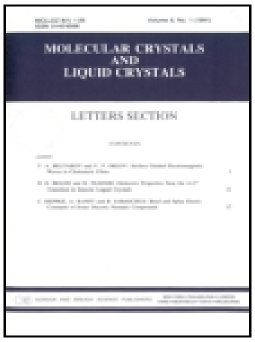

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Dependence of liquid crystallinity on molecular rigidity

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ABSTRACT

A novel homologous series of liquid crystals (LC) of chalconyl derivatives is synthesized and studied with a view to understanding and establishing the effects of molecular structure on liquid crystal properties. The novel series consists of 12 homologues. Nematogenic LC property commences from C_3 and continues up to C_{14} and the smectogenic mesophase is exhibited from C_4 to C_{16}. The C_3 homologue is a monotropic nematic and the rest of the homologues are enantiotropically smectic and nematic or only smectic (C_{16}). Transition curves Cr-Sm, Sm-N, Cr-I, and N-I behave in normal manner with exhibition of odd-even effect, showing phase behaviors of the series.

KEYWORDS

Enantiotropic; liquid crystal; nematic; smectic; thermotropic

Introduction

Applicability of thermotropic liquid crystal (LC) substances in liquid crystal devices and chalconyl substances in pharmaceutical and medicinal treatment have inspired the synthesis of novel chalconyl substances of liquid crystal property, which may be useful to mankind in both the ways [1]. Many thermotropic [2,3] and lyotropic [4–9] substances have been reported to date. The present investigation is planned with a view to synthesize novel LC substances and to understand and establish the relations between molecular structure and thermotropic LC properties [10–16]. The novel LCs consist of three phenyl rings, two central bridges, viz., –COO– and –CH=CH–CO– with two flexible end groups –OR and –Cl ($R = C_nH_{2n+1}$). The results of the novel investigation are evaluated and compared with a known structurally similar homologous series and interpreted in terms of molecular rigidity and flexibility [17–20]. Evaluated results can be useful to the other groups of researchers who are working with LC substances because every researcher in LCs requires novel substances [21–23].

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated by suitable alkylating agents by the modified method of Dave and Vora [24]. β-4-Hydroxy phenyl α-4'-chlorobenzoyl ethylene was prepared by a well-known method [25]. 4-n-Alkoxy benzoic acids were converted to corresponding acid chlorides using freshly distilled thionyl chloride and condensed with an ice cold solution of

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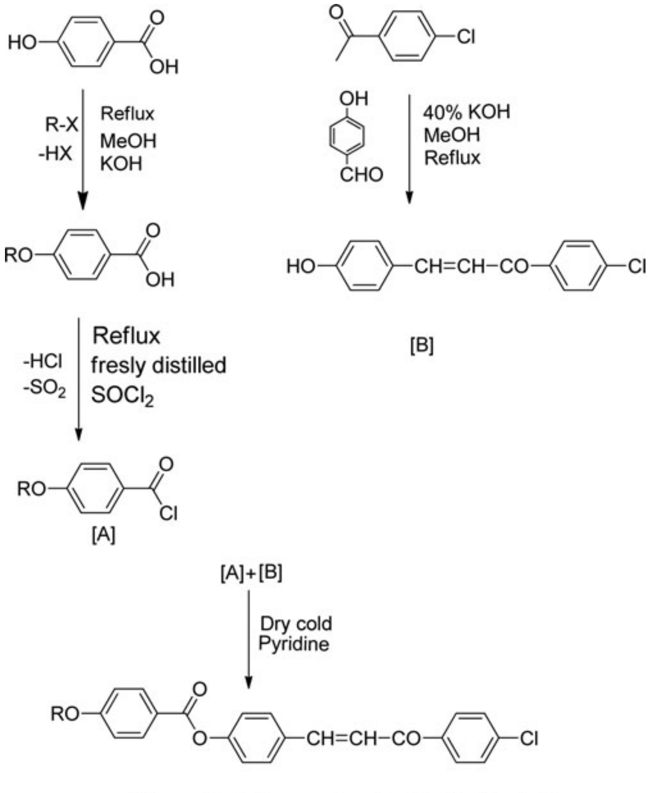
chalcone in pyridine [26]. Final products were individually decomposed in a 1:1 hydrochloric acid aqueous solution, filtered, washed, dried, and purified until the homologue gave constant transition temperatures.

4-Hydroxy benzoic acid, alkyl halides, KOH, thionyl chloride, methanol, ethanol, pyridine, 4-hydroxy benzaldehyde, 4-chloro acetophenone, etc., were used as received except solvents that were dried and purified prior to use. The synthetic route of the novel homologous series is shown in Scheme 1.



Where, R= C_nH_{2n+1} and n= 1to8,10,12,14and 16.

Scheme 1. Synthetic route to the novel series.

Characterization

Some members of the novel series as the representative members were characterized by elemental analysis (Table 1), infrared spectroscopy, ^{1}H NMR spectra, and mass spectroscopy. Microanalysis was performed on a EuroEA Elemental Analyzer. IR spectra were recorded on

Table 1. Elemental analysis for (1) ethyloxy, (2) hexyloxy, and (3) tetradecyloxy derivatives.

		Elements% found			Elements% calculated		
Sr. no.	Molecular formula	C	H	O	C	H	O
1	$C_{24}H_{19}ClO_4$	70.91	4.68	15.69	70.85	4.71	15.73
2	$C_{28}H_{27}ClO_4$	72.69	5.86	13.79	72.64	5.88	13.82
3	$C_{36}H_{43}ClO_4$	75.11	7.51	11.10	75.17	7.54	11.13

a Shimadzu FTIR Model -IRAffinity-1S (MIRacle 10), ^{1}H NMR spectra were recorded on a Bruker spectrometer using $CDCl_3$ as a solvent, and mass spectra were recorded on a Shimadzu GC-MS Model No. QP-2010. The liquid crystal behavior and the type of textures were determined by a miscibility method on microscopic observations.

Analytical data

Spectral data

^{1}H NMR in ppm for propyloxy derivative

1.04–1.08 (t, 3H,–CH_3 of –OC_3H_7 group), 1.81–1.89 (m, 2H, Ar–O–CH_2–$\underline{CH_2}$), 3.93–4.02 (2H, t, Ar–O–$\underline{CH_{2}}$-), 6.96–8.15 (4H of phenyl ring with n-propoxy group), 7.26–7.84 (4H of middle phenyl ring), 7.68–7.84 (4H of phenyl ring with chloro group), 7.96–7.98 (d, 1H, –$\underline{CH}$=CH–CO–), 7.44–7.48 (d, 1H, –CH=$\underline{CH}$–CO–). The NMR data are consistent with the molecular structure.

^{1}H NMR in ppm for pentyloxy derivative

0.93–0.96 (t, 3H,–CH_3 of –OC_5H_{11} group), 1.35–1.37 (m, 2H, CH_3–$\underline{CH_2}$–$(CH_2)_3$–O–), 1.39–1.41(m, 2H, CH_3–CH_2–$\underline{CH_2}$–$(CH_2)_2$–O–), 1.79–1.86 (m, 2H, CH_3–$(CH_2)_2$–$\underline{CH_2}$–CH_2–O–), 4.02–4.06 (t, 2H, CH_3–$(CH_2)_3$–$\underline{CH_2}$–O–), 6.96–8.15 (4H of phenyl ring with n-pentyloxy group), 7.26–7.84 (4H of middle phenyl ring), 7.69–7.84 (4H of phenyl ring with chloro group), 7.96–7.98 (d, 1H, –$\underline{CH}$=CH–CO–), 7.44–7.47 (d, 1H, –CH=$\underline{CH}$–CO–). The NMR data are consistent with the molecular structure.

IR in cm^{-1} for butyloxy derivative

3070 (=C–H Str. of phenyl nucleus), 2956 and 2870 (CH_2 sym. and asym. stra.), 1720 (aromatic C=O Str.), 1656 (aromatic C=C str.), 1506 (C–C aromatic str.), 1471 (C–H bend alkanes), 1321 (aromatic and aliphatic C–O str.), 1166 (Ar–O str.), 848 (C–H oop. phenyl ring), 806 (C–Cl str.), 758 (C–H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

IR in cm^{-1} for decyloxy derivative

3070 (=C–H Str. of phenyl nucleus), 2920 and 2850 (CH_2 sym. and asym. stra.), 1722 (aromatic C=O Str.), 1656 (aromatic C=C str.), 1512 (C–C aromatic str.), 1469 (C–H bend alkanes), 1328 (aromatic and aliphatic C–O str.), 1174 (Ar–O str.), 848 (C–H oop. phenyl ring), 806 (C–Cl str.), 759 (C–H oop. bending of phenyl ring). The IR data are consistent with the molecular structure.

Mass spectra of hexyloxy derivative

m/z (rel.int%): 462 $(M)^+$,257,223,205,165,139,121,93,65

Mass spectra of octyloxy derivative

m/z (rel.int%): 490$(M)^+$,315,233,194,165,139,121,111,93,65

Table 2. Transition temperatures in °C.

		Transition temperatures in °C		
Compound no.	R=n-alkyl chain C_nH_{2n+1}	Sm	N	Isotropic
1	1	–	–	164.4
2	2	–	–	156.5
3	3	–	(138.8)	141.6
4	4	135.2	140.1	154.9
5	5	119.8	131.9	141.2
6	6	118.5	135.8	145.7
7	7	114.6	140.2	150.1
8	8	110.1	144.4	152.3
9	10	102.6	149.0	158.0
10	12	101.7	150.3	164.0
11	14	96.0	147.8	168.2
12	16	82.0	–	145.1

Sm, Smectic; N, Nematic; () indicate monotropy.

Result and discussion

β-4-Hydroxy phenyl α-4'-chlorobenzoyl ethylene (M.P. 178 °C; Yield 77.8%) is a nonliquid crystal component. However on linking it with 4-n-alkoxy benzoic acids yielded LC compounds from C_3 number of a series. C_3 homologue is a monotropic nematic. C_{16} homologue is enantiotropic smectic only and the rest of the LC homologues (C_4 to C_{14}) are enantiotropically smectic in addition to nematic. C_1 and C_2 members are nonliquid crystals (NLC). Transition temperatures (Table 2) were plotted versus the number of carbon atoms present in n-alkyl chain of the last n-alkoxy terminal end group. Transition curves showing phase behaviors are obtained on linking like or related points as depicted in a phase diagram (Fig. 1). Cr-I or Cr-Sm transition curve descends continuously with exhibition of minor odd-even effect as series is ascended and behave in normal manner. Sm-N or Sm-I transition curve initially rises and passes through maxima at the C_{12} homologue and then descends as series is ascended with exhibition of odd-even effect. N-I transition curve initially descends and then rises up to C_{14} homologue with exhibition of odd-even effect. Thus, Sm-N or Sm-I transition curve behaved in expected normal manner, but N-I (or vice versa) transition curve behaved in abnormal manner from and beyond C_6 homologue. Curves for odd and even members are merging into

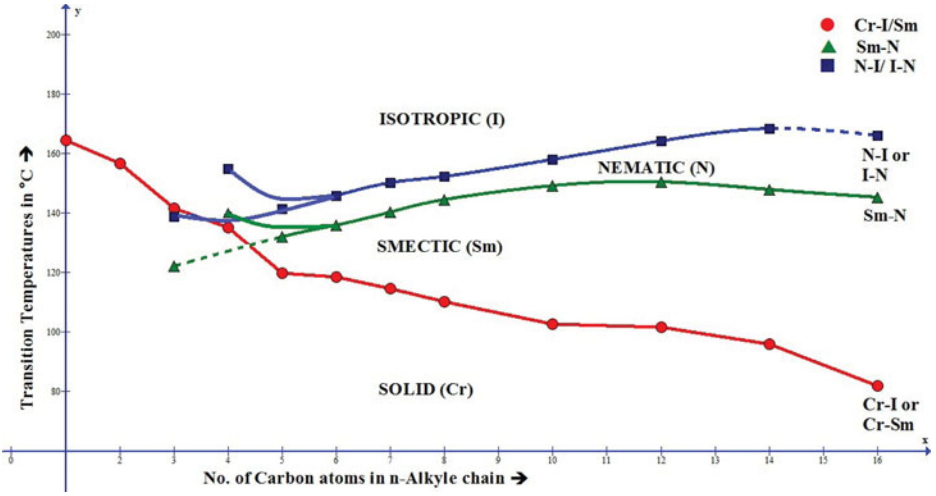


Figure 1. Phase behavior of series.

each other at the C_6 members of a series and then curves (N-I and Sm-N/I) propagated as a single transition curve from and beyond C_6 homologues. Thus, odd-even effect disappears for higher homologues from and beyond C_6 number of a series. LC properties vary from homologue to homologue in the present same series in usual manner. Thus, series under present discussion is partly smectogenic and partly nematogenic with middle ordered melting type. The exhibition of mesomorphic tendency from C_3 homologue to C_{16} homologues is due to increase in molecular length by linking 4-hydroxyl chalconyl derivative with 4-n-alkoxy benzoic acids, which increases length to breadth ratio, ratio of the polarity to polarizability, molecular rigidity and flexibility, permanent dipole moment across the long molecular axis, dipole–dipole interactions, dispersion forces, etc., to disalign the molecules perpendicular or/and at an angle less than 90° due to a suitable magnitude of anisotropic forces of intermolecular end to end and lateral attractions on floating surface under the influence of exposed thermal vibrations. Thus, mesomorphic homologues resisted thermal vibrations for certain degree of temperature for exhibition of only smectic or only nematic or smectic and nematic mesophase formation. C_4 to C_{14} members of a present series resisted exposed thermal vibrations and arranged or sliding layered organization to show smectic phase and then at higher temperature the same molecules arrange themselves or statistically parallel orientation ordered organization of higher entropy value under floating condition on the surface. The C_{16} homologue does not exhibit the nematic phase due to poor end to end attractions of the molecules. Thus, smectic and nematic mesophases appear for the C_4 to C_{14} homologues and the C_{16} homologue shows solely a smectic phase. The C_3 homologue transforms into isotropic state without an exhibition of a mesomorphic state, but on supercooling the isotropic state melts and a nematic mesophase is generated in a monotropic manner. Non-mesomorphicity of C_1 and C_2 is attributed to their high melting points due to low flexibility of the short alkyl chains. Exhibition of an odd-even effect in the alternation of transition temperature is attributed to the sequentially added methylene unit at the left n-alkyl chain. Disappearance of odd-even effect from and beyond $C\text{-}_6$ number of a novel series is attributed to the coiling, bending, flexing, or coupling of longer n-alkyl chain with the major axes of the core structure of higher homologues. Thus, transition curves in a phase diagram for higher homologues prolong as a single curve, from and beyond C_6 homologue. The deviation from normal behavior of N–I transition curve is attributed to the polarity and polarizability induced by a tail group −Cl and the uncertainty in the molecular length and the status of longer n-alkyl chain of left end group, which disturbs the suitable magnitudes of molecular flexibility; operating N–I transition temperatures. N–I transition curve is extrapolated to C_{16} homologue to predict its N–I transition temperature, which is not realizable in actual practice due to insufficient end to end intermolecular cohesion. Similarly Sm–N transition curve is also extrapolated for C_3 [27–30] to determine its latent transition temperature (L.T.T.) for smectic, but it is not realizable due to its high crystallizing tendency. Variations in LC properties from homologue to homologue in the same series is attributed to the changing molecular length by a $-CH_2$ unit, which affects the suitable magnitudes of anisotropic forces of end to end and lateral attraction or cohesive energy.

Some LC properties of presently investigated homologous series-1 are compared with the other structurally similar known homologous series-X [31] and Y [32] as shown in Fig. 2.

Homologous series-1 of present investigation and the homologous series-X and Y chosen for comparison are identical with respect to three phenyl rings, central bridge −COO− linking first and middle phenyl rings, para-substituted flexible tail group −Cl as well as the left n-alkoxy terminal end group for the same homologue from series to series. But, they differ with respect to central bridges linking middle and third phenyl rings as −CH=CH−CO−,

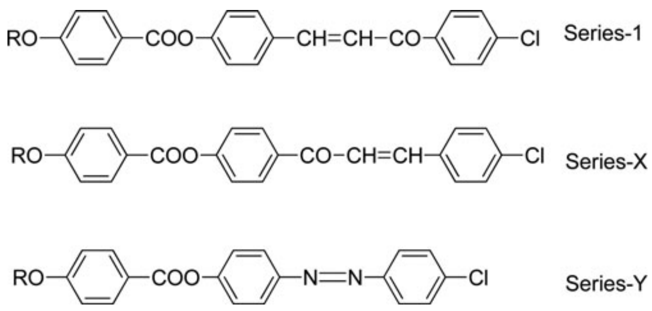


Figure 2. Structurally similar series.

–CO–CH=CH–, and –N=N–. Therefore, observed difference in LC properties and the degree of liquid crystallinity can be attributed to the differing features (central bridges or molecular rigidity) of the molecules under comparative study. Table 3 represents some LC properties of present series-1 and the series-X and Y chosen for comparison.

Table 3 indicates that,

- Homologous series-1 and Y are smectogenic in addition to nematogenic character, whereas series-X that is an isomeric with present series-1 is only nematogenic.
- Thermal stability for smectic of present series-1 is lower than a series-Y by 6.14 and smectic mesophase is destabilized till the last member of a series-X.
- Nematic thermal stability of series-1 is higher than an isomeric series-X and the lower than an azoester series-Y.
- Smectic mesophase commences earlier for series-1 (C_4) than a series-Y (C_6) but it does not commence till the last member of a series-X.
- Total mesophase (Sm+N) of present series-1 is more than a series-X but it is less than a series-Y under comparison.
- Nematic mesophase commences from presenting series (C_3) than a series X (C_5) but it commences later than a series-Y (C_1).
- Odd-even effect is exhibited by all the homologous series under comparative study.

Homologous series-1 of present investigation and an isomeric series-X differ only by displacement of –CO– group between middle and third phenyl ring as para-substituted –Cl group. The displacement of –CO– group bonded directly to either middle phenyl ring or last third phenyl ring, which affects the extent of molecular noncoplanarity. Therefore, the suitable magnitudes of anisotropic forces of intermolecular end to end and lateral attractions as a consequence of varying molecular rigidity and flexibility undergo variations. Thus, lamellar

Table 3. Average thermal stabilities in °C.

Series →	1	X	Y
Smectic-Nematic or Smectic-Isotropic	142.66 (C_4-C_{16})	—	148.8 (C_6-C_{16})
Commencement of smectic mesophase	C_4	—	C_6
Nematic-Isotropic	154.3 (C_4-C_{14})	149.4 (C_5-C_{14})	217.6 (C_1-C_{10})
Commencement of nematic phase	C_3	C_5	C_1
Total Mesophase length range (Sm+N)	19.7(C_4) to 72.2(C_{14})	14.0(C_7) to 25.0 (C_{12})	16.0 (C_{16}) to 121.0 (C_2)

packing of molecules in the crystal lattices is favored for the novel, present series-1, while it hinders for an isomeric series-X. Hence, variations arise in degree of molecular planarity due to positional difference of same –CO– group at the end phenyl ring or middle phenyl ring causing difference in the formation at smectic and nematic phase one after another or the formation at only nematic phase excluding formation of smectic phase. The degree of molecular planarity in case of series-Y favors sliding layered molecular arrangement, simultaneously prior to statistically parallel orientational order of molecules under floating condition on the surface resisting exposed thermal vibrations for definite range of temperature like present series-1 to emerge smectic and nematic phase one after another.

Difference in molecular resistivity due to very minor change in molecular structure by changing molecular rigidity through central bridges, –CH=CH–CO–, –CO–CH=CH–, –N=N– linking middle and third phenyl ring with para-substituted –Cl group, causes difference in permanent dipole moment across the long molecular axis, dispersion forces, electronic and dipole interactions, extent of planarity, etc., which results into the suitable magnitudes of thermal resistivity (ΔH) toward exposed thermal vibrations of different range of temperature (including zero degree difference at temperature), which facilitate or hinder the mesophase stabilization and formation of either one or both type at LC state or states. Thus, based on the suitable magnitudes of thermal resistivity against thermal vibrations with relevant molecular arrangement in floating condition can stabilize more or less either of the mesophase with different degree of thermal stability. Highest thermal stability of nematic of series-Y and the lowest at series-X as compared to series-1 is attributed to the rigidity played and contributed by uncommon central bridges. Commencement of mesophase formation early or late depends upon magnitudes of intermolecular end to end and/or lateral attractions that vary for the same homologue from series to series. Thus, present investigation novel series is partly smectic and partly nematic with middle ordered melting type.

Conclusion

- Novel chalconyl ester derivatives are synthesized, which are thermotropically liquid crystalline. In which –CO– group position for –CH=CH–CO– from middle phenyl ring induces smectic and nematic mesophase and the –CO– group attached at the middle phenyl ring direction (–CO–CH=CH–) hinders the smectic mesophase formation.
- The group efficiency order derived on the basis of (i) thermal stabilities, (ii) early commencement of mesophase, and (iii) total mesophase length range for smectic and nematic are as under.
    - (i) Smectic: –N=N– > –CH=CH–CO– > –CO–CH=CH–
    - (ii) Nematic: –N=N– > –CH=CH–CO– > –CO–CH=CH–
    - (iii) Smectic: –CH=CH–CO– > –N=N– > –CO–CH>CH–
    - (iv) Nematic: –N>N– > –CH=CH–CO– > –CO–CH=CH–
    - (v) Smectic + Nematic: –N=N– > –CH=CH–CO– > –CO–CH=CH–
- Liquid crystal properties and the degree of liquid crystallinity of substances are very sensitive and susceptible to the molecular structure.
- The novel compounds may be useful for devices to be operated between 62.0 °C and 82.0 °C by the study of binary systems. Chalconyl LC substances are biologically active compounds, which may be pharmaceutically and medicinally useful.
- Molecular rigidity and flexibility vary from substance to substance depending on molecular structure in which central bridge and position can play an important role.

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