



Liquid crystalline materials with lateral polar chloro substituent

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Abstract

Twelve novel liquid crystalline materials of the homologous series 4-(4'-*n*-alkoxy benzyloxy)-3-chloro benzoic acid have been synthesized. All members of the series exhibit mesomorphism. The smectic mesophase is exhibited by the very first member along with nematic phase which persists up to *n*-dodecyl homologue. The last two members exhibit only smectic phases. The prepared materials are characterized by elemental analysis and spectroscopically. Mesomorphism has been studied by polarizing microscopy and differential scanning calorimetry. Mesogenic behaviour of series is discussed by taking into consideration other structurally similar materials to signify the influence of lateral substituent.

Keywords: Liquid crystalline material, Lateral polar substituent, Mesomorphism.

Introduction

Innovation in the area of novel materials has importance in shaping life of modern society. Research in material science has resulted in the development of many devices with specific applications. Liquid crystalline compounds are class of materials that has triggered massive research activity and has resulted in commercial development of many materials of interesting applications. Liquid crystals are recognised as orientationally ordered fluids formed by shape-anisotropic organic molecules¹⁻⁶. Thermotropic liquid crystals exhibit mesomorphism based on the variations of temperature and the range of temperature depending upon their individual molecular rigidity and flexibility generated from respective molecular structure⁷⁻⁸. For potential commercial applications, the existence of mesophases at lower temperatures is of very high importance. Lateral substituents play an important role in order to decrease the phase transition temperatures. Many researchers have reported their work on different short lateral substituents⁹⁻¹⁴. Report on different short and long lateral groups in three benzene ring system of our past work, also suggested that presence of lateral substituents depresses thermal stabilities of mesophases^{15,16}. However, the lateral substituent on the system comprising two phenyl rings is expected to reflect more in the depression of transition temperatures due to significantly change in length to breadth ratio. Keeping this in view, synthesis, characterization and mesogenic properties of novel compounds, having two benzene rings connected *via* ester group and possess a polar chloro substituent at the middle benzene nucleus, are reported in this communication.

Materials and methods

Requisite starting materials such as *p*-hydroxybenzoic acid, thionylchloride, *n*-bromo alkane, ethyl alcohol, KOH, bleaching powder, toluene *p*-sulphonamide, were used as received.

Solvents were purified and dried by standard methods before use. C and H percentage are obtained from a Coleman elemental analyzer. Compounds were analysed for Fourier transform infrared spectroscopy on Shimadzu 8400 FTIR instrument. ¹HNMR spectra is obtained from 60 MHz Perkin-Elmer spectrometer by taking tetramethylsilane as references. Leitz Laborlux 12 POL microscope equipped with a heating stage was used to investigate liquid crystalline properties of the compounds. Thermodynamic parameters ΔH and ΔS for transition, are obtained by calorimeter (Mettler TA 4000).

Experimental: Preparation of Materials: 4-*n*-Alkoxy benzoic acids and respective benzoyl chlorides are prepared following the procedure reported by Dave and Vora¹⁷. 3-Chloro-4-hydroxy benzoic acid was prepared by known method¹⁸. The series, namely, 4-(4'-*n*-alkoxybenzyloxy)-3-chloro benzoic acids was synthesized by condensing equimolar quantity of 3-chloro-4-hydroxy benzoic acid and 4-*n*-alkoxybenzoylchloride respectively, in dry pyridine at 5°C. The reaction mixture was then poured into aqueous HCl (50%). The product was washed with diluted NaOH solution and H₂O successively. The resultant compound has been purified by recrystallizing with glacial acetic acid till steady transition temperature is attained (Table-1). The elemental analysis has been found in consonance with the theoretical values (Table-2). Scheme-1 shows the route for preparation of compounds.

Spectral Data: FTIR (KBr) spectra (cm⁻¹): *n*=C₇H₁₅: 2951(C-H str., aromatic, Ar), 2932 (C-H str., aliphatic, Ali), 1735 (C=O str., ester), 1419, 1246, 1167 (aryl ether), 1057, 840, and 761 (Spectrum is shown in Figure-1).

n=C₁₂H₂₅: 2950 (C-H str., Ar), 2917 (C-H str., Ali), 1738 (Carbonylstr., ester), 1424,1258, 1166 (aryl ether), 1054, 845, and 760 (Spectrum is shown in Figure-2).

Proton NMR Spectra (δ ppm): $n=C_{12}H_{25}$: $\delta = 0.9$ (m, 3H, Methyl), 1.3 (s, 20H, $-(CH_2)_{10}-$), 4.0 (t, 2H, $-Ar-(OCH_2)-$), and 6.8-8.3 (m, 7H, Ar-H) (Spectrum is shown in Figure-3).

DSC Analysis: The phase transition enthalpies for the C-16 member have been obtained by DSC and data are recorded in Table-3.

Table-1: Transition temperatures ($^{\circ}C$) of Series I.

n-Alkyl C_nH_{2n+1} . Group (n) =	Transition Temperatures ($^{\circ}C$)			
	Sm C	Sm A	N	I
Series I				
1	185	--	210	280 (d)
2	160	--	185	255 (d)
3	172	--	190	260 (d)
4	145	--	165	245
5	130	--	145	236
6	108	--	137	228
7	109	--	130	215
8	90	--	130	205
10	85	--	125	185
12	96	--	128	180
14	95	125	--	155
16	86	130	--	145

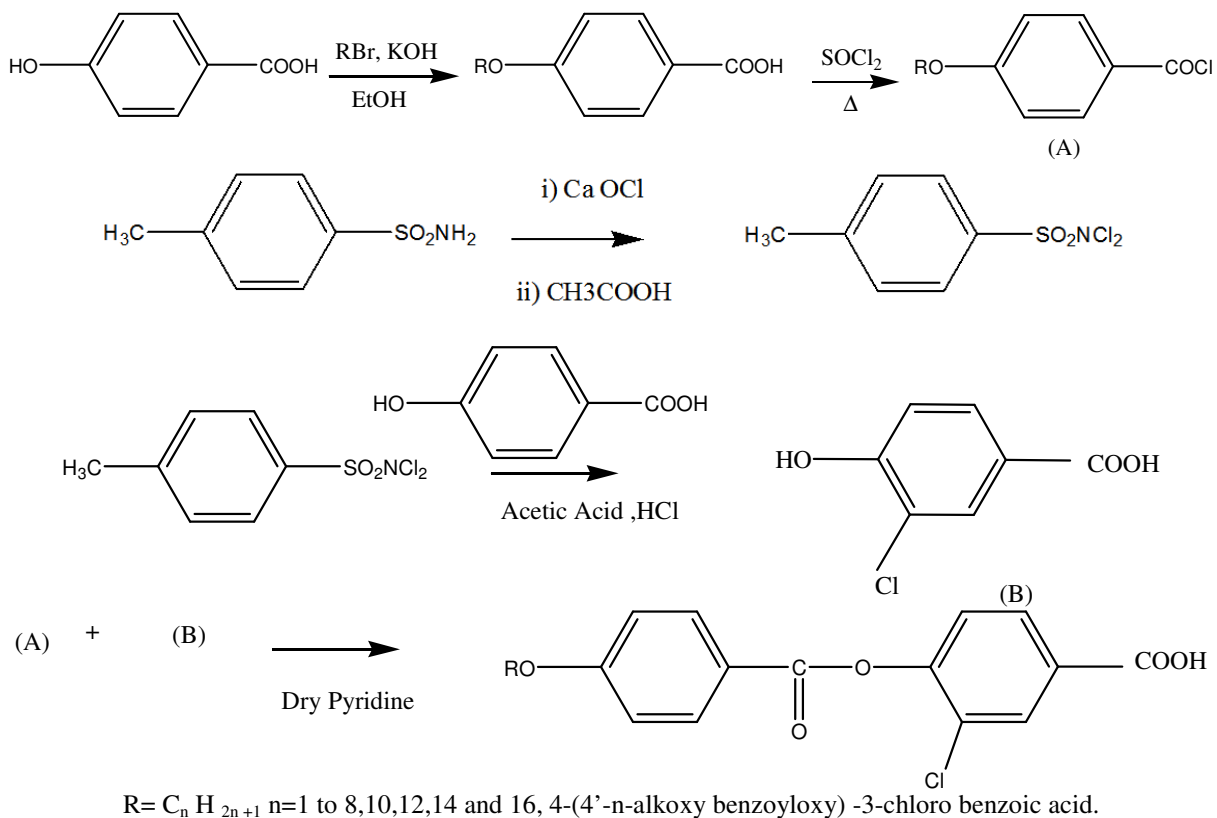
d-decomposition, Sm-Smectic, N-Nematic, I- Isotropic.

Table-2: Elemental analysis for Butyloxy, Octyloxy, Decyloxy and Tetradecyloxyderivative.

Molecular formula	C % found (% calculated)	H % found (% calculated)
$C_{18}H_{17}O_5Cl$	61.45 (61.97)	4.52 (4.87)
$C_{22}H_{25}O_5Cl$	65.78 (65.26)	6.35 (6.18)
$C_{24}H_{29}O_5Cl$	66.94 (66.58)	7.16 (6.70)
$C_{29}H_{37}O_5Cl$	68.36 (68.78)	7.39 (7.57)

Table-3: DSC Data.

Member	Transition	Peak temperature (microscopic reading)	Δ (H/Jg $^{-1}$)	Δ (S/Jg $^{-1}$ K $^{-1}$)
Hexadecyl	Cr – Sm	81.2 (86)	18.931	0.0534
	Sm-Iso	134.5 (130)	8.932	0.021



Scheme-1: The route of synthesis of series I compounds.

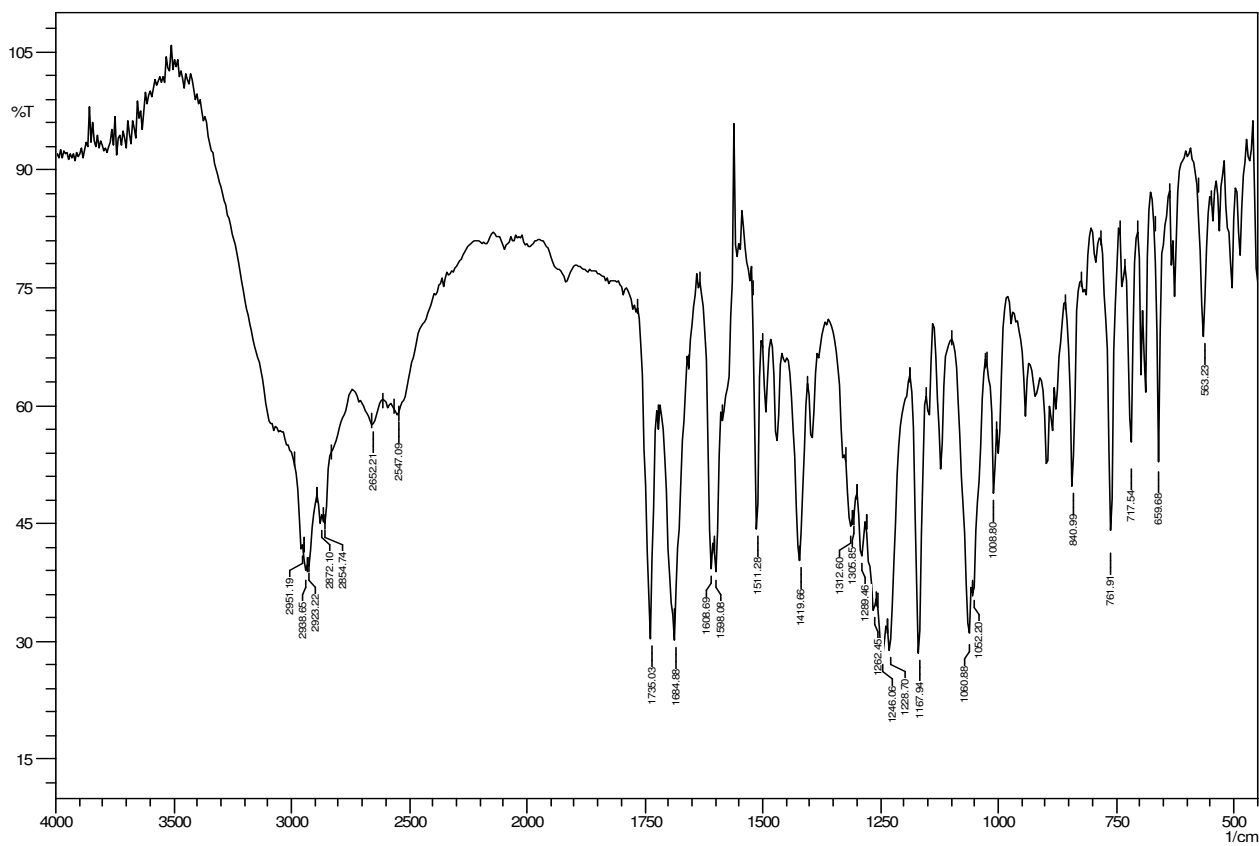


Figure-1: FTIR Spectrum of 4-(4'-n-heptyloxy benzoyloxy)]-3-chloro benzoic acid.

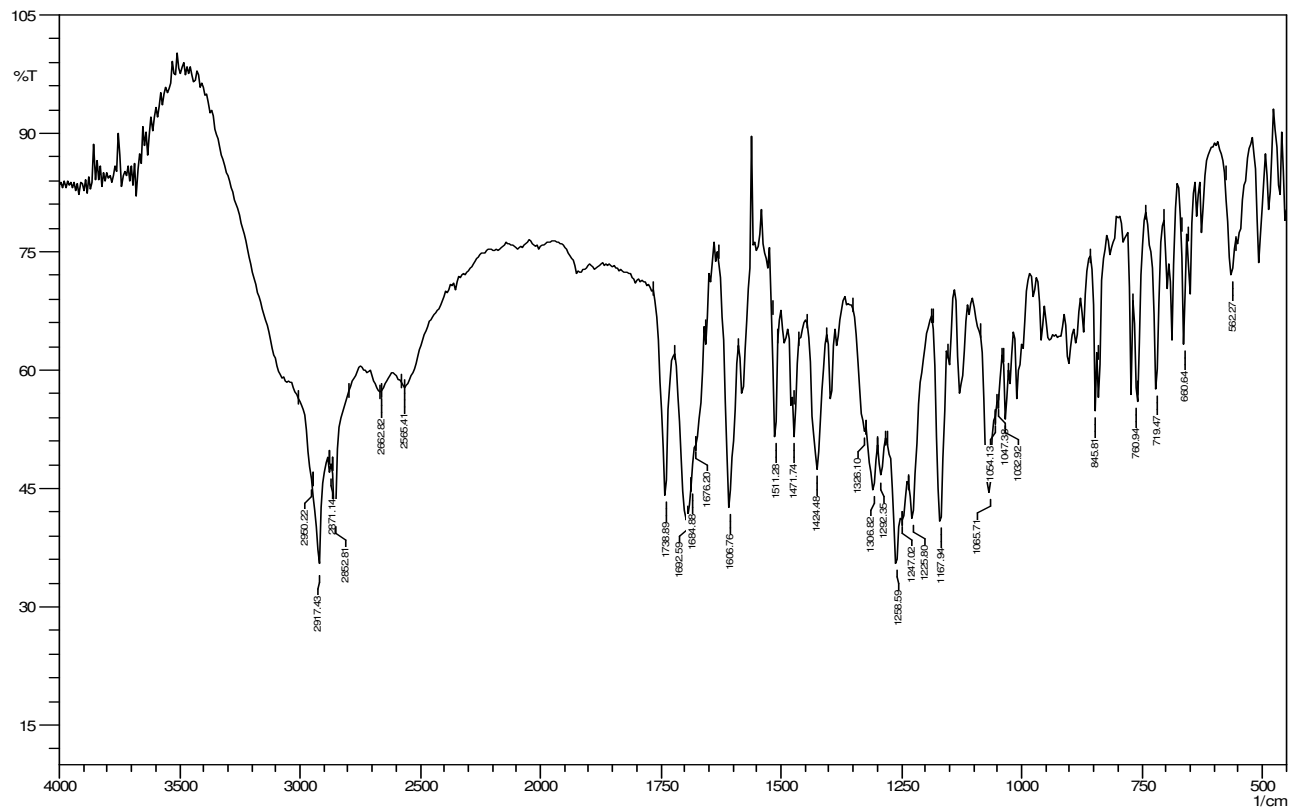


Figure-2: FTIR Spectrum of 4-(4'-n-dodecyloxy benzoyloxy)]-3-chloro benzoic acid.

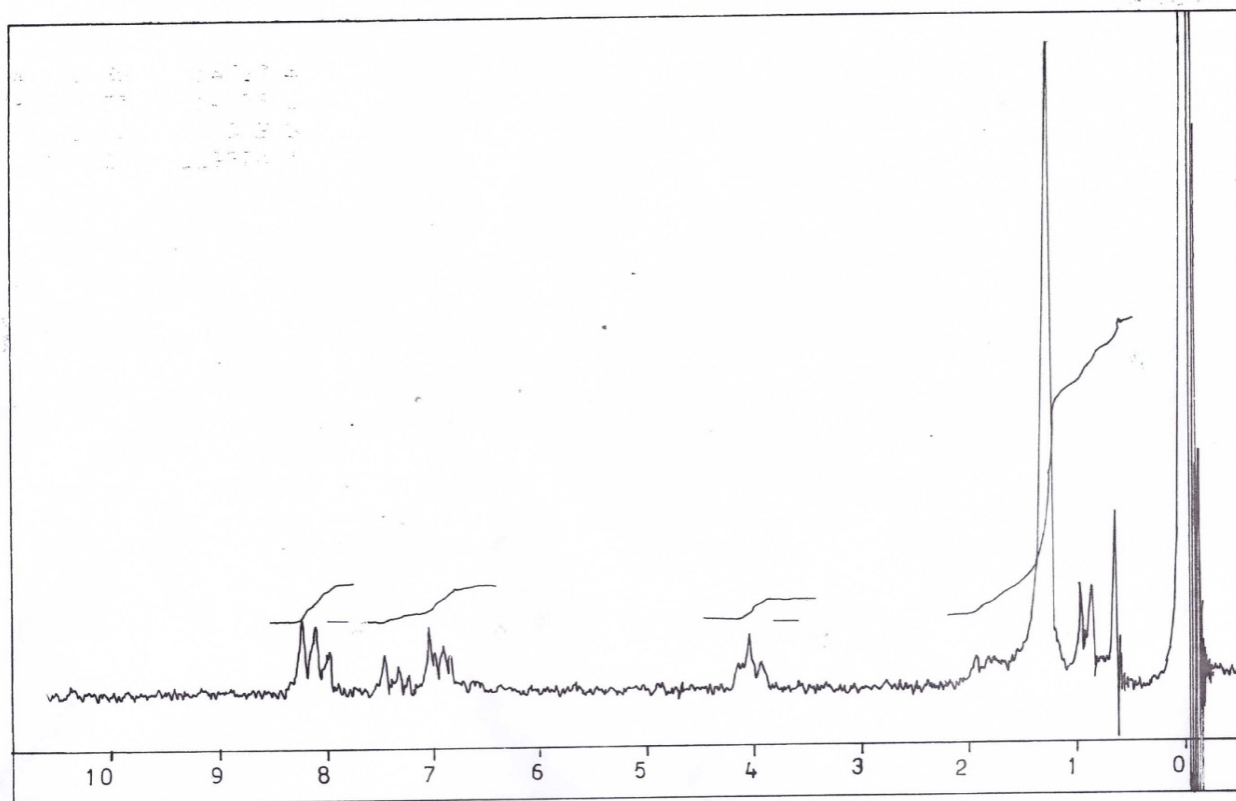


Figure-3: ¹H NMR Spectrum of 4-(4'-n-dodecyloxy benzoyloxy)]-3-chloro benzoic acid.

Results and discussion

In the present study, twelve homologues of the series 4-(4'-*n*-alkoxy benzoyloxy)-3-chloro benzoic acids are prepared and their mesogenic characteristics are investigated. Each member of present series is found to exhibit liquid crystalline properties with good phase lengths. The smectic mesophase is exhibited by the very first member along with nematic phase which persists till C₁₂ homologue. The C₁₄ and C₁₆ homologues show smectic phases alone. The plot of transition temperatures against the number of carbon atoms in alkoxy chain is shown in Figure-4. Nematic-isotropic and smectic-nematic transitions show a steady fall with increase in carbon chain length. Ranges of nematic and smectic phases are found from 52-91°C and 15-60°C, respectively.

In order to correlated molecular structure and mesogenic properties, *n*-octyloxy member (compound 1) is compared with other structurally similar compounds A¹⁹ and B²⁰ reported in literature. Figure-5 shows molecular structures and transition temperatures of these compounds under comparison.

Looking to mesogenic properties of compound 1 and compound A, it is observed that smectic and nematic phase ranges of compound 1 are lowered by 10°C and 45°C, respectively, than that of compound A. Figure-5 shows that the molecular structures of these materials are similar in all aspects but differ in side group. *n*-Octyloxy homologue has a lateral -Cl substituent, while it is absent in compound A. The presence of -Cl group in the side position in *n*-octyloxy derivative leads to an increase in molecular breadth and forces apart the molecular axes of the molecules, so reducing the strength of intermolecular attractions. Both smectic and nematic mesophases depend to a greater and lesser extent on the cohesive forces to maintain the parallel orientations of the molecules. Therefore, substitution leading to an increase in molecular breadth will decrease the smectic and nematic thermal stabilities²¹.

Hence, breadth increasing effect due to lateral chloro group of *n*-octyloxy derivative (compound 1) causes depression in smectic and nematic transition temperatures in comparison to compound A.

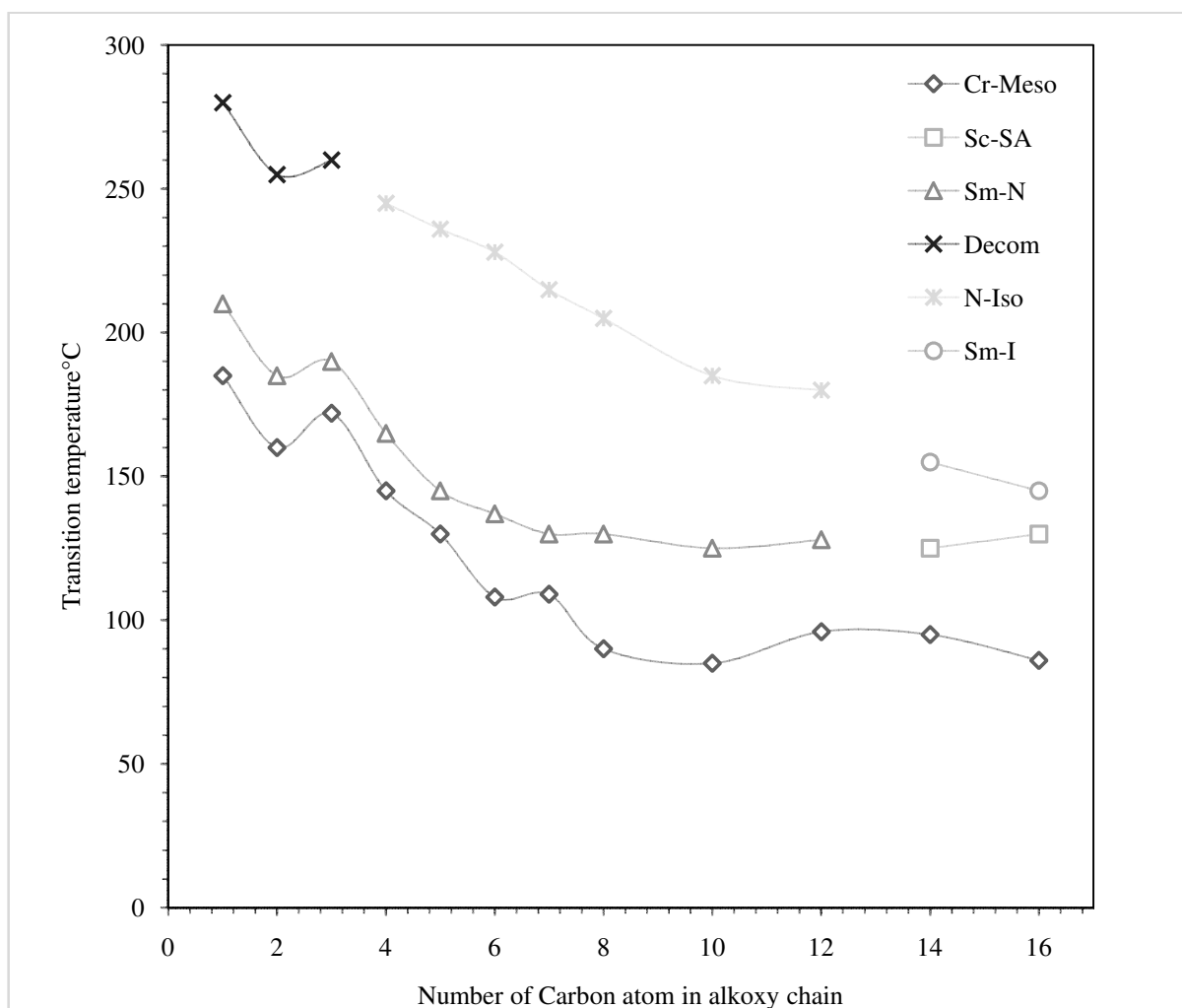


Figure-4: The phase behaviour of series.

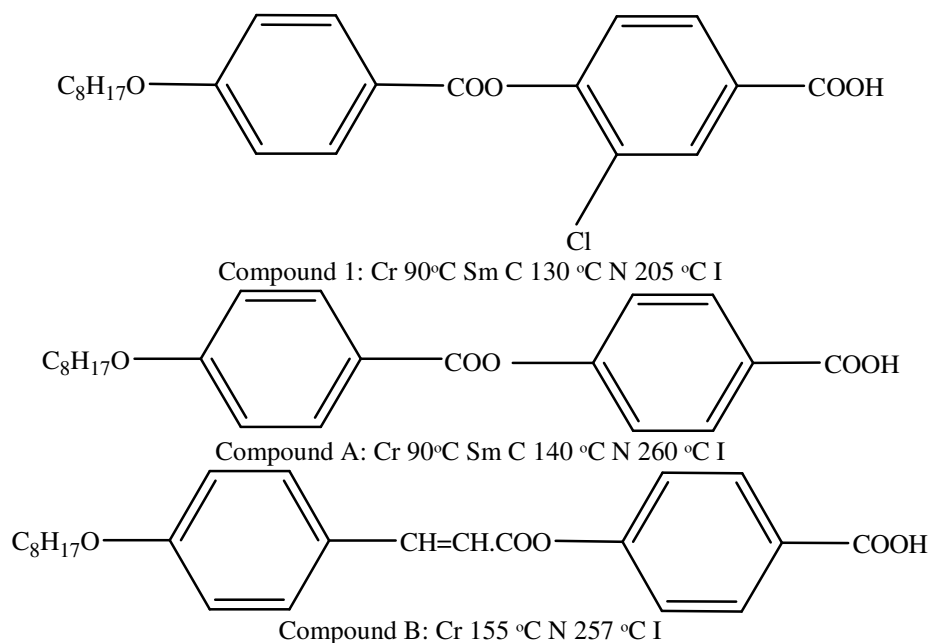


Figure-5: The comparative molecular structures and transition temperatures of compounds 1, A and B.

Figure-5 shows that material with lateral chloro group exhibits enantiotropic smectic and nematic phases with the ranges of temperature $40^\circ C$ and $75^\circ C$, respectively, while material without lateral group exhibits only nematic phase with temperature range of $102^\circ C$. The nematic phase range was found lower (by $27^\circ C$) with lateral group containing material. The difference in phase lengths of these materials can be correlated with the structures of these compounds. The comparison of structures of these compounds shows that compound 1 differs with compound B in two aspects. Firstly compound 1 has two $-COO-$ central linkages in place of $-COO-$ and vinyl carboxy $-CH=CH.COO-$ linkages of compound B. Secondly compound 1 has a chloro group in lateral position whereas compound B is without any lateral group. Both these factors i.e. presence of longer $-CH=CH.COO-$ linkage increases length of themolecules and absence of lateral group resulting in higher length to breadth ratio of compound B. For the liquid crystalline compounds, type and length of mesogenic phase depends on the shape, size and polarizability of the molecules. Higher length of the molecules are known to enhance its polarizability and such compounds would exhibit liquid crystalline property with broader phase length²¹. Therefore, the higher length of molecules of compound B causes terminal attractions to become stronger and gives rise to wider nematic phase length than that of compound 1. Further compound 1 exhibits smectic mesophase which is not observed in compound B. This may be due to the presence of short lateral polar chloro group which introduces an additional dipole moment into the molecule. The dipole may reinforce lateral intermolecular attraction in compound 1 and increases its polarizability. This factor causes increase in lateral cohesive forces that hold together the compound in more ordered layered structure of

smectic phase. Therefore compound 1 exhibits smectic mesophase.

It is interesting to note that smectic mesophase is exhibited by the very first member in series and polymorphism of the smectic phase is also observed.

Conclusion

In this paper, we have presented, synthesis and characterization of a homologous series composed of two phenyl rings, joined through central ester linkages and possess a chloro group in the lateral position. The study revealed that lateral chloro group results in the depression of nematic mesophase of the present system due to change in length to breadth ratio but high polarity of chloro group favours formation of parallel molecular arrangement resulting in an early exhibition of smectic mesophase. The knowledge of structure–property relationship is important in the design of novel liquid crystalline materials to developed new advanced applications.

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