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Synthesis, characterization and study of liquid crystal properties of new homologous chalcone series

B. B. Jain and R. B. Patel

Chemistry Department, K.K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India

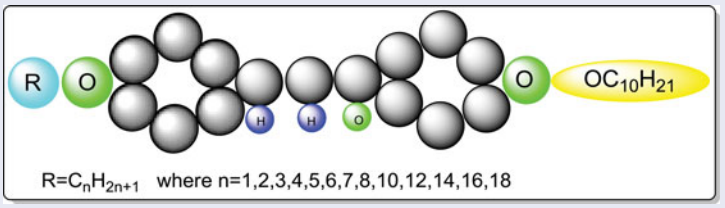
ABSTRACT

One new mesogenic homologous series of chalconyl derivative with two ring (3/-(4/- (decyloxy) phenyl-1-(4-(alkoxy) phenyl) prop-2-en-1-one) has been synthesized and characterized by a combination of elemental analysis and standard spectroscopic methods. In the series, the lower members (C_4 and C_5) exhibit only enantiotropic nematic mesophase but middle and higher members exhibit enantiotropic nematic as well as smectic mesophase. The nematic mesophase commence from C_4 homologue and smectic mesophase (smectic-A type texture) commence from C_6 homologue as enantiotropic and persists up to the last member synthesized. The mesomorphic properties of present series were compared with other two structurally similar series to study the effects of change of meta and para position on the mesomorphism.

KEYWORDS

Enantiotropic; liquid crystal; mesomorphism; nematic; smectic

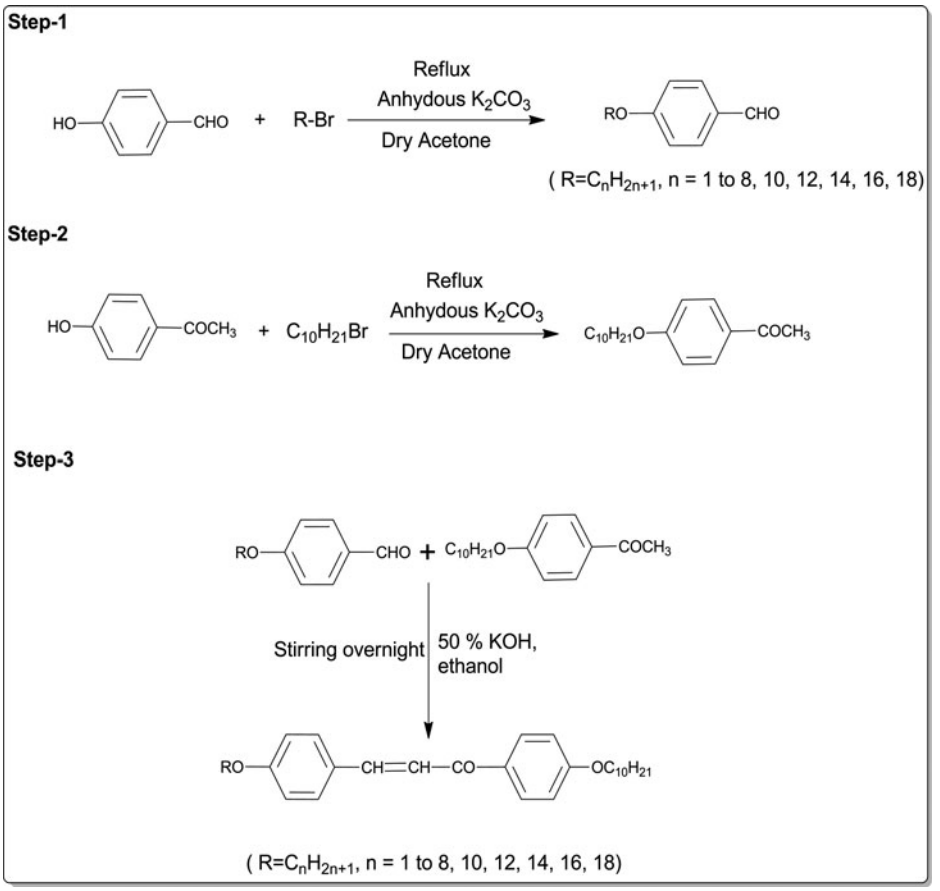
GRAPHICAL ABSTRACT



Introduction

Liquid crystals [1] flow like liquid on a surface and possesses optical properties like crystals. These substances are neither fully crystal nor liquid. The chalconyl derivatives with two ring and −CH═CH-COO- as central linkage exhibit thermotropic liquid crystal properties (LC) with biological activity, which is very useful for society in the manufacture of LC devices and the pharmaceutical preparations [2–9]. This work includes synthesis, characterization by analytical, thermal and spectral data and results and discussion on the basis of thermometric data and thermal behaviors of novel series. The object of this work to understand the effect of molecular structure on liquid crystal properties with reference to changing molecular flexibility through lateral groups of the present and analogous series [10–15].

CONTACT B. B. Jain bijendrajain1988@gmail.com Chemistry Department, K.K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad, Gujarat, India.



Scheme 1. Synthetic route to the series.

Experimental

Synthesis

Alkylation of 4-hydroxy benzaldehyde to give 4-n-alkoxy benzaldehyde is carried out by reported method [16] and 4-n-alkoxy acetophenone is obtained by alkylation of 4-hydroxy acetophenone by reported method [17] Thus, the chalconyl homologue derivatives (C) were prepared by usual establish method [18]. Homologues were filtered, washed with ethanol solution dried and purified until constant transition temperatures obtained using an optical polarizing microscope equipped with a heating stage. Alkyl halides, EtOH, KOH, 4-hydroxy acetophenone, 4-hydroxy benzaldehyde, etc., required for synthesis were used as received except solvents which were dried and distilled prior to use. The synthetic route to the series is mentioned below as Scheme 1.

Characterization

Representative homologues of a series were characterized by elemental analysis, Infrared spectroscopy, ^{1}H NMR spectra, IR spectra were recorded on Perkin-Elmer spectrum GX, ^{1}H NMR spectra were recorded on Bruker using $CDCl_3$ as solvent. Microanalysis was performed

Table 1. Elemental analysis for (1) hexyloxy (2) decyloxy (3) tetradecyloxy and (4) octadecyloxy derivatives.

		%Elements found		%Elements theoretical	
Sr. No	Molecular formula	C	H	C	H
1	$C_{31}H_{54}O_3$	78.42	11.36	78.48	11.39
2	$C_{35}H_{62}O_3$	79.21	11.64	79.24	11.69
3	$C_{39}H_{70}O_3$	79.84	11.90	79.86	11.94
4	$C_{43}H_{78}O_3$	80.33	12.08	80.37	12.14

Table 2. Texture of nematic phase of C_8, C_{12}, C_{16}, C_{18} by miscibility method.

Sr. No.	Homologue	Texture
1	C_8	Threaded
2	C_{12}	Threaded
3	C_{16}	Schlieren
4	C_{18}	Schlieren

on Perkin-Elmer PE 2400 CHN analyzer (Table 1). Transition temperature (Table 3) and LC properties (Textures) were determined using an optical polarizing microscopy equipped with heating stage and digital camera (POM). Texture images of nematic phase were determined by miscibility method (Table 2), thermodynamic quantities enthalpy (ΔH) and entropy ($\Delta S = \Delta H/T$) are qualitatively discussed.

Analytical data

IR spectra in cm−1 for hexyloxy and decyloxy derivatives

Hexyloxy: 2912 (C–H str. of alkane), 2848 (C–H str. of –(CH_2-)n group of $-OC_6H_{13}$ alkyl chain, 1602–1656 (C=O str. of carbonyl carbon of chalconyl group), 1610 (C=C str. of alkene), 1512, 1563 (C=C str. of aromatic ring), 997 (C–H bending of alkene), 1180 (C-O str. of ether linkage), 1286, 1245 (C-O str. of carbonyl group), 778 Polymethylene (-CH_2-) of $-OC_{10}H_{21}$, 680 Polymethylene (-CH_2-)n of $-OC_6H_{13}$, 828 (−C–H- def. m di-substituted-Para),IR data confirms the molecular structure.

Table 3. Transition temperature in °C.

		Transition temperatures in °C		
Sr. no	R = n-alkyl group	Smectic	Nematic	Isotropic
1	C_1	—	—	89.0
2	C_2	—	—	91.0
3	C_3	—	—	83.0
4	C_4	—	61.0	75.0
5	C_5	—	58.0	70.0
6	C_6	50.0	60.0	71.0
7	C_7	46.0	53.0	66.0
8	C_8	48.0	54.0	69.0
9	C_{10}	42.0	50.0	64.0
10	C_{12}	49.0	57.0	67.0
11	C_{14}	45.0	54.0	63.0
12	C_{16}	43.0	56.0	68.0
13	C_{18}	51.0	61.0	72.0

Decyloxy: 2914 (C–H str. of alkane), 2850 (C–H str. of –(CH_2-)n group of $-OC_{10}H_{21}$ group, 1601–1660 (C=O str. of carbonyl group of chalconyl group), 1608(C=C str. of alkene), 1514, 1568 (C=C str. of aromatic ring), 1002, (C–H bending of alkene), 1186 (C-O str. of ether linkage), 1238, 1252 (C-O str. of carbonyl group), 774 Polymethylene (-CH_2-) of $-OC_{10}H_{21}$, 826 (−C–H- def. m di-substituted-Para), IR data confirms the molecular structure.

1HNMR spectra in $CDCl_3$ in δ ppm for heptyloxy and dodecyloxy derivative

Heptyloxy: 0.87 (t, -CH_3 of polymethylene $-C_7H_{15}$ and $-C_{10}H_{21}$), 1.77 (p, CH_3-CH_2-CH_2-CH_2-CH_2- of $-OC_7H_{15}$ and $-OC_{10}H_{21}$), 1.26 (m, $-CH_2$-CH_2-CH_2- of $-OC_7H_{15}$ and $-OC_{10}H_{21}$), 1.35 (q, -CH_2-CH_3), 4.04(t,-OCH_2-CH_2-), 7.62 (d,-CH = CH-), 7.42, 7.27 & 7.82 (para substituted phenyl ring), 7.54 & 7.95 (phenyl ring with alkoxy chain). NMR data confirms the molecular structure.

Dodecyloxy: 0.88 (t, -CH_3 of $-C_{12}H_{25}$ and $-C_{10}H_{21}$), 1.82(CH_3-CH_2-CH_2-CH_2-CH_2-CH_2 of -$OC_{12}H_{25}$ and $-OC_{10}H_{21}$), 1.28 (polymethylene $-CH_2$-CH_2-CH_2- of $-OC_{12}H_{25}$ and $-OC_{10}H_{21}$), 1.34 (q, -CH_2-CH_3), 4.06 (t, -OCH_2-CH_2-), 7.59 (d, -CH = CH-),7.44, 7.26, and 7.83 (para substituted phenyl ring), 7.56 and 7.97 (phenyl ring with alloy chain), NMR data confirms the molecular structure.

Homlologous Series: RO–⟨⟩–CH=CH–CO–⟨⟩–$OC_{10}H_{21}$

Result and discussion

The novel homologous series have been synthesized by reaction between 4-n-alloy benzaldehyde and 4-decyloxy acetophenone which include thirteen homologues. In present series C_1-C_3 are nonmesomorphic and C_4-C_{18} homologues are enantiotropically nematic which includes C_6 to C_{18} homologues as the enantiotropically smectic in addition to nematic character. The transition temperature Table 3 determined with the help of polarizing optical microscope (POM) equipped with the hot stage and plotted against the number of carbon atoms present in n-alkyl chain 'R' of –OR group and then transition curves Cr-N/I, N-I and Sm-N are obtain on linking like or related transition points as shown in a phase diagram (Fig. 1). Transition Curve for Cr-N/I adopted zigzag path of rising and falling manner with overall descending manner and behaved in normal manner. N-I transition curve initially descended up to C_{10} homologue and then ascended to C_{12} homologue and descended to C_{14} homologue and then ascended to $C_{16}-C_{18}$ homologue with exhibition of very narrow and short odd-even effect up to C_9 homologue. Sm-N transition curve rises from C_8 to C_{12} and descended after passing through maxima at C_{12}, till the last homologue C_{18} with absence of odd-even effect. Thus, all the transition curves behaved in normal manner. Thermal stabilities are 54.8 °C and 68.5 °C for smectic and nematic, respectively whose maxima to minimum phase lengths are 06 °C to 13.0 °C and 10 °C to 14.0 °C, respectively. Thus, novel homologous series is low melting type series. Analytical, spectral and thermal data supported molecular structures of homologues.

Homlologous Series: RO–⟨⟩–CH=CH–CO–⟨⟩–$OC_{10}H_{21}$

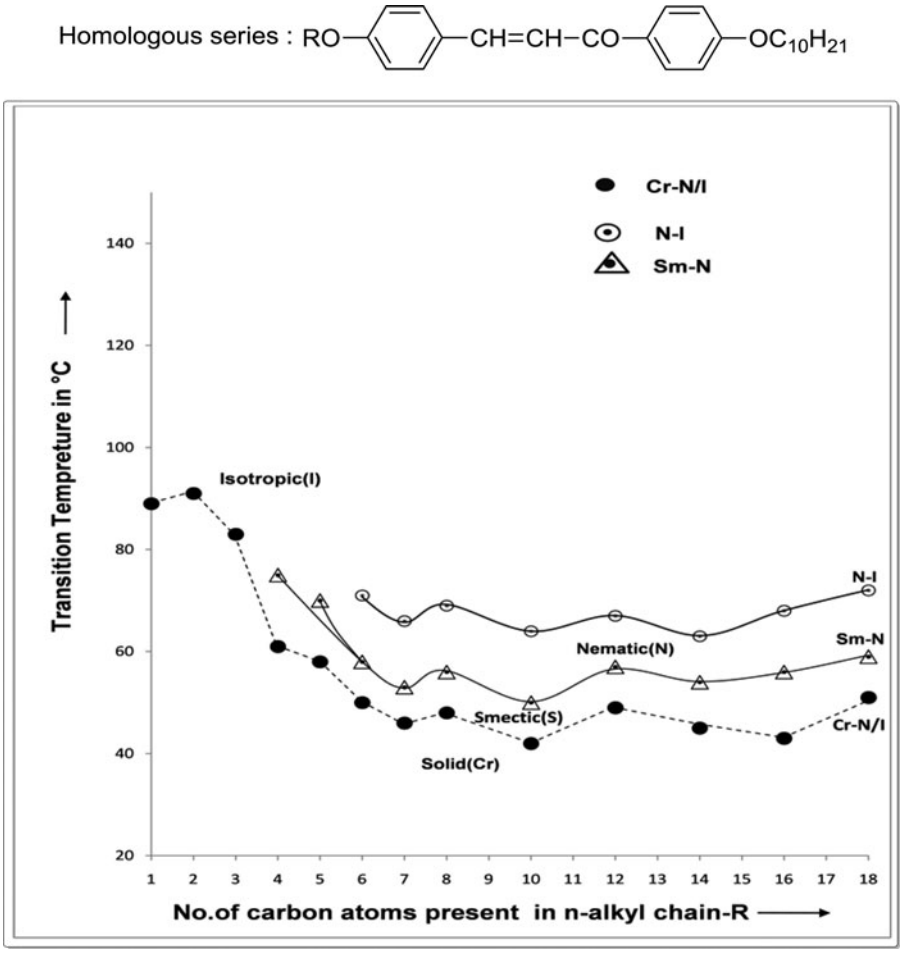


Figure 1. Phase behavior of series.

The changing style of LC properties from homologue to homologue in the present novel series is observed. The exhibition of mesomorphism by C_4-C_{18} homologues of a present novel series is attributed to the suitable magnitudes of anisotropic forces of intermolecular cohesions and closeness as a consequence of fittest molecular rigidity, polarizability and favorable flexibility. The flexibility from homologue to homologue in the same series undergo variations keeping molecular rigidity and the part of flexibility due to para substituted $-OC_{10}H_{21}$ right end tailed unaltered. The nonmesomorphic behaviors of C_1-C_3 homologues is due to the low magnitudes of dispersion forces and low magnitudes of dipole–dipole interactions leading to high crystallizing tendency and inducing unsuitable magnitudes of anisotropic forces of end to end attractions. Diminising of odd-even effect for higher homologues beyond C_9 homologue of longer n-alkyl chain 'R' of –OR and $-OC_{10}H_{21}$ right end flexible groups is attributed to coiling, bending, flexing and coupling with the major axes of core structure of a molecule.

The condensation of nonmesomorphs 4-n-alkoxy benzaldehydes with 4-n-decyloxy acetophenone extends molecular lengths, polarity and polarizability, rigidity and flexibility, permanent dipole moment across the long molecular axis, intermolecular end to end and lateral attractions, suitable magnitude of dispersion forces and dipole-dipole interaction etc. Which induces resistivity and disalignment of molecules at an angle ninety degree or/and less than

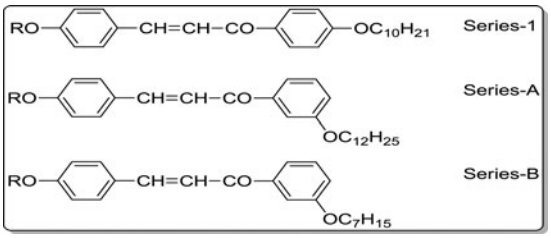


Figure 2. Structurally analogous series.

ninety degree with the plane of floating surface under the influence of exposed thermal vibrations to maintain the floating with statistically parallel orientational order and/or with sliding layered molecular arrangement for different range or ranges of temperatures to facilitate only nematic or smectic plus nematic mesophase formation for C_4-C_{18} homologues. The variations in LC properties and the degree of mesomorphism from homologue to homologue in the same series or from series to series for the same homologue is attributed to the changing magnitudes of molecular rigidity and flexibility due to varied molecular polarity and polarizability and other related parameters concerning suitable magnitudes of intermolecular cohesions and closeness. The LC properties of presently investigated homologous Series-1 are compared with structurally similar series A [19] and B [20] as under in Fig. 2.

Homologous seires-1, A and B are identical with respect to two phenyl rings and one central bridge –CH=CH-CO- contributing to total molecular rigidity and the left n-alkoxy terminals –OR for the same homologue from series to series. However, they differ with tailed end group viz. para $-OC_{10}H_{21}$, meta $-OC_{12}H_{25}$, meta $-OC_7H_{15}$ for the same homologue from series to series and homologue to homologue in the same series which partly contributes to the total molecular flexibility. Therefore, variations in liquid crystal (LC) properties are due to differing features of their molecular structures which differs with respect to flexibility of tailed end groups differing by $-CH_2$-CH_2- and their position of substitutions para or meta as shown in Figure 2. Following Table 4 represents some evaluated thermometric data indicating mesogenic behaviors and the degree of mesomorphism for the series-1, A and B under comparative study.

From Table 4, it is clear that,

- Smectogenic mesomorphism commences from C_6 homologue in series-1 whereas it commences C_4 and C_{10} homologue in series-A and B, respectively
- Nematogenic mesomorphism commences from C_4 homologue in series-1 whereas it commences from C_2 and C_7 homologue in series –A and B, respectively.
- Thermal stability for smectic is less for the series –1 as compared to series A.
- Thermal stability for nematic is more for series-A as compared to series 1 and series-X.

Table 4. Thermal stability in °C.

Series →	Para $-OC_{10}H_{21}$	Meta $-OC_{12}H_{25}$	Meta $-OC_7H_{15}$
Sm-I or Sm-N Commencement of smectic phase	54.8 (C_8-C_{16}) C_6	56.0 (C_4-C_5) C_4	Fraction of 1°C or 1°C (C_{10} - C_{18}) C_{10}
N-I Commencement of nematic phase	68.5 ($C_{10}-C_{4/10}$) C_4	70.5 (C_2-C_5) C_2	66.0 (C_7 - C_8) C_7
Total mesophase lengths in °C minimum to maximum	06.0 to 25.0 C_8 C_{16}	05.0 to 29.0 $C_{10/14}$ C_4	07.0 to 15.0 $C_{10/14/16}$ C_{12}

- Homologous series under comparison are predominantly nematogenic and partly smectogenic in enantiotropic and/or monotropic condition.

The present novel series-1 has para substituted $-OC_{10}H_{21}$ group whereas Series -A and B have meta substituted lateral $-OC_{12}H_{25}$ and $-OC_7H_{15}$ groups so there are difference in the geometry of series-1 as compared to series-A and B. Thus, the two opposing effects of intermolecular attractions due to para and meta substituted tail ended n- alkoxy groups play role in facilitating smectic and/or nematic mesophase formation through predominancy of either molecular polarity or polarizability factor. The dipole moment, magnitudes of dipole-dipole interactions, molecular rigidity and flexibility, length of breath ratio, intermolecular closeness all are play important role in mesomorphism and the degree of mesomorphism. The increasing order of nematic thermal stability is attributed to the increasing order of intermolecular cohesions corresponding to increasing number of carbon atoms present from Series-A ($-OC_{12}H_{25}$ (m)) to series-1 ($-OC_{10}H_{21}$(p)) to Series-B ($-OC_7H_{15}$(m)) due to increasing order of polarities and polarizability caused by their lateral groups or para substitutents for the same homologue in series A, 1 and B, respectively. The alternation of nematic thermal stability or mesophase lengths are related with the combined effects of molecular rigidity in combition with flexibility and the unexpected status of both ended n-alkoxy end groups, which may fluctuate with the status of flexible groups and their polarity or polarizability. Therefore, it may acquire increasing or decreasing or alternating order of facilitating or stabilizing mesophase or mesophases in enantiotropic manner. Thus, present chalconyl homologous series is predominantly nematogenic and partly smectogenic of low melting type and shorter mesophase lengths.

Conclusions

- Novel homologous series of single central bridge linking two phenyl rings and n-alkoxy terminal groups is enantiotropically nematogenic and smectogenic.
- The group efficiency order derived on the basis of (a) thermal stability (b) early commencement of mesophase (c) mesophaselengths for smectic and nematic are as under
  (1) **Smectic**
  $-OC_{12}H_{25} > -OC_{10}H_{21} > -OC_7H_{15}$
  Nematic
  $-OC_{12}H_{25} > -OC_{10}H_{21} > -OC_7H_{15}$
  (2) **Smectic**
  $-OC_{12}H_{25} > -OC_{10}H_{21} > -OC_7H_{15}$
  Nematic
  $-OC_{12}H_{25} > -OC_{10}H_{21} > -OC_7H_{15}$
  (3) **Sm ± N**

  Upper: $-OC_{12}H_{25} > -OC_{10}H_{21} > -OC_7H_{15}$
  Lower: $-OC_7H_{15} > -OC_{10}H_{21} > -OC_{12}H_{25}$
- Mesomorphism is depended on suitable magnitudes of molecular rigidity and flexibility.
- Present investigation may be useful for LC devices, Their pharmaceutical or biological activity may be exploited for pharmaceutical preparation and agricultural production to reduce the consumption of insecticides and pesticide as they are antibacterial and antifungal.
- Present study supports and raises credibility to the conclusions drawn earlier.

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