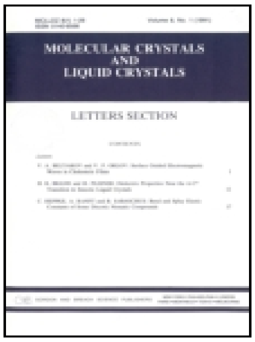

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Dependence of thermotropic mesomorphism on lateral nitro group

Ravindra Solanki and R. B. Patel

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

ABSTRACT

A novel homologous series RO-C_6H_4-COO-C_6H_3-(NO_2)-CO-CH=CH-$C_6H_4OC_{18}H_{37}$(n) para of chalconyl ester derivatives have been synthesized and studied with view to understanding the effect of an ortho substituted nitro group on thermotropic liquid crystal (LC) behavior. The novel homologous series consists of thirteen homologues (C_1 to C_{18}). The C_1 to C_4 homologues are nonliquid crystal (NLC) and the rest of the homologues (C_5 to C_{18}) homologues are enantiotropically nematogenic without exhibition of a smectic phase even in the monotropic condition. Transition temperatures were determined by an optical polarizing microscope (POM) equipped with a heating stage. Texture of nematic phase are threaded or Schlieren. Analytical, thermal and spectral data supported molecular structure of homologues. Thermal stability for nematic is 147.1°C whose mesophase lengths vary between 16.0 and 32.0°C the C_7 and C_{18} homologues, respectively, and their mesogenic exhibition range between 96.0 and 166.0°C. Thus, the present novel series is middle ordered melting type, Group efficiency order is derived from comparative study of structurally similar series. The transition curves of a phase diagram behaved in normal manner except C_{10} and C_{16} homologues. Odd-even effect is observed for N-I transition curve. Group efficiency order derived is: -$OC_{12}H_{25}$ (*n*) > -$OC_{18}H_{37}$ (*n*) > -$OC_{18}H_{37}$ (*n*).

KEYWORDS
Nematic; liquid Crystal; smectic; enantiotropy; mesogen

Introduction

Mesogenic [1] materials have been exploited in the benefit of mankind and to the society as a whole for electronic display devices and many other fields [2–4]. The present investigation is planned with a view to understanding and establishing the effect of molecular structure on liquid crystal (LC) properties [5–9]. A novel homologous series of chalconyl ester containing three phenyl rings bonded through carboxy and chalconyl group is proposed to synthesize and their thermotropic properties will be studied. Moreover, the chalconyl group being bioactive group, which is antibacterial, antimalarial anticancer, antifungal, etc., which may be studied by groups of biological scientists of pharmacy, medicine, etc. [10–14] in the benefit of society as a whole. Thus, synthesis of novel compounds may be multi beneficiary to researchers of scientific and technology community by synthesizing proposed novel compounds. Number of homologous series of ester, azo-ester, chalconyl ester derivatives of monomers, dimer and polymers have been reported till the date [15–26]. Group efficiency order will be derived with

CONTACT Ravindra Solanki ✉ ravindrasolanki19@gmail.com Chemistry Department, K. K. Shah Jarodwala Maninagar Science College, Gujarat University, Ahmedabad-8, Gujarat, India.

reference to presence and absence of nitro group. The experimental data will be discussed and interpreted on the basis of molecular rigidity and flexibility [27–30].

Experimental

Synthesis

4-Hydroxy benzoic acid was alkylated using suitable alkylating agent (R-X) to convert it into 4-*n*-alkoxy benzoic acids (A) by modified method of Dave and Vora [31], α-3-Nitro-4-Hydroxy benzoyl β-4$'$-*n*-Octadecyloxy phenyl ethylene (B) was prepared by usual established method [32]. 4-*n*-Alkoxy benzoic acids and α-3-Nitro-4 Hydroxy benzoyl β-4$'$-*n*-Octadecyloxy phenyl ethylene were condensed in 1,3-dicyclohexylcarbodiimide (DCC), 4-dimethyl amino pyridine (DMAP) and CH_2Cl_2 [33] to obtain α-4-(4$'$-*n*-Alkoxy benzoyloxy) 3-nitro benzoyl-β-4$'$-*n*-Octadecyloxy phenyl ethylene. Final products were filtered, washed, dried and purified till the constant transition temperatures obtained. The synthetic route to the novel homologous series of ethylene derivatives is under mentioned in Scheme 1.

Characterization

Representative homologues of a series were characterized by elemental analysis, Infra red 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 on Perkin-Elmer PE 2400 CHN analyser (Table 1). Transition temperature and LC properties (Textures) were determined using an optical polarising microscopy equipped with heating stage. Textures of some homologues for the nematic phase determined by miscibility method (Table 2).

Analytical data

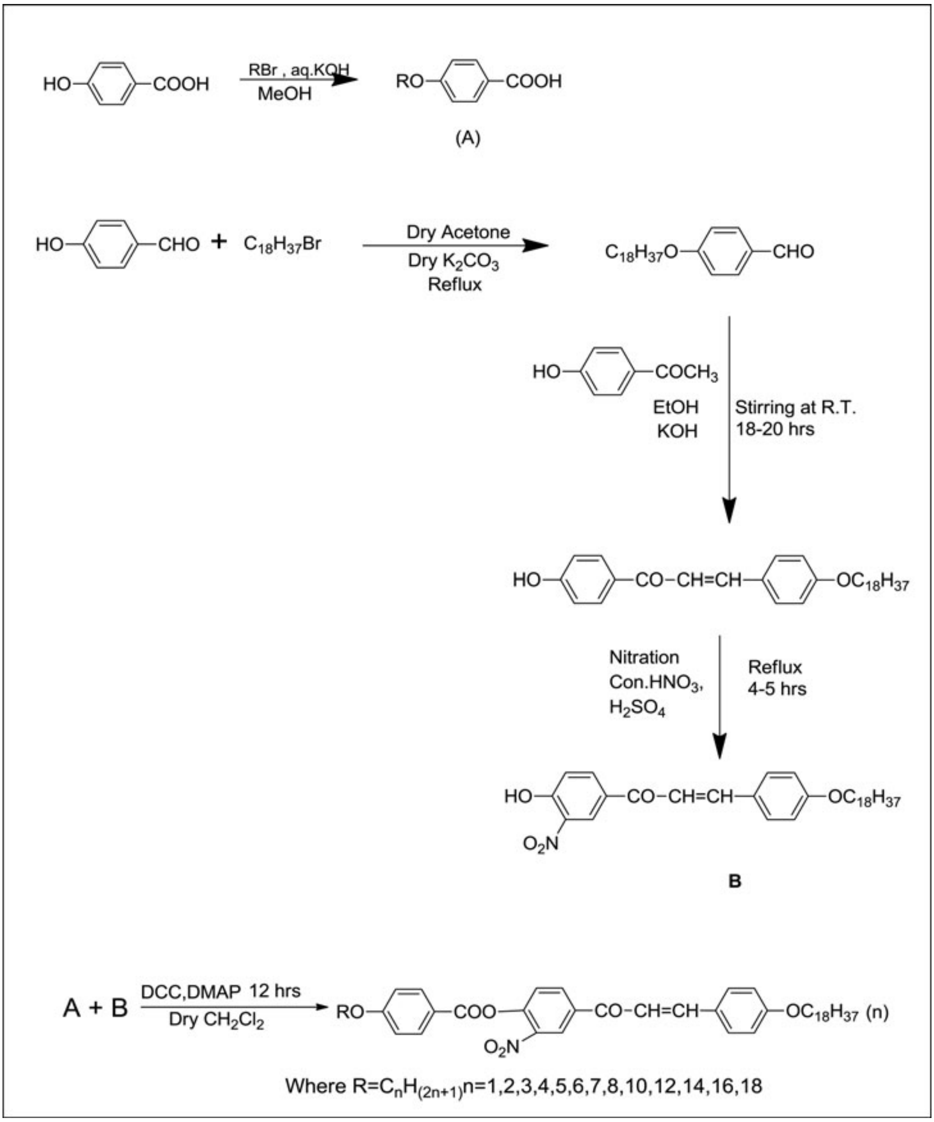
IR spectra (KBr) in cm^{-1} for pentyloxy, decyloxy derivatives

Pentyloxy. 675, 725 (C-H alkane), 761 Poly methylene $(\text{-CH}_2\text{-})_n$ of -OC_5H_{11}, 835,(-C-H- def. di-substituted-Para & Ortho aromatic ring), 894 Poly methylene ($\text{-CH}_2\text{-}$) of $\text{-OC}_{18}H_{37}$, 1074 (-C-H- def. hydrocarbon), 1114 and 1172(-C-O-) Str, 1259 and 1303 and 1321(C=O str in $(CH_2)_n$ Chain), 1384 (-N-O str Symmetric), 1512 (-N-O str Asymmetric),1581 (-C=C-)str, 1606,1616 (-C=O in CH=CH- group), 1730 (-COO- ester group), 2927 and 3033 (-C-H str in CH_3).

Decyloxy. 667 (C-H- alkane), 725 Poly methylene ($\text{-CH}_2\text{-}$)n of $\text{-OC}_{10}H_{21}$,829 and 894(-C-H- def. m di-substituted-Para & Ortho aromatic ring), 975 (-C-H- def. hydrocarbon), 1022,1072, 1122, 1172,1215,1255(-C-O-) Str, of $C_{18}H_{37}$,1301 and 1336 (-C-O str in -(CH_2)n chain, 1386 (-N-O str Symmetric)1421 (-C-H- def. in CH_2),1512 (-N-O str Asymmetric) and 1548 (-C=C-)str, 1608 (-C=O in CH=CH- group), 1722 (-COO- ester group), 2856 and 2923 and 3035,3064 (-C-H str in CH_3).

^{1}H NMR spectra in $CDCl_3$ in δ ppm for octyloxy & octadecyloxy derivative

Octyloxy. 0.90 (t, -CH_3 of -C_8H_{17}), 1.32–1.80 (m, n-poly methylene groups of-OC_8H_{17}), 1.55–1.76 (m, n-poly methylene groups of $\text{-OC}_{18}H_{37}$), 4.10–4.20(s,$\text{-OCH}_2\text{-CH}_2$-of$OC_{18}H_{37}$),



Scheme 1. Synthetic route to the series.

4.0–4.2 (s,-OCH_2-CH_2-of OC_8H_{17}), 7.58 and 8.20(s,-CO-CH=CH), 8.5–8.9 (s, p-di substituted phenyl ring).

Octadecyloxy. 0.88(t, -CH_3 of -$C_{18}H_{37}$), 1.3–1.43(m, n-poly methylene groups of -$OC_{18}H_{37}$), 1.5–1.7(m, n-poly methylene groups of - $OC_{18}H_{37}$),4.1(s, -OCH_2-CH_2-of $OC_{18}H_{37}$), 4.1–4.4(s,-OCH_2-CH_2- of $OC_{18}H_{37}$), 6.94–7.15 (s, substituted benzene), 6.9–7.2(s, -CO-CH=CH), 7.6–7.8(s, p-substituted phenyl ring).

Results and discussion

The transition temperatures of novel chalconyl ester derivatives of lateral -NO_2 group are relatively higher than the other structurally similar series and the ten to twenty persent lower than the corresponding *n*-alkoxy dimeric acids for the same homologue. The nematic mesophase

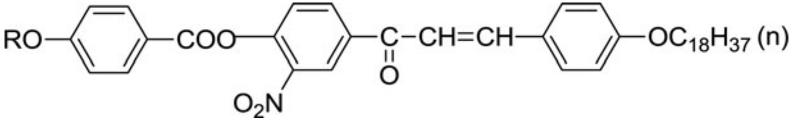
Table 1. Elemental analysis for butyloxy, heptyloxy, tetradecyloxy, hexadecyloxy derivatives.

		Elements found %			Elements calculated %		
Sr. No.	Molecular formula	C	H	N	C	H	N
1	C_4	74.90	7.80	1.78	74.05	8.20	1.90
2	C_7	73.90	8.10	1.70	74.70	8.60	1.80
3	C_{14}	74.89	8.95	1.50	75.96	9.20	1.60
4	C_{16}	76.10	8.92	1.30	76.27	9.50	1.50

Table 2. Textures of Nematic phase by miscibility method for C_7, C_{10}, C_{16}, C_{18}.

Sr. No.	Homologue	Texture
1	C_8	Threaded
2	C_{12}	Threaded
3	C_{14}	Schlieren
4	C_{18}	Schlieren

Table 3. Transition Temperatures in °C for Homologous series:



Homologous series: α-4-(4′-*n*-Alkoxy benzoyloxy) benzoyl-β-4′-*n*-Octadecyloxy 3-nitro phenyl Phenyl ethylenes

		Transition temperatures in (°C)		
Compound no.	*n*-alkyl chain C_nH_{2n+1}	Smectic	Nematic	Isotropic
1	C_1	–	–	196.0
2	C_2	–	–	189.0
3	C_3	–	–	184.0
4	C_4	–	–	168.0
5	C_5	–	118.0	165.0
6	C_6	–	138.0	166.0
7	C_7	–	112.0	128.0
8	C_8	–	120.0	150.0
9	C_{10}	–	138.0	161.0
10	C_{12}	–	124.0	145.0
11	C_{14}	–	112.0	139.0
12	C_{16}	–	116.0	142.0
13	C_{18}	–	96.0	128.0

formation commences from C_5 homologue without exhibition of smectic property till the last homologue (C_{18}). Transition temperature (Table 3) as determined by POM were plotted against the number of carbon atoms present in *n*-alkyl chain “R” of -OR group and then Cr-N as well as N-I transition curves are obtained by linking like or related points as depicted in a phase diagram (Fig. 1) as shown in Fig. 1.

The Cr-N/I transition curve follows a zigzag path of rising and falling with overall descending tendency and behaved in normal manner. *N-I* transition curve behaves in normal manner except at C_8 homologue for which *N-I* transition point deviates from expected place below the ten to eleven degree Celsius temperature *N-I* transition curve for odd member lye below the curve for even members showing odd-even effect unusual manner. The texture of nematic phase are threaded or Schlieren as determined by miscibility method of some representative members of a series and by direct observation of texture on the heating top of POM, for other

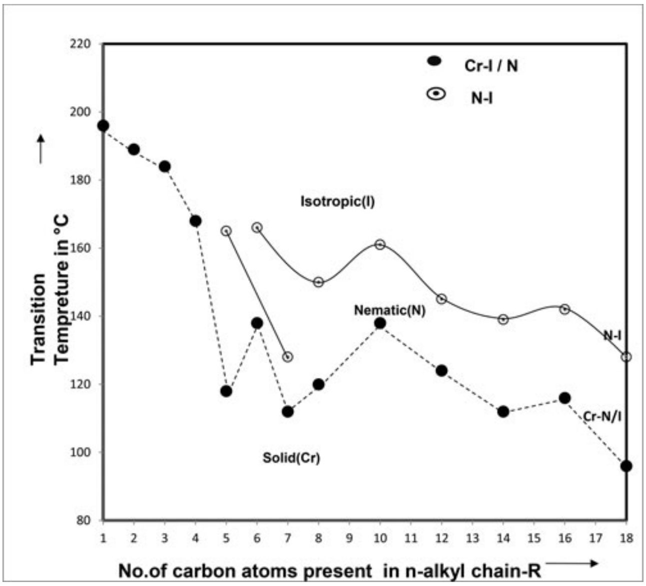


Figure 1. Phase behavior of the series.

homologues of a series. Analytical, thermal, and spectral data conformed the molecular structure of homologues. The variation in mesogenic properties, behaviors and mesophase lengths, etc. from homologue to homologue in present novel series is observed. Thus, present series is only nematogenic without exhibition of smectogenic character and middle ordered melting type whose transition temperatures vary between 96.0 and 196.0°C.

Dimerization of n- alkoxy acids disappears by esterification process by braking of hydrogen bonding which may lower transition temperature but the increase of transition temperature is attributed due to the polarizability induced by laterally substituted highly polar -NO_2 group. The exhibition of only nematogenic property is attributed to the position of -NO_2 group in the sequential order of its group efficiency as nematogenic functional group. Absence of smectogenic character indicates absence of lamellar packing of molecules. The nonmesomorphicity of C_1–C_4 homologues and absence of smectogenic property is due to their high crystallizing tendency. The exhibition of nematic property (C_5–C_{18}) homologues is attributed to the suitable magnitudes of anisotropic forces of intermolecular attraction and closeness as a consequence of favorable molecular rigidity and flexibility caused by suitable magnitudes of dispersion force and dipole- dipole interaction which maintains the floating of homologue on the surface under the influence of exposed thermal vibrations with statistically parallel orientational order to facilitate formation of nematic mesophase for definite range of temperature. The odd-even effect observed for *N-I* transition curve is due to the odd and even number of carbon atom present in *n*-alkyl chain “R” of -OR group. The disappearance of odd-even effect from C_7 or C_8 is attributed to the longer *n*-alkyl chain “‘R” of -OR and -$C_{18}H_{37}$ of -$OC_{18}H_{37}$ (*n*) which may coil or band or flex or couple to lye with principal axes of core structure of molecule, modifying magnitudes of molecular rigidity and flexibility affecting possibility of mesophase and the degree of mesomporphism. The appearance of deviation in transition temperature for C_8 homologue below expected transition temperature is attributed to the unexpected status of n-alkyl chain or chains. The variations in mesogenic properties behavior and the degree of mesomorphism from homologue to homologue in the present novel homologous series is due to the sequentially and progressively added methylene unit or units in

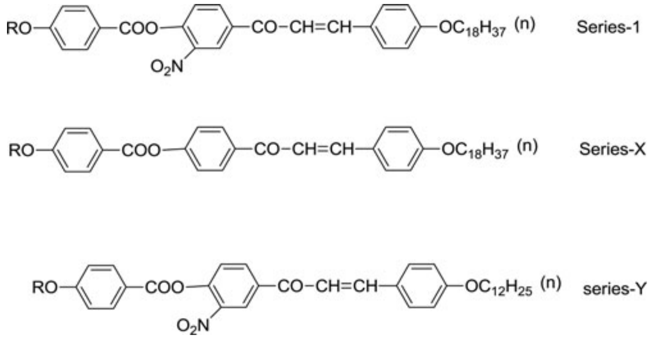


Figure 2. Structurally Similar analogous Series.

n-alkyl chain “‘R” of -OR group. The changing mesogenic behavior of present novel series -1 are compared with structurally similar analogous series-X [34] and Y [35] as mention below in Fig. 2.

From above Fig. 2, it is clear that, homologous series 1, X and Y are identical with respect to three phenyl rings, two central bridge and left n- alkoxy terminal which contributes to the total molecular rigidity and partly contributes to the molecular flexibility for the same homologue from series to series, but, differs from homologue to homologue in the same series. Homologous series-1 and X differs respect to presence and absence of lateral -NO_2 group which partly contributes to total molecular flexibility, molecular polarizability and polarity. Homologous series 1 and Y are identical in all respect but, differs with respect to terminally situated -$OC_{18}H_{37}$ (*n*) and -$OC_{12}H_{25}$ (*n*) group contributing to total molecular flexibility for the same homologue from series to series. Thus, mesomorphic properties behavior and degree of mesomorphism will depend upon differing features of series 1, X and Y under comparative study, of analogous series. The thermotropically mesogenic some properties of homologous series 1, X and Y are recorded in Table 4 as shown below for comparative study.

Table 3 represent comparative data of present investigated chalconyl ester homologous series 1 and structurally similar analogous series X and Y selected for comparative study purpose as under.

- Homologous series 1, X, and Y are nematogenic only without exhibition of smectic property.
- Mesomorphism commence from C_5 homologue in all the three series under comparison.
- Thermal stability for nematic is in decreasing order from series Y to serie —1 to series-X.
- Upper mesophase lengths are in increasing order from series-1 to series -X to series -Y but the lower mesophase lengths are in decreasing order from series-Y to series- 1 to series-X.

Table 4. Relative thermal stability in °C.

Series →	Series-1	Series-X	Series-Y
Sm-I or Sm-N			
Commencement of Smectic phase	—	—	—
N-I or I-N	147.1	122.0	182.5
Commencement of nematic phase	(C_5–C_{18})	(C_5–C_{18})	(C_5–C_{18})
	C_5	C_5	C_5
Total	16.0 to 32.0	7.0 to 38.0	17.0 to 45.0
Mesophase length from t_1 to t_2 °C	C_7 C_{18}	C_7 C_{12}	C_{14} C_5

From above comparative points it is clear that, the exhibition of only nematogenic character and the commencement of nematic phase are identically same which suggests that the end to end intermolecular cohesion and closeness are nearly equivant as a consequence of equivalent molecular rigidity and flexibility induced by three phenyl rings, two similar central bridges and terminally situated flexible n- alkoxy group. However, the difference in the magnitudes of thermal stability among the series 1, X and Y can be attributed to the presence and absence of laterally substituted flexible nitro group whose group polarizability and polarity factor predominates and contribute more to the intermolecular end to end cohesion and attractions, Thus, energy stored (ΔH) by the molecules of same homologue from series to series containg lateral nitro group have (series- 1 and *Y*) higher resistivity toward exposed thermal vibration leading to higher thermal stability for nematic as compared to the corresponding thermal stability of series-X and order of lower mesophaselengths.

Conclusions

- Homologous series-1 of present investigation is enantiotropically nematogenic whose mesophaselengths minimum to maximum vary between 16.0 and 32.0°C and middle ordered melting type.
- The group efficiency order derived (i) on the basis of thermal stability, (ii) early commencement of mesophase and (iii) upper mesophase lengths for nematic are as under.
  (i) Nematic

$$\begin{array}{ccccc} -\mathrm{OC}_{12}\mathrm{H}_{25}(n) & > & -\mathrm{OC}_{18}\mathrm{H}_{37}(\mathrm{n}) & > & -\mathrm{OC}_{18}\mathrm{H}_{37}(\mathrm{n}) \\ \mathrm{With}-\mathrm{NO2} & & \mathrm{With}-\mathrm{NO2} & & \mathrm{Without}-\mathrm{NO2} \end{array}$$

  (ii) Nematic

$$\begin{array}{ccccc} -\mathrm{OC}_{18}\mathrm{H}_{37}(\mathrm{n}) & = & -\mathrm{OC}_{18}\mathrm{H}_{37}(\mathrm{n}) & = & -\mathrm{OC}_{12}\mathrm{H}_{25}(\mathrm{n}) \\ \mathrm{With}-\mathrm{NO2} & & \mathrm{Without}-\mathrm{NO2} & & \mathrm{With}-\mathrm{NO2} \end{array}$$

  (iii) (Nematic ± Smectic)

$$\begin{array}{ccccc} -\mathrm{OC}_{12}\mathrm{H}_{25}(\mathrm{n}) & > & -\mathrm{OC}_{18}\mathrm{H}_{37}(n) & > & -\mathrm{OC}_{18}\mathrm{H}_{37}(\mathrm{n}) \\ \mathrm{With}-\mathrm{NO2} & & \mathrm{Without}-\mathrm{NO2} & & \mathrm{With}-\mathrm{NO2} \end{array}$$

- Mesomorphism is very sensitive and susceptible to the molecular structure as a consequence of
- molecular rigidity and flexibility.
- Study of binary system can be useful to manufacture electronic display devices. Chalconyl derivatives being bioactive molecules which may be applied or exploited in pharmaceutical preparation and in agricultural production of healthy cropes to act as antibacterial as well as antifungal material which may reduce the consumption of insecticide and pesticides.
- Present investigation supports and raises credibility to the conclusion drawn earlier.

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