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