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Research

Green Synthesis and Mesomorphic Characteristics of a Phenoxyethyl tail with Alkoxy Benzoate Homologous Series

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Abstract:

A novel mesogenic homologous series of phenoxyethyl-tailed benzoates, namely 4-((3-phenoxypropanoyl) oxy) phenyl 4-*n*-alkoxybenzoate (Series **PX*n***), was synthesized and systematically investigated to evaluate the influence of terminal alkoxy chain length and phenoxyethyl moiety on mesomorphic behavior. The compounds were prepared via conventional and green synthetic routes and characterized by FT-IR, and ^{1}H NMR spectroscopy. Mesophase behavior was examined using polarizing optical microscope (POM) and differential scanning calorimetry (DSC). The lower homologues (**PX*1*** & **PX*2***) were found to be non-mesogenic, while intermediate members exhibited monotropic nematic or Smectic A (SmA) phases. Notably, **PX*3*** & **PX*4*** displayed monotropic nematic and smectic A mesophase. Higher homologues (***n*** **≥ 5**) displayed enantiotropic SmA mesophases with decreasing transition temperatures upon increasing alkyl chain length. Differential scanning calorimetry (DSC) thermograms exhibited distinct phase transition temperature, indicating a clear homologous dependence of the thermal properties. Structural comparison further revealed that the presence of the phenoxyethyl terminal group and the benzoyloxy central linkage plays a crucial role in modulating molecular polarizability and mesophase stability. Overall, this study emphasizes the structure–property relationship that governs phase transition behavior in phenoxyethyl-based liquid crystalline systems.

Keywords: Homologous series, phenoxyethyl tail, monotropic, enantiotropic, smectic A, nematic

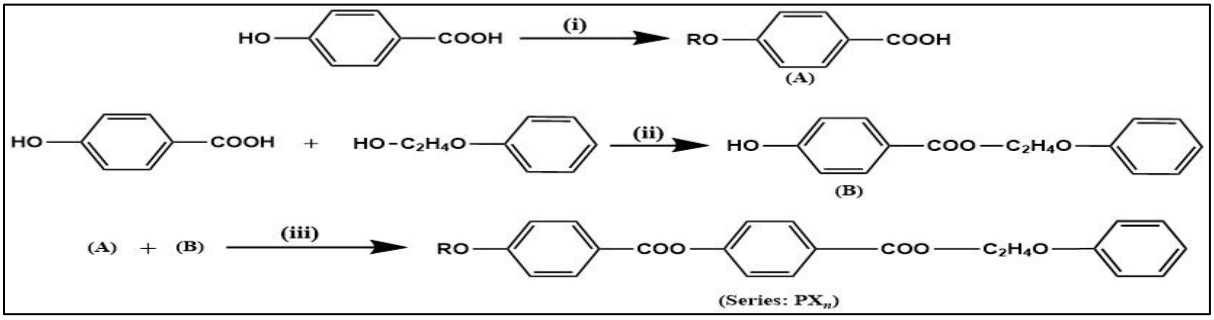
1. Introduction

The mesomorphic behavior of liquid crystalline compounds primarily depends on their molecular arrangement, where even minor variations in molecular geometry can lead to significant changes in mesomorphic properties. Numerous mesogenic homologous series containing central linkages such as -COO-, -N = N-, -CH = N-, -CH = CH-, -C ≡ C-, -CH = CH-COO-, -CONH-, etc., along with alkyl and/or alkoxy terminal chains, have been reported [1–4]. In recent years, cinnamic acid ester (C6H5–CH = CH–COO–) has gained considerable attention in molecular design for the development of novel liquid crystalline materials. The presence of the conjugated –CH = CH–COO– unit imparts rigidity and planarity to the molecular framework, which favors mesophase formation. Compounds containing this moiety are known to exhibit desirable properties such as relatively low melting points, high clearing temperatures, and suitable mesophase temperature ranges, making them attractive for both fundamental studies and practical applications [5–14]. Earlier investigations by Jones and Ratto [15] demonstrated that esters of cinnamic acid not only possess low melting points but also exhibit wide nematic mesophase ranges along with relatively high nematic–isotropic transition temperatures. These characteristics highlight their potential as efficient mesogenic materials and justify their continued exploration in liquid crystal research. Zhang et al. [16] reported that cinnamates act as effective photoalignment materials, making them useful in liquid crystal displays. Cinnamate esters have been widely studied and are well documented in liquid crystal research [17–25]. Vora and Rajput [26] showed that binary mixtures of cinnamate esters exhibit a wide range of smectic and nematic mesophases. Sadashiva et al. [27] synthesized and characterized esters of trans-4-n-alkoxycinnamic acid and related derivatives, which displayed ferroelectric and antiferroelectric phases. Kashyap et al. [28] conducted a comparative study on benzoate- and cinnamate-linked homologous series. Thaker and Kanojiya [29] investigated mesomorphic properties of biphenyl-based compounds with azo-ester and azo-cinnamate linkages. Doshi et al. [30] reported the synthesis and mesomorphic behavior of n-butyl-4-(4′-n-alkoxy cinnamoyloxy) cinnamates. Doshi and Patel [31] reported cis-cinnamate esters, specifically n-hexyl-4-(4′-n-alkoxy cinnamoyloxy) cinnamates. They also described a homologous series of 4-(4′-n-alkoxybenzoyloxy)benzyl cinnamates [32]. Serrano et al. [33] investigated the synthesis, characterization, and photoreactivity of liquid crystalline cinnamates, examining their behavior in the presence of a small amount of triplet sensitiser across different temperatures and phases. Kawatsuki et al. [34] synthesized side-chain liquid crystalline polymers containing cinnamoyl biphenyl mesogens and studied their photoreaction properties. Zhang et al. [35] developed a novel photoalignment system using layer-by-layer self-assembled long side-chain cinnamate polyelectrolytes. The photosensitive and photo-cross-linking nature of cinnamoyl groups enables their application in in-plane switching LEDs, IPS-LCDs, and biomaterials [36–39]. Additionally, cinnamoyl-based liquid crystals with reactive vinyl groups are useful in optical data storage, photonic devices, and liquid crystal polymer actuators [40-41]. Jay C. Panchal et al. reported the synthesis of novel liquid crystalline Schiff base compounds containing an ester moiety, along with DFT analysis and mesomorphic investigations. They also developed a new series of rod-like nematic liquid crystals derived from [1,1′-biphenyl]-4-yl (E)-4-((4-n-alkoxybenzylidene) amino) benzoate (X_nI) and 4-benzoylphenyl (E)-4-((4-(n-alkoxy) benzylidene) amino) benzoate (X_nII), and performed a comparative study between the XnI and XnII series. [42-43]. Vinod et al. reveal pyrazolo[1,5-a] pyrazine moieties were synthesized through alkylation, condensation, and esterification with various 4-((4-alkoxybenzylidene) aminobenzoic acids [44].

Phenoxy ring is a compelling aromatic core for the preparation of liquid crystalline compounds. It expands the breadth of the molecules, which can decrease the mesogenic characteristics. However, the phenoxy ethyl derivative may reveal rich phase transition, if the molecule is perfectly designed. In continuation of our work on liquid crystalline phenoxy ethyl derivatives, we have prepared new mesogenic homologous series viz. Phenoxy ethyl-4-*n*-alkoxy benzoyloxy benzoates **(**Series **PX*n*)** to analyze the effect of phenoxy moiety and ester central linkages on phase transition.

2. Experimental

4-hydroxybenzoic acid, 2-phenoxyethan-1-ol, Potassium hydroxide, Methanol, n-alkyl halides, N, N’-Dicyclohexylcarbodiimide, 4-Dimethylaminopyridine, Tetrahydrofuran, Sulfuric acid (H_2SO_4). Thin layer chromatography was performed (Merck). Infrared spectra (IR) were recorded using a Shimadzu IR-408 spectrophotometer with potassium bromide (KBr) pellets, while proton nuclear magnetic resonance spectra (400 MHz) were obtained using a Bruker Avance Neo-spectrometer with deuterated chloroform. Phase appearance and transition were analysed via thermal polarizing optical microscopy (POM) employing a polarizing optical microscope with a heating stage. Leica DM 2500P polarizing optical microscope with a connected with a Linksys temper ature control unit in conjunction with Leica DFC295 camera for image capture. Sample preparation: thin film of powder sample was sand wiched between a glass slide and coverslip. The enthalpies associated with changes in phases, quantified in kilojoules per mole, were determined through the utilization of a Shimadzu DSC-60 plus system, a type of differential scanning calorimeter (DSC). operating at a scanning rate of 10°C per minute.



Scheme PX$_n$: R=C$_n$H$_{2n+1}$.

[***n*** (number of carbon) = 1 to 8,10,12,14,16,18]. (i) R-Br, KOH, Methanol (ii) Conc. H_2SO_4 (iii) DCC (N, N′-Dicyclohexylcarbodiimide), DMAP (4- Dimethylaminopyridine), THF (tetrahydro furan).

Synthesis

2.1 Synthesis of 4-*n*-Alkoxybenzoic acids (A)

4-*n*-alkoxybenzoic acid (A) was synthesized starting from 4-hydroxybenzoic acid [45]. A mixture of 4-hydroxybenzoic acid (0.1 mol), 1-bromoalkane (0.12 mol), and potassium hydroxide (0.25 mol) was dissolved in methanol and refluxed for 7–8 hours. Subsequently, 25 mL of 10% potassium hydroxide solution was added, and the reaction mixture was further refluxed for 2 hours. After cooling to room temperature, the mixture was acidified using a cold 1:1 mixture of hydrochloric acid and ice. The resulting solid product was filtered, collected, and recrystallized from methanol. The purity of the compounds was confirmed by thin-layer chromatography.

2.2 Green synthesis

0.1 mol 4-hydroxybenzoic acid, 0.12 mol 1-bromoalkane, 0.1 mol KOH, and 0.005 mol tetrabutylammonium bromide (TBAB, 5 mol%) as phase-transfer catalyst were suspended in 150 mL water. The mixture was vigorously stirred and heated at 90–95 °C for 7–8 h. Subsequently, 25 mL of 10% aq. KOH was added, and heating continued for 2 h to hydrolyze any ester intermediates. The reaction mixture was cooled to 5 °C, acidified to pH ~2 with 1:1 cold aq. HCl, and the precipitated alkoxy acid collected by filtration, washed with cold water (2 × 20 mL), and dried under vacuum. The product was recrystallized from minimal ethanol or acetic acid until constant transition temperature was obtained.

2.3 Synthesis of *β*-Phenoxyethyl-4-hydroxybenzoate [B]:

β-Pheoxyethyl-4-hydroxy benzoate was synthesized by using conventional method of esterification [46]. 0.125 Mole of 4-Hydroxybenzoic acid, 0.25 mole of phenoxyethanol and 0.018 mole of concentrated sulphuric acid were taken in a round bottom flask. Mixture was refluxed on a sand bath for five-six hours. The whole mass was allowed to cool and poured into about 250 ml of saturated sodium hydrogen carbonate. The organic compounds were extracted by ether. The ether extract was dried on anhydrous magnesium sulphate and evaporated on a rotary evaporator. The residue was distilled under reduced pressure and the solid ester obtained was crystallized repeatedly from methanol till constant melting point was obtained. M. P.: 121°C yield 81%.

Green synthesis

0.125 mol 4-hydroxybenzoic acid, 0.25 mol phenoxyethanol, and Novozym 435 (lipase B from Candida antarctica, 10 wt% relative to acid) were suspended in 200 mL phosphate buffer (pH 7.0, 0.1 M). The mixture was stirred at 45 °C for 24 h under orbital shaking (150 rpm). Progress was monitored by TLC (EtOAc:hexane 1:1). After completion, the enzyme was filtered off, and the product extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with brine (50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by short-path distillation under reduced pressure, followed by recrystallization from minimal methanol to afford the pure ester as a white solid.

Synthesis of 2-Phenoxy ethyl 4-(4-*n*-Alkoxybenzoyloxybenzoate [C]:

0.1 Mole of 4-(4’-*n*-Alkoxybenzoic acids) **[A],** 0.1 mole of *β*-Phenoxyethyl-4-hydroxybenzoate [**B**], 0.1 mole of DCC [47] and 0.1 mole of DMAP were dissolved in dry THF and stirred at room temperature for overnight. The insoluble solid was removed through filtration. The crude product was repeatedly crystallized from the ethanol. All the compounds of the present series were synthesized with the same method. Yield in general is 60-65%. The elemental analysis of all the compounds was found to be satisfactory and all are listed in table.

Green synthesis

The target esters were prepared via aqueous esterification. Equimolar amounts (0.1 mol each) of 4-(4'-n-alkoxybenzoic acid) [A] and β-phenoxyethyl 4-hydroxybenzoate [B] were dissolved in 300 mL water containing $NaHCO_3$ (0.2 mol) and DMAP (0.01 mol, 10 mol%). T3P® (50 wt% in water, 0.11 mol) was added dropwise at 0 °C, and the mixture stirred at room temperature for 12–18 h (TLC monitoring: EtOAc:hexane 1:1). The precipitated product was filtered, washed with cold water (2 × 50 mL) and brine (50 mL), and recrystallized from minimal ethanol to give pure esters. This protocol was applied to all homologues, yielding 75–85%.

3. Characterizations

4-((3-phenoxypropanoyl)oxy)phenyl 4-ethoxybenzoate (PX$_2$)

IR Spectrum (KBr) νmax/Cm^{-1}: 2954, 2870, 1721 (-COO-), 1603, 1510, 1259, 1157, 1061, 844. **^{1}H-NMR Spectrum** (400 MHz, $CDCl_3$) δ in ppm: 7.99 (d, 2H, ArH), 7.25 (t, 2H, ArH), 7.18 (d, 2H, ArH), 7.17 (d, 2H, ArH), 7.13 (d, 2H, ArH), 6.93 (t, H, ArH), 6.91 (d, 2H, ArH), 4.37 (t, 2H, H_2C-O-Ph), 3.97 (t, 2H, H_2C-O-Ar), 2.19 (t, 2H, H_2C-C-O-Ph), 0.99 (t, 3H, CH_3).

4-((3-phenoxypropanoyl)oxy)phenyl 4-butoxybenzoate (PX$_4$)

IR Spectrum (KBr) νmax/Cm^{-1}: 2954, 2870, 1721 (-COO-), 1603, 1510, 1259, 1157, 1061, 844. **^{1}H-NMR Spectrum** (400 MHz, $CDCl_3$) δ in ppm: 7.62 (d, 2H, ArH), 7.60 (t, 2H, ArH), 7.40 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.19 (d, 2H, ArH), 6.99 (t, H, ArH), 6.18 (d, 2H, ArH), 4.14 (t, 2H, H_2C-O-Ph), 4.05 (t, 2H, H_2C-O-Ar), 2.11 (t, 2H, H_2C-C-O-Ph), 1.85-1.12 (m, 4H, CH_2 X 2), 0.99 (t, 3H, CH_3).

4-((3-phenoxypropanoyl)oxy)phenyl 4-(pentyloxy)benzoate (PX$_5$)

IR Spectrum (KBr) νmax/Cm^{-1}: 2954, 2870, 1721 (-COO-), 1603, 1510, 1259, 1157, 1061, 844. **^{1}H-NMR Spectrum** (400 MHz, $CDCl_3$) δ in ppm: 7.62 (d, 2H, ArH), 7.60 (t, 2H, ArH), 7.40 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.19 (d, 2H, ArH), 6.99 (t, H, ArH), 6.18 (d, 2H, ArH), 4.14 (t, 2H, H_2C-O-Ph), 4.05 (t, 2H, H_2C-O-Ar), 2.11 (t, 2H, H_2C-C-O-Ph), 1.85-1.12 (m, 6H, CH_2 X 3), 0.99 (t, 3H, CH_3).

4-((3-phenoxypropanoyl)oxy)phenyl 4-(hexyloxy)benzoate (PX$_6$)

IR Spectrum (KBr) νmax/Cm^{-1}: 2954, 2870, 1721 (-COO-), 1603, 1510, 1259, 1157, 1061, 844. **^{1}H-NMR Spectrum** (400 MHz, $CDCl_3$) δ in ppm: 7.62 (d, 2H, ArH), 7.60 (t, 2H, ArH), 7.40 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.19 (d, 2H, ArH), 6.99 (t, H, ArH), 6.18 (d, 2H, ArH), 4.14 (t, 2H, H_2C-O-Ph), 4.05 (t, 2H, H_2C-O-Ar), 2.11 (t, 2H, H_2C-C-O-Ph), 1.85-1.12 (m, 8H, CH_2 X 4), 0.99 (t, 3H, CH_3).

4-((3-phenoxypropanoyl)oxy)phenyl 4-(octyloxy)benzoate (PX$_8$)

IR Spectrum (KBr) Vmax/Cm^{-1}: 2954, 2870, 1721 (-COO-), 1603, 1510, 1259, 1157, 1061, 844. **^{1}H-NMR Spectrum** (400 MHz, $CDCl_3$) δ in ppm: 7.62 (d, 2H, ArH), 7.60 (t, 2H, ArH), 7.40 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.19 (d, 2H, ArH), 6.99 (t, H, ArH), 6.18 (d, 2H, ArH), 4.14 (t, 2H, H_2C-O-Ph), 4.05 (t, 2H, H_2C-O-Ar), 2.11 (t, 2H, H_2C-C-O-Ph), 1.85-1.12 (m, 12H, CH_2 X 6), 0.99 (t, 3H, CH_3).

4-((3-phenoxypropanoyl)oxy)phenyl 4-(dodecyloxy)benzoate (PX$_{12}$)

IR Spectrum (KBr) νmax/Cm^{-1}: 2954, 2870, 1721 (-COO-), 1603, 1510, 1259, 1157, 1061, 844. **^{1}H-NMR Spectrum** (400 MHz, $CDCl_3$) δ in ppm: 7.62 (d, 2H, ArH), 7.60 (t, 2H, ArH), 7.40 (d, 2H, ArH), 7.30 (d, 2H, ArH), 7.19 (d, 2H, ArH), 6.99 (t, H, ArH), 6.18 (d, 2H, ArH), 4.14 (t, 2H, H_2C-O-Ph), 4.05 (t, 2H, H_2C-O-Ar), 2.11 (t, 2H, H_2C-C-O-Ph), 1.85-1.12 (m, 20H, CH_2 X 10), 0.99 (t, 3H, CH_3).

Result and discussion

conventional Method vs green method

The **table 1** compares yields obtained via conventional and green methods for the synthesized compounds. For Compound A (4-*n*-Alkoxybenzoic acid), the green method shows a higher yield (76%) than the conventional method (70%). Similarly, Compound B (β-Phenoxyethyl-4-hydroxybenzoate) exhibits a smaller improvement of around 2%. A significant enhancement is observed for Compound C (2-Phenoxyethyl 4-(4-*n*-alkoxybenzoyloxy) benzoate), where the green method (75–85%) outperforms the conventional method (60–65%). Overall, green method providing approximately 10–20% higher yield compared to the conventional method the green approach provides better yields.

Table: 1. Comparison between conventional Method vs green method.

Compound	Name of Compound	Conventional Method Yield (%)	Green Method Yield (%)
A	4-n-Alkoxybenzoic Acid	70%	76%

B	β-Phenoxyethyl-4-hydroxybenzoate	81%	83%
PX$_n$	2-Phenoxyethyl 4-(4-n-alkoxybenzoyloxy) benzoate	60–65%	75–85%

Mesomorphic behaviour

In this study, a series of derivatives of 2-Phenoxyethyl 4-(4-n-alkoxybenzoyloxy) benzoate **PX$_n$** were investigated for their mesomorphic behavior. It was found that **PX$_3$** to **PX$_{16}$** the derivatives exhibited mesogenic properties. The derivatives with *n*-alkoxy groups ranging **PX$_3$** to **PX$_4$** demonstrated monotropic nematic and smectic A mesophase. The nematic and smectic A mesophases (**PX$_3$** & **PX$_4$**) exhibited monotropic behavior, meaning they transitioned from the isotropic phase to the nematic liquid crystalline phase upon cooling. On the other hand, the derivatives with n-alkoxy groups, specifically **PX$_5$** to **PX$_{12}$** exhibited an enantiotropic smectic A mesophase. Smectic A phase was also enantiotropic, allowing reversible transformation with temperature changes. **Table 2** exhibited the transition temperature data for these **PX$_n$** derivatives, providing valuable information about the temperature. Additionally, **Fig. 1** demonstrated the mesomorphic behavior of the **PX$_n$** compounds, showing their clearing and melting points of all derivatives.

Table 2: Transition temperatures (ºC) of the series PX$_n$ compound

Compound No.	R= -C_nH_{2n+1} *n* =	Cr-SmA	SmA-N	SmA/N-I
1	1	-	-	112
2	2	-	-	106
3	3	-	(86)	101
4	4	(70)	-	99
5	5	85	-	96
6	6	79	-	92
7	7	77	-	92
8	8	78	-	89
9	10	76	-	87
10	12	70	-	76
11	14	66	-	73
12	16	62	-	70

()=monotropic value; Cr=crystalline solid; SmA=smectic A phase; N=nematic phase; I=isotropic liquid phase.

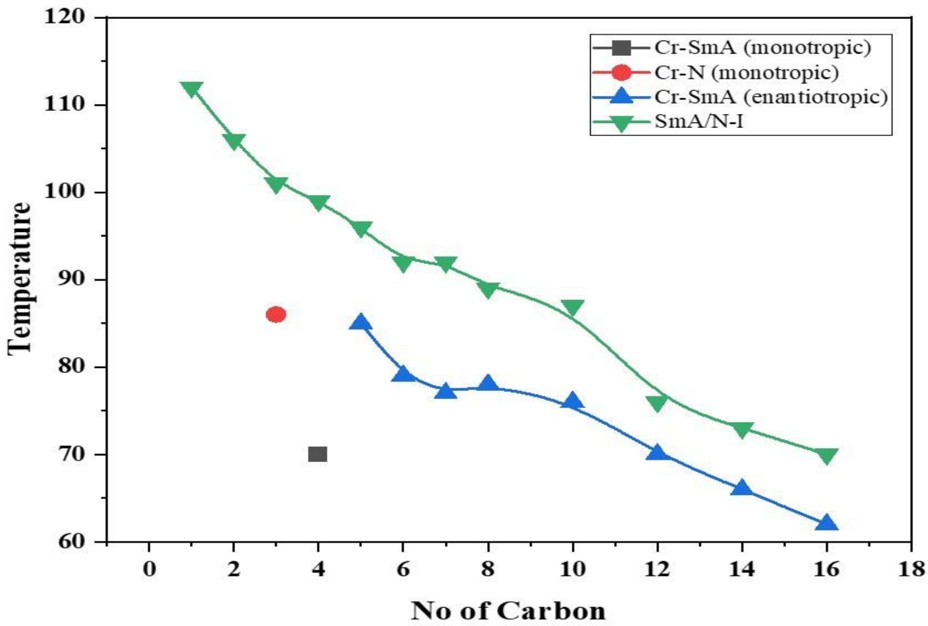


Fig. 1. LCs phase behaviour of series **PX$_n$**.

Polarising optical microscope study

The mesomorphic characteristics in every derivative within the synthesized Series **PX*n*** was conducted utilizing a polarized optical microscope equipped with a heating and cooling platform. The experimental procedure involved creating a slender sample layer by carefully placing the derivatives between coverslip and glass slide, forming a sandwich-like arrangement. This method allowed for the subsequent analysis of mesogenic characteristics. The derivatives of series **PX*n*** were discovered to exhibit mesogenic properties. **PX*1*** and **PX*2*** are non-mesogenic compounds. Notably, derivative **PX*3*** exhibited monotropic nematic phase at 86 ˚C to the isotropic (101 ˚C) phase, (POM texture shown in **Fig. 2**) while **PX*4*** displayed monotropic smectic A mesophase is exhibited in the cooling stage at 70 ˚C as well as isotropic range is 99 ˚C. On other hand **PX*5*** to **PX*16*** demonstrated enantiotropic smectic A phase on heating from the 85 ˚C to 62 ˚C followed by isotropic range at 96 ˚C to 70 ˚C.

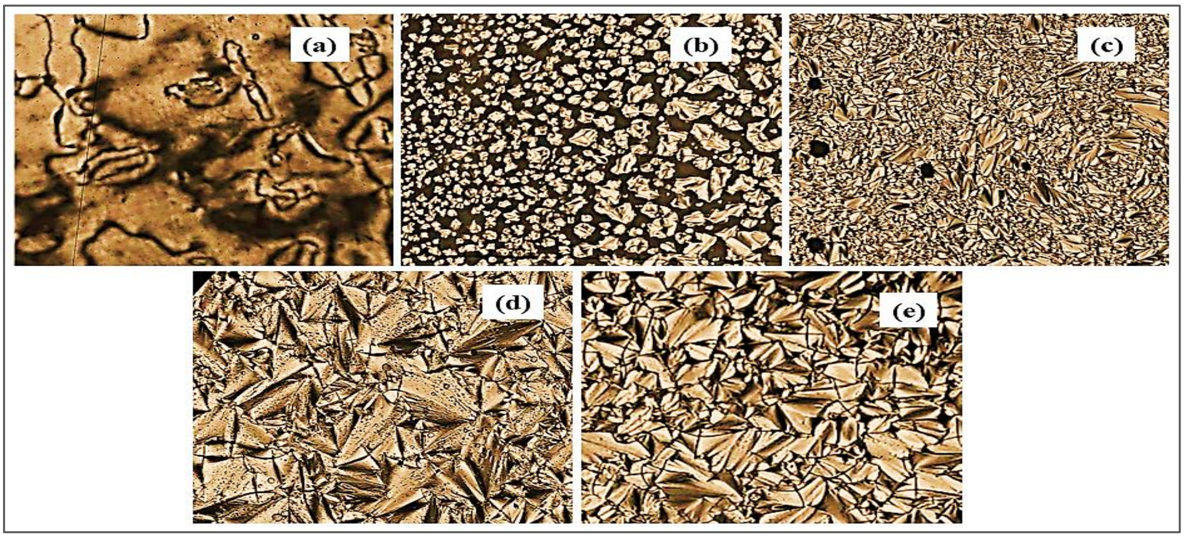


Fig. 2 Optical microphotographs of (a) Cr-N monotropic at 86 ˚C and Cr-I at 101 ˚C of compound PX*3*. (b) monotropic smA-I at 70 ˚C and Cr-I at 99 ˚C of compound PX*4*. (c, d & e) Optical microphotographs of Cr-SmA at 79, 78 & 70 ˚C and SmA-I at 92, 89 & 76 ˚C of compound PX*6*, PX*8* & PX*12*.

Differential scanning calorimetry analysis (DSC)

Calorimetry is an effective technique for studying phase transitions, as it provides precise data that helps in understanding the properties of the phases involved. In the present study, measurements were carried out to determine the enthalpy values of the mesogenic homologues in the **PX*n*** series. The enthalpies of phase transitions during heating were recorded in kJ/mol at a scanning rate of 10 ˚C per minute. The thermal stability of these compounds was verified by obtaining consistent thermograms over multiple heating cycles. **Figure 3** presents the DSC thermograms of the **PX*n*** compounds obtained during the first heating cycle at a rate of 10 ˚C per minute.

PX*3* showed two clear peaks while cooling, at 86 ˚C and 101 ˚C. These represent the transitions from an isotropic state to monotropic nematic state and crystalline state to an isotropic state (Cr-I). The enthalpy changes for these transitions are 51.6230 kJ/mol and 0.8231 kJ/mol, respectively. As well as compound **PX*4*** showed two clear peaks while cooling, at 70 ˚C and 99 ˚C. These represent the transitions from an isotropic state to monotropic nematic state and crystalline state to an isotropic state (Cr-I). The enthalpy changes for these transitions are 45.1118 kJ/mol and 0.5869 kJ/mol. Additionally, **PX*12*** showed two clear peaks while heating, at 86 ˚C and 103 ˚C. These represent the transitions from crystalline to smectic A (Cr-SmA) and from the smectic A to an isotropic state (SmA-I). The enthalpy changes for these transitions are 44.8821 kJ/mol and 0.5582 kJ/mol, respectively. **Table 3** shows the phase sequences, transition temperatures, as well as enthalpies and entropies for the mesogenic members within Series **PX*n***. Notably, the data underscores the remarkable stability exhibited by all the mesomorphic compounds, with particular emphasis on the heightened stability observed in the lower members of the homologous series **PX*n***.

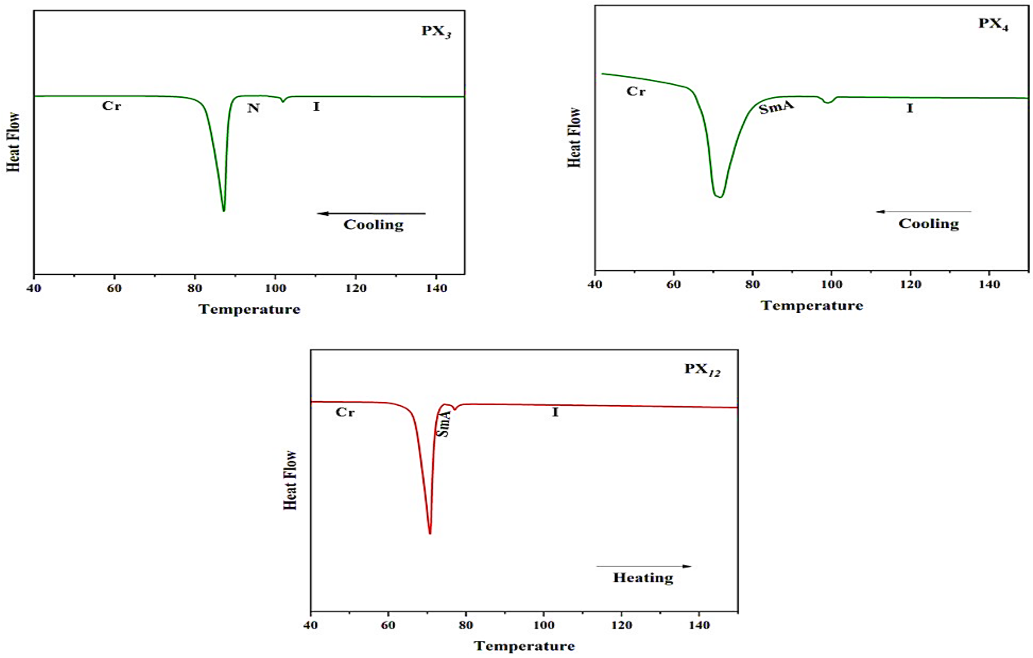


Fig. 3 DSC thermogram of series PX$_n$. (PX$_3$, PX$_4$ & PX$_{12}$).

Table:-3 Phase transition temperatures (°C), enthalpy change, entropy change and normalised entropy of the series- PX$_n$ by DSC and POM measurement.

Compound	Transition	Peak temp./°C	ΔH/kJmol^{-1}	ΔS/kJmol^{-1} K^{-1}
PX$_3$	Nematic (monotropic)	86	51.623	0.14376
	Cr-I	101	0.8231	0.00220
PX$_4$	SmA (monotropic)	70	45.1118	0.13152
	Cr-I	99	0.5869	0.00157
PX$_{12}$	Cr-SmA	86	44.8821	0.12502
	SmA-Isotropic	103	0.5582	0.00148

Conclusion

A novel homologous series of 4-((3-phenoxypropanoyl) oxy) phenyl 4-*n*-alkoxybenzoate (Series **PX$_n$**) was successfully synthesized using both conventional and green methodologies and were characterized by FT-IR and ^{1}H-NMR spectroscopy. Their mesomorphic properties were investigated using a polarizing optical microscope (POM) and differential scanning calorimetry (DSC). The lower homologues (**PX$_1$** and **PX$_2$**) were non-mesogenic, whereas the intermediate members exhibited monotropic nematic or smectic A (SmA) phases. In particular, **PX$_3$** and **PX$_4$** showed monotropic nematic as well as SmA mesophases. The higher homologues (n ≥ 5) displayed enantiotropic SmA mesophases, with transition temperatures decreasing as the alkyl chain length increased. Overall, this study emphasizes the structural property relationship that governs phase transition behaviour in phenoxy ethyl-based liquid crystalline systems.

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