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Synthesis, and Characterization of Mesomorphic Homologous Series of *n*-alkoxybenzaldehyde Derivatives

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ABSTRACT

A new homologous series of liquid crystals based on *n*-alkoxybenzaldehyde, consisting of ten homologues, has been synthesized. This series exhibits a middle-order melting behavior, displaying both nematic and smectic mesophases. The transition curve between solid, isotropic, and mesomorphic states follows a zig-zag pattern, with alternating increases and decreases. The texture of the nematic phase is droplet-nematic texture, while the smectic phase shows a focal conic fan-shaped structure. The thermal stability and mesomorphic properties of this series are compared to those of structurally similar compounds. Analytical data confirm the molecular structure of the compounds, and transition temperatures are determined using an optical hot-stage polarizing microscope.

Keywords: Nematic, Smectic, Liquid crystals

1. INTRODUCTION

Recent interest in the design and development of liquid crystalline (LC) materials has grown due to their versatile functionality and wide range of applications [1-5]. Among the

efforts to create novel mesogenic cores, the incorporation of long-chain alkoxy groups from acid derivatives has been extensively studied, particularly for understanding the structure-property relationships. These studies focus on how changes in flexibility and rigidity affect key properties such as melting point, transition temperatures, and mesophase morphology. Such research shows that even minor adjustments in molecular structure can lead to significant changes in mesomorphic properties [6-9]. In this context, the Schiff base functionality (-CH=N-) acts as a linking bridge between the rigid core groups [10-14]. As a result, this structure can help maintain molecular linearity, ensuring good thermal stability and facilitating the formation of distinct phases.

Numerous researchers have explored liquid crystalline (LC) materials for a variety of applications. Shang et al. provided a comprehensive review on the recent advancements of LC materials in the biomedical field [15-18]. Their work covers the fundamental concepts of LC materials and their functionalized derivatives, highlighting their potential for applications such as drug development, artificial implants, disease diagnosis, and health monitoring. The article also presents key insights for the future development of LC-based technologies in these areas. Rabbi et al. focused on the characterization techniques for thermotropic and lyotropic LC materials, offering a detailed review of their properties and their promising applications in optoelectronics [16]. In another study, Wang et al. discussed the current progress in 4D printing of liquid crystalline elastomers, exploring the synthetic tools available to control molecular orientation and induce macroscopic changes in properties. Their research delves into the interactions between external stimuli, adjustable LC behaviors, and the programmable topological features of printed structures [19].

The studies reported so far highlight the growing interest and significance of liquid crystalline (LC) materials in the field of materials science. In this work, we aim to investigate the mesomorphic behavior of a novel homologous series of liquid crystals (LC), consisting of *n*-alkoxybenzaldehyde derivatives with varying alkyl chain lengths. The LC materials were synthesized by combining Ambroxol with the Schiff base of an aromatic aldehyde. The resulting homologous series, with alkyl chain lengths ranging from C₁ to C₁₆, were characterized using various instrumental techniques.

2. EXPERIMENTAL

2. 1. Materials & Methods

To carry out our experimental work, all other chemicals and reagents used were of analytical grade. 4-hydroxybenzaldehyde, alkyl bromides of C₁ to C₁₆ *n*-alkyl chains and Ambroxol were procured from Avra Synthesis Private Ltd. Hyderabad, India. Double distilled water was used for each experimental work. TLC plates (silica gel 60 F254 silica-aluminum plates) were purchased from Merck, India.

2. 2. Synthesis of liquid crystal

Firstly, to synthesize 4-*n*-Alkoxybenzaldehydes was refluxed with corresponding *n*-alkyl bromides in the presence of potassium carbonate (1 equiv.) and acetone as a solvent by using reported method [20]. Then after, the prepared *n*-alkoxybenzaldehyde reacted with 4-((2-amino-3,5-dibromobenzyl)amino)cyclohexan-1-ol in the presence of Ethanol reflux condition 5-6 hrs.

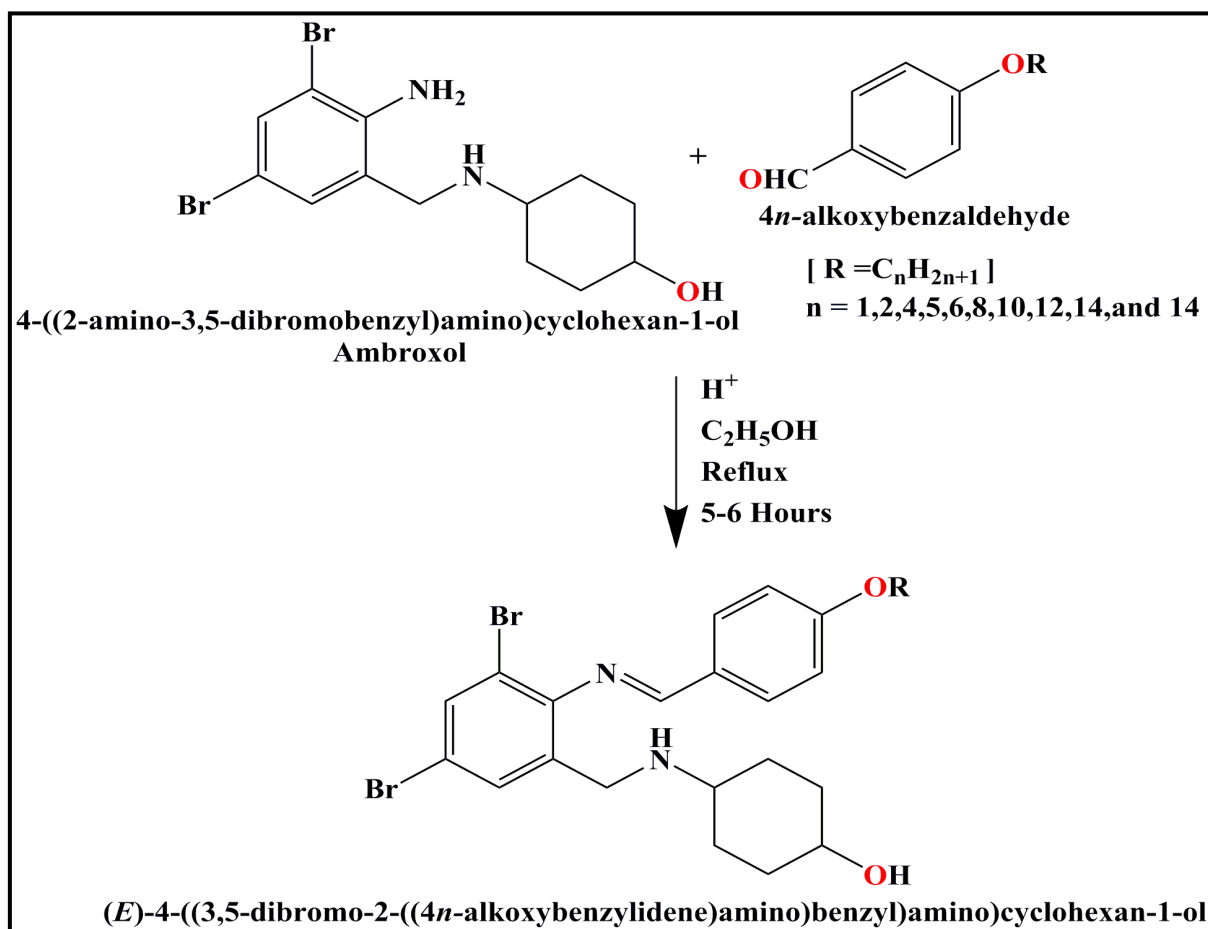


Figure 1. Synthetic scheme for *n*-alkoxybenzaldehyde derivatives.

2. 3. Characterization

Thermal analysis was conducted using differential scanning calorimetry (DSC) on a Perkin Elmer Thermal Analyzer, with a heating rate of 10 °C/min. Fourier-transform infrared (FT-IR) spectra were obtained using the KBr pellet method and analyzed in the range of 3500–500 cm⁻¹ with a Bruker TENSOR 27 instrument. Proton Nuclear Magnetic Resonance (¹H-NMR) spectra were recorded on a Bruker Avance (400 MHz) spectrometer in CDCl₃ solvent, with tetramethylsilane (TMS) as the internal standard. The mesophase was identified using a polarizing optical microscope (POM), employing a Nikon Eclipse LV-100 POL with a temperature-controlled heating stage.

2. 4. Spectral Data

FT-IR (KBr): $\nu_{\max}/\text{cm}^{-1}$

Sample C₈: ~1021, ~1136, ~1110 (-C-H hydrocarbon), ~1277 (-C-H bending), ~1213 (ether linkage), ~3365 (N-H), ~1510 and ~601 (aromatic ring), ~2932 and ~2857 (-C-H str), ~719, ~787 and ~861 (*p*-di substituted phenyl ring), ~822 poly(-CH₂)_n group). ~1260 (-C=N-), ~3350 (-OH).

Sample C₁₀: ~1022, ~1135,~1111 (-C-H hydrocarbon), ~1276 (-C-H bending), ~1213 (ether linkage), ~3367 (N-H), ~1510 and ~603 (aromatic ring), ~2933 and ~2859 (-C-H str), ~719, ~787 and ~861 (*p*-di substituted phenyl ring), ~822 poly(-CH₂)_n group). ~1265 (-C=N-), ~3354 (-OH).

Sample C₁₂: ~1025, ~1138,~1113 (-C-H hydrocarbon),~1277 (-C-H bending), ~1213 (ether linkage), ~3365 (N-H), ~1510 and ~601 (aromatic ring), ~2936 and ~2859 (-C-H str), ~719, ~787 and ~864 (*p*-di substituted phenyl ring), ~827 poly(-CH₂)_n group), ~1266 (-C=N-), ~3354 (-OH).

¹H-NMR (CDCl₃)

Sample C₈: 0.87-0.90 (3H, t; -CH₃ of -OC₈H₁₇ group), 1.32-1.77 (2H, m; -CH₂-CH₂-O-), 4.06-0.88 (2H, m; -CH₂-(CH₂)₇-O), 8.64 (1H, s; -N=CH-), 4.08 (1H of -OH), 7.27-7.62 (4H, m;*p*-di-substituted phenyl ring containing -OC₈H₁₇ chain), 7.93-7.38 (2H, middle phenyl ring), 1.47-1.72 (*p*-di substituted cyclohexane ring).

Sample C₁₀: 0.87-0.90 (3H, t; -CH₃ of -OC₁₀H₂₁ group), 1.33-1.76 (2H, m; -CH₂-CH₂-O-), 4.06-0.88 (2H, m; -CH₂-(CH₂)₈-O), 8.63 (1H, s; -N=CH-), 4.08 (1H of -OH), 7.26-7.62 (4H, m;*p*-di-substituted phenyl ring containing -OC₁₀H₂₁ chain), 7.92-7.38 (2H, middle phenyl ring), 1.47-1.71 (*p*-di substituted cyclohexane ring).

Sample C₁₂: 0.87-0.90 (3H, t; -CH₃ of -OC₁₂H₂₅ group), 1.34-1.76 (2H, m; -CH₂-CH₂-O-), 4.08-0.88 (2H, m; -CH₂-(CH₂)₈-O), 8.63 (1H, s; -N=CH-), 4.08 (1H of -OH), 7.27-7.62 (4H, m;*p*-di-substituted phenyl ring containing -OC₁₂H₂₅ chain), 7.92-7.38 (2H, middle phenyl ring), 1.46-1.70 (*p*-di substituted cyclohexane ring).

Sample C₁₄: 0.87-0.91 (3H, t; -CH₃ of -OC₁₄H₂₉ group), 1.34-1.79 (2H, m; -CH₂-CH₂-O-), 4.08-0.88 (2H, m; -CH₂-(CH₂)₈-O), 8.61 (1H, s; -N=CH-), 4.08 (1H of -OH), 7.28-7.61 (4H, m;*p*-di-substituted phenyl ring containing -OC₁₄H₂₉ chain), 7.91-7.38 (2H, middle phenyl ring), 1.47-1.74 (*p*-di substituted cyclohexane ring).

3. RESULTS & DISCUSSION

The prepared LC samples of (E)-4-((3,5-dibromo-2-((4n-alkoxybenzylidene)amino)benzyl)amino)cyclohexan-1-ol derivatives have been analyzed for elemental (CHN) analysis. The obtained data are found to be well matched with theoretical values of corresponding samples (**Table 1**).

Table 1. CHN Analysis.

Samples	Molecular Formula	Elements % Found (% Calculated)		
		C	H	N
C ₁	C ₂₁ H ₂₄ Br ₂ N ₂ O ₅	50.71 (50.83)	4.41 (4.48)	5.57 (5.65)

C ₂	C ₂₂ H ₂₆ Br ₂ N ₂ O ₅	51.70 (51.78)	5.01 (5.14)	5.37 (5.49)
C ₄	C ₂₄ H ₃₀ Br ₂ N ₂ O ₅	53.48 (53.55)	5.57 (5.62)	5.11 (5.20)
C ₅	C ₂₅ H ₃₂ Br ₂ N ₂ O ₅	54.27 (54.36)	5.76 (5.84)	5.01 (5.07)
C ₆	C ₂₆ H ₃₄ Br ₂ N ₂ O ₅	55.03 (55.14)	5.94 (6.05)	4.81 (4.95)
C ₈	C ₂₈ H ₃₈ Br ₂ N ₂ O ₅	56.48 (56.58)	6.37(6.44)	4.67 (4.71)
C ₁₀	C ₃₀ H ₄₂ Br ₂ N ₂ O ₅	57.81 (57.89)	6.77 (6.80)	4.42 (4.50)
C ₁₂	C ₃₂ H ₄₆ Br ₂ N ₂ O ₅	59.01 (59.08)	7.01 (7.13)	4.22 (4.31)
C ₁₄	C ₃₄ H ₅₀ Br ₂ N ₂ O ₅	60.13 (60.18)	7.31 (7.43)	4.03 (4.13)
C ₁₆	C ₃₆ H ₅₄ Br ₂ N ₂ O ₅	61.02 (61.19)	7.61 (7.70)	3.83 (3.90)

3. 1. POM Texture Analysis

POM analysis was performed using a glass slide, where the samples were sandwiched and covered with a cover slip to identify the phase transition temperatures of the synthesized LC derivatives. In this study, microphotographs of the textures observed for the C₈ and C₁₀ samples are shown in **Figure 2**. The image of sample C₈ clearly demonstrates a nematic phase at 117 °C under heating conditions. In contrast, sample C₁₀ exhibits a droplet-type texture characteristic of the smectic A phase at 84 °C and 98 °C upon heating.

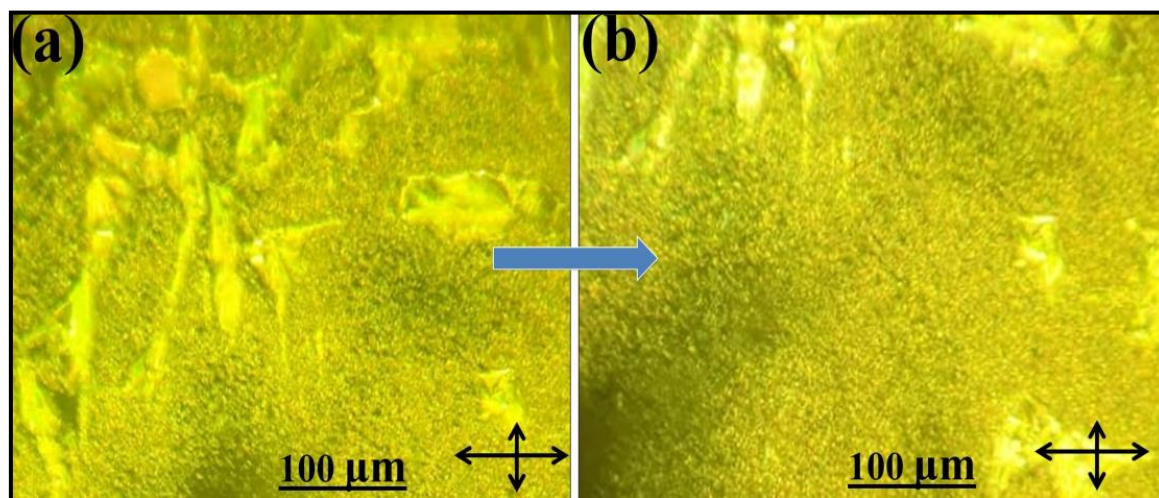


Figure 2. POM images for the texture of Samples C₈(A) Nematic marble texture and C₁₀ (B) Nematic marble texture

The prepared LC samples were further examined for their phase behavior, with phase transition temperatures recorded using a polarizing microscope with a heating stage (Table 2).

Table 2. Phase transition temperatures (°C) of the synthesized LC samples (heating scan).

Samples	Smectic	Nematic	Isotropic
C ₁	--	159	165
C ₂	--	154	161
C ₄	--	150	157
C ₅	--	135	141
C ₆	--	131	136
C ₈	--	117	125
C ₁₀	84	98	106
C ₁₂	75	85	95
C ₁₄	68	78	86
C ₁₆	69	75	83

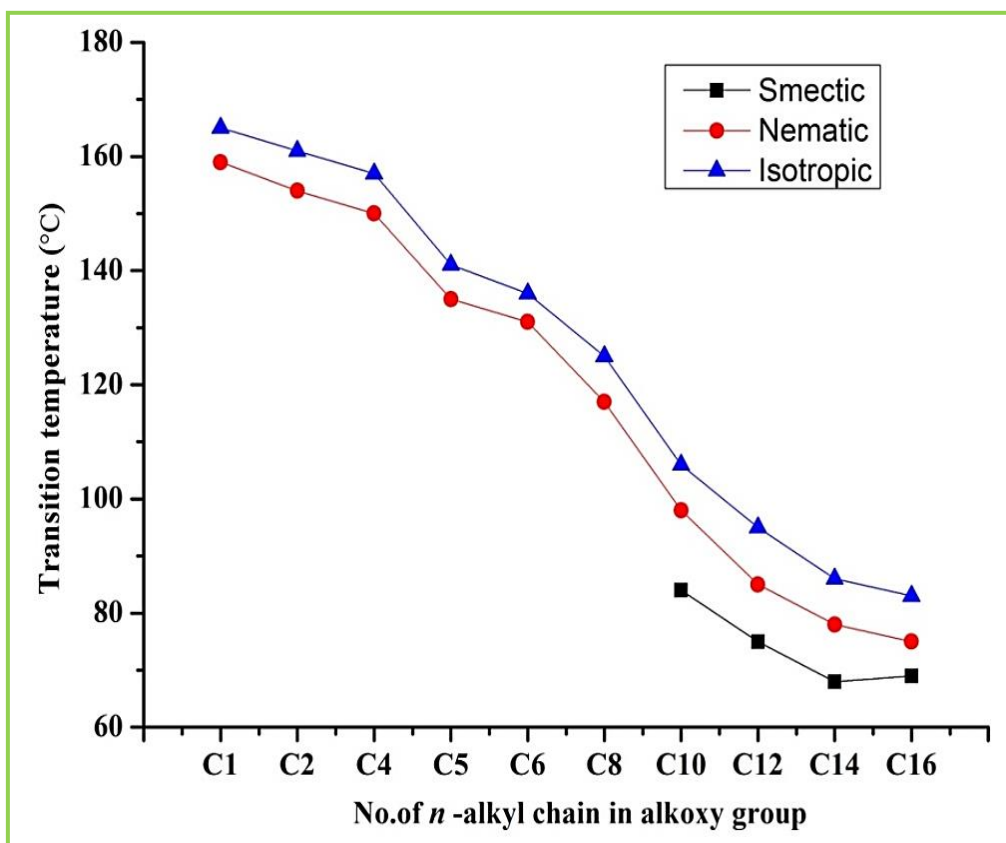


Figure 3. Phase diagram for the synthesized samples.

The focus of this study was to investigate the effect of varying aliphatic alkyl side chains substituted in the *n*-alkoxy group on the mesomorphic properties. To visualize this, a plot of transition temperature versus the number of carbon atoms in the alkyl chain was created, as shown in **Figure 3**.

The results indicate that among the samples in this series, C1, C2, C3, C5, and C7 do not exhibit liquid crystalline behavior due to their high crystallinity. This behavior is attributed to the presence of weak dispersion forces and limited dipole-dipole interactions, which result in insufficient anisotropic intermolecular forces. The adverse effects of both molecular rigidity and flexibility contribute to these samples' inability to form mesophases.

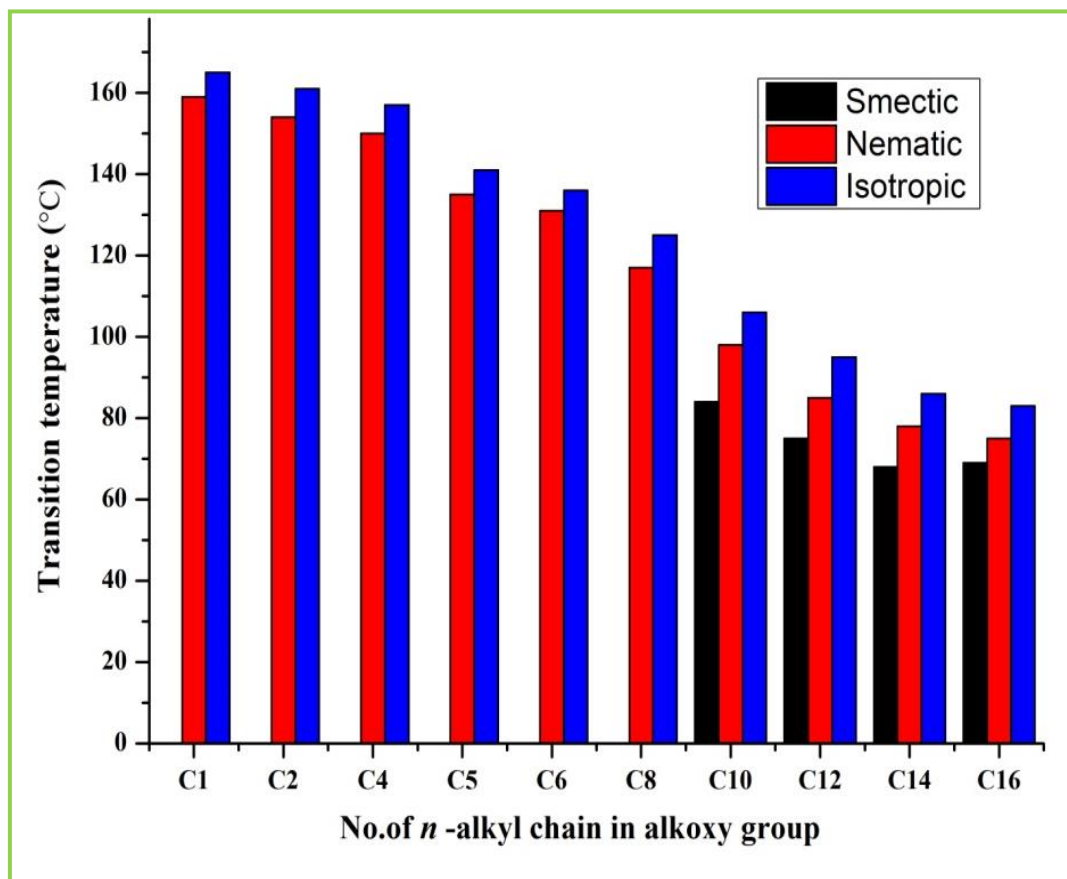


Figure 4. Phase comparison for the synthesized samples.

3. 2. Thermal Analysis

In this study phase transition temperatures were determined through thermal analysis using DSC thermograms. The phase transition temperatures is presented in the corresponding figures. Figures 5 and 6 show the DSC thermograms for the C10 and C14 samples, respectively. In Figure 5, three exothermic peaks are observed at 84 °C, 116 °C, and 144 °C during the heating cycle, which correspond to the smectic and nematic phases (Table 3). Similarly, the DSC thermogram of C14 (Figure 6) shows two exothermic peaks at 69 °C in the heating cycle, further supporting the presence of both smectic and nematic phases.

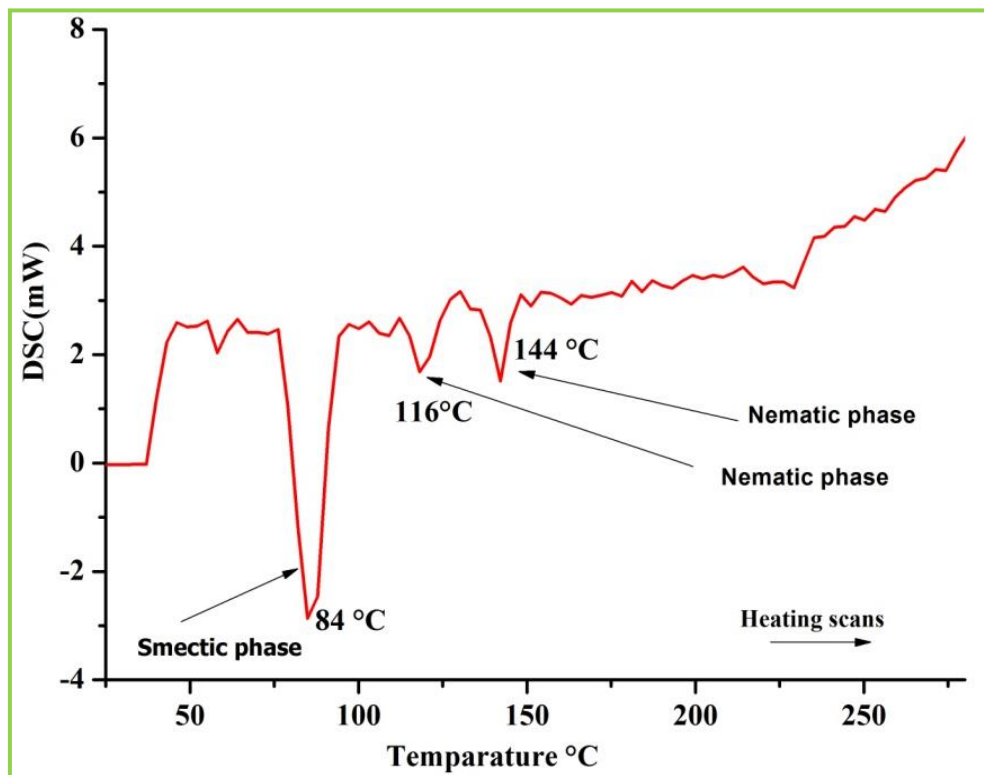


Figure 5. DSC Thermograph for the sample C₁₀

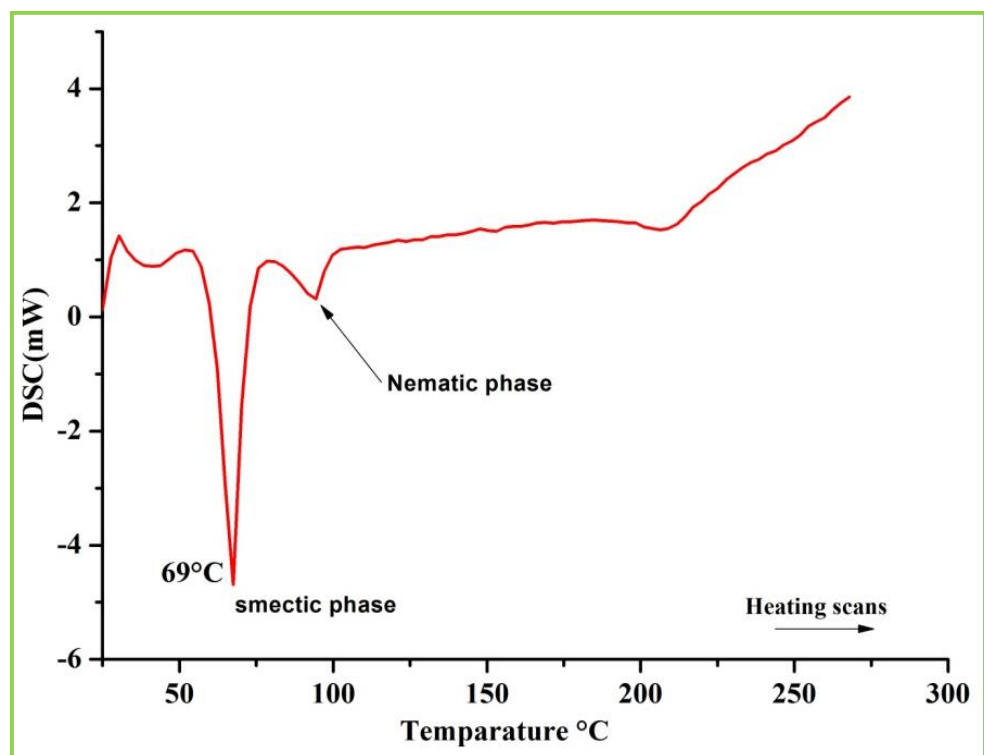


Figure 6. DSC Thermograph for the sample C₁₄

4. CONCLUSIONS

In this work, we synthesized a series of n-alkoxybenzaldehyde derivatives by varying the alkyl chains at the terminal moieties as alkoxy groups. The structural identification of the synthesized compounds was confirmed through spectral and thermal analyses. The series was found to exhibit nematogenic behavior with a short-range liquid crystallinity, displaying a smectic phase. The observed mesogenic properties and transition temperatures were influenced by the size of the alkyl chains, indicating that mesomorphism is sensitive to the molecular structure. For practical applications, the smectogenic and nematogenic homologues with transition temperatures below 80 °C could be useful in device applications.

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