

Contents lists available at GrowingScience

## Current Chemistry Letters

homepage: www.GrowingScience.com

**Synthesis and characterization of acrylamide substituted sulfanilamide based calamitic LCs: effect of terminal group on phase behavior****Lakshman Meena<sup>a</sup>, Vinay S. Sharma<sup>b\*</sup>, Hitendra Mali<sup>b</sup>, Jigar Y. Soni<sup>a\*</sup>**<sup>a</sup>Department of Chemistry, Faculty of Basic and Applied Science, Madhav University, Sirohi, India<sup>b</sup>Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad, India**CHRONICLE***Article history:*

Received March 20, 2023

Received in revised form

June 17, 2023

Accepted October 9, 2023

Available online

October 12, 2023

*Keywords:*

Sulfanilamide

Liquid Crystal

Nematic

Calamitic

Enantiotropic

**ABSTRACT**

In the present study, we have prepared two phenyl ring substituted sulfanilamide bearing acrylamide linking groups. The four derivatives (C<sub>1</sub>-C<sub>4</sub>) were prepared by changing the left n-alkoxy terminal group. The liquid crystalline properties of the synthesized sulfanilamide-based compounds were investigated using POM and DSC studies. All four materials exhibit nematic liquid crystalline properties during both heating and cooling. They also demonstrate a broad temperature range and thermal stability. Further, we have studied the structure-property relationship to gain a better understanding of the effect of the linking group and variable alkoxy tail group on mesomorphic behavior. The results indicate that thermal stability, mesophase temperature range, and liquid crystalline properties depend on the linking group and variable alkyl chain length.

© 2024 by the authors; licensee Growing Science, Canada.

**1. Introduction**

Thermotropic liquid crystals are mesogenic compounds that depend solely on changes in ambient temperature for their mesomorphism.<sup>1</sup> Mesomorphism may be changed with changing molecular geometry. To date, various homologous series have been reported, which include azo, ester, chalconyl, vinyl ester, and Schiff base groups as linking groups.<sup>2,3</sup> A thermotropic liquid crystal molecule consists of a central part, typically a linker rod, used to connect aromatic rings through various linking units. It also has end tails, which are composed of either straight alkyl or alkyloxy chains with a polar substituent at the terminal end to enhance flexibility and maintain molecular alignment stability.<sup>4</sup> The flexibility of an LC molecule is determined by the number of carbon atoms present in the alkyl chain. Depending on the type of substituents and their combinations, it is possible to form both nematic and smectic C-type mesophases.<sup>5</sup> Because of its unique ability to flow like a liquid while exhibiting optical properties like crystals, the study of the liquid crystalline state is a multidisciplinary field that offers benefits to both humans and various industries.<sup>6</sup>

In literature, various types of calamitic liquid crystals with small molecular systems have been reported, featuring two phenyl rings linked by different types of linking units.<sup>7-10</sup> Small molecular system-based liquid crystals are primarily applicable at an industrial level for large-scale synthesis and purification processes. Calamitic liquid crystals with lower molecular mass typically consist of 1,4-disubstituted phenyl terminal cores with lateral and terminal side groups, as well as the presence of flexible alkoxy side groups.<sup>11</sup> Additionally, structural variations can be achieved by introducing polar groups, such as fluorine or cyano, at both the lateral and terminal positions of the rigid core to create liquid crystalline materials.<sup>12</sup> In the nematic mesophase, the presence of longitudinal molecular axes aligns themselves parallel to the director axis, displaying a long-range orientational order that can be observed with different types of texture patterns under POM studies.<sup>13</sup> In smectic thermotropic liquid crystals, there is a coexistence of outlined orientational order and translational order. The molecules are arranged in equidistant planes, creating a periodic layered structure with a specific layer

\* Corresponding author. Tel : +91-9979937124 ++91-6351469588

E-mail address [vinaysharma3836@gmail.com](mailto:vinaysharma3836@gmail.com) (V.S. Sharma) [drjigarsoni@gmail.com](mailto:drjigarsoni@gmail.com) (J.Y. Soni)

thickness.<sup>14</sup> The selection of a mesogenic core, terminal groups, and a flexible chain are essential parameters for designing small molecular system-based liquid crystals. A para-substituted phenyl ring is used to confirm that the molecules have structural linearity and large molecular polarizability with respect to terminal and lateral side groups which further impact on the exhibition of liquid crystalline phase.<sup>15</sup> Till the date, different type of liquid crystalline compound based on chalcone group was reported in the literature with different types of mesogenic properties.<sup>16-21</sup> Apart from this, our research group reported two phenyl ring based linear and non-linear single chalcone substituted imidazolium based LCs.<sup>22</sup> These imidazolium based ionic compounds displayed smectic C and nematic type mesogenic properties. Understanding the generation and behavior of the nematic mesophase in small molecular systems is crucial for various applications, including liquid crystal displays, optical devices, and materials with tunable optical properties.<sup>23-25</sup>

Sulfonamides belong to an important class of synthetic antimicrobial drugs that are pharmacologically used as broad spectrum for the treatment of human and animal bacterial infections.<sup>26,27</sup> Sulfonamides are organo-based sulphur containing compounds having five or six-membered heterocyclic rings.<sup>28</sup> In present investigation, we have synthesized sulfonamide based liquid crystal and focused on the study of the effect of central linking group as well as molecular structure on the liquid crystalline properties. Addition to this, we also investigate the effect of the variable alkyloxy side chain (-OR) on the mesomorphic behavior. On other hand, we have studied the structure-property relationship for more understanding the exhibition and variation on liquid crystalline, mesophase temperature range and thermal stability. This report aims to elucidate the correlation between the mesomorphic properties of chalcone-linked ester and cinnamate mesogens. This includes the number of side chains, the variation of their position, their length and branching. The structure-property relationships of the number of alkyl chains, their position, length and structure were studied.

## 2. Experiment

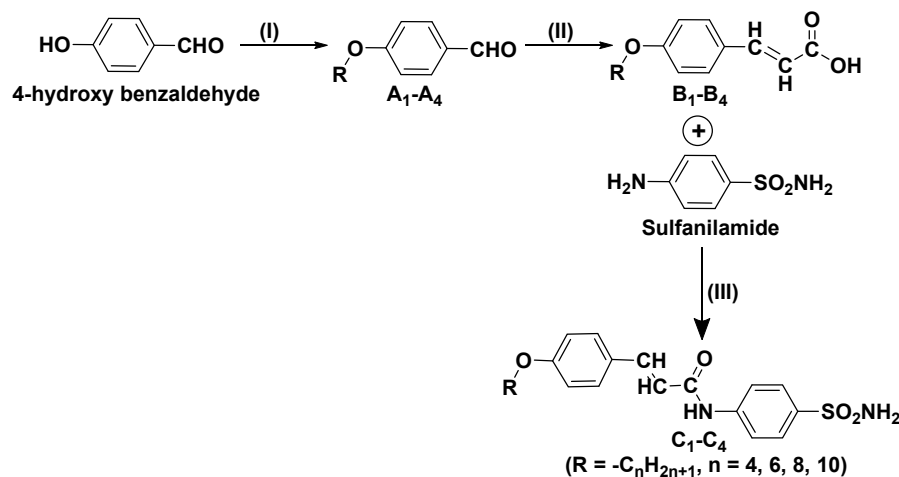
### 2.1 Materials

The following materials were acquired from Avra Chemicals, India for synthesis: 4-hydroxy benzaldehyde, sulphanilamide, and anhydrous potassium carbonate ( $K_2CO_3$ ), sodium nitrite ( $NaNO_2$ ), and resorcinol. Alkyl bromides (R-Br) were purchased from S.R.L. India. Malonic acid, pyridine, di-cyclohexyl carbodiimide (DCC), dimethylamino pyridine (DMAP), and hydrochloric acid (HCl) were purchased from JSK Chem Ltd. The solvents were dried and further purified by the reported method.

### 2.2 Measurements

Melting points were taken on the Opti-Melt (automated melting point system). The FT-IR spectra were recorded as KBr pellets on Shimadzu in the range of  $3800-600\text{ cm}^{-1}$ . The texture images were studied on a trinocular polarizing optical microscope (POM) equipped with a heating plate and a digital camera. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a 400 MHz in Bruker Advance in the range of 0.5 ppm to 16 ppm using  $CDCl_3$  solvent. The phase transition temperatures were measured using the Shimadzu DSC-60 plus on the heating and cooling cycle. The miscibility method was employed to assess the texture images of the nematic phase. The newly synthesized compound is placed between a glass slide and a coverslip for POM measurements, with both heating and cooling rates set at  $2.0\text{ }^\circ\text{C}/\text{min}$ . Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (Mettler Toledo) under constant nitrogen flow at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

### 2.3 Reaction and Scheme



**Scheme 1.** (i) alkyl bromide (R-Br), anhydrous  $K_2CO_3$ , acetone, reflux, (v) malonic acid, piperidine, pyridine, reflux for 4 h, (vi) DCC, DMAP, DCM, 24 hr, rt.

### 3. Result and discussion

In the present study, we have prepared newly calamitic-shaped two phenyl ring-based compounds and investigated their liquid crystalline properties. We have prepared four derivatives by using a central substituted acrylamide group and variable alkoxy side chain at terminal position. The target acrylamide-based compounds (**C<sub>1</sub>-C<sub>4</sub>**) have been prepared by the reaction of 4-n-alkoxy cinnamic acid derivatives (**B<sub>1</sub>-B<sub>4</sub>**) with sulfanilamide. The liquid crystalline properties of the synthesized compounds were studied by using a polarizing optical microscope (POM) and further confirmed by differential scanning calorimetry (DSC) analysis.

#### 3.1 POM discussion

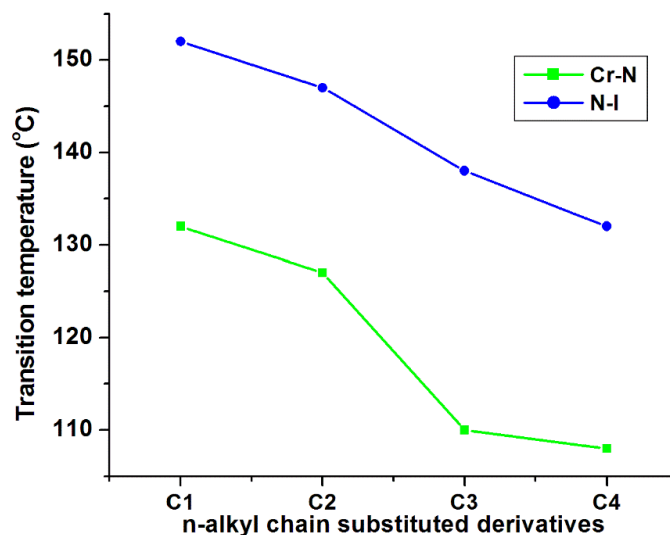
The liquid crystalline properties of the newly synthesized calamitic-shaped acrylamide-based materials were examined using a polarizing optical microscope during both heating and cooling cycles. For the POM analysis, the compound is sandwiched between a coverslip and a glass slide, and then scanned during both heating and cooling cycles. The compound **C<sub>1</sub>** with butyloxy tail group shows nematic mesophase at 132.0 °C and further transforms into isotropic liquid at 152.0 °C respectively. Similarly, compound **C<sub>2</sub>** with octyloxy, compound **C<sub>3</sub>** with octyloxy, and compound **C<sub>4</sub>** with decyloxy tail group displayed nematic mesophase at 127.0 °C, 110.0 °C, and 108 °C and further transform into isotropic liquid at 147.0 °C, 138.0 °C, 132.0 °C respectively. All four chalconyl-amide-based derivatives exhibited enantiotropic mesogenic behavior. The transition temperatures of the compounds, as determined from the POM study, are listed in Table 1.

**Table 1.** Transition temperature of the acryl amide based compounds (**C<sub>1</sub>-C<sub>4</sub>**) in °C.

Comp.	alkyl chain (-R)	Transition temperatures in °C		
		Cr	N	I
<b>C<sub>1</sub></b>	<b>C<sub>4</sub></b>	-	132.0	152.0
<b>C<sub>2</sub></b>	<b>C<sub>6</sub></b>	-	127.0	147.0
<b>C<sub>3</sub></b>	<b>C<sub>8</sub></b>	-	110.0	138.0
<b>C<sub>4</sub></b>	<b>C<sub>10</sub></b>	-	108.0	132.0

(Cr = solid crystal; N = nematic phase; I = isotropic phase)

The number of alkoxy tails, their positions, and the length of side alkyl chains in a compound can indeed influence its transition temperature.<sup>32</sup> These factors impact the compound's overall molecular structure and properties, which, in turn, affect its physical behavior. The alkyl chains in a compound can contribute to its polarity, rigidity, polarizability, dipole moment, and molecular interactions.<sup>33</sup> An acrylamide group is not a combination of a vinyl group and an amide group; instead, it is a distinct functional group derived from acrylic acid. Acrylamide finds extensive applications in various sectors, including industry and research, with diverse uses such as in polymer production, the creation of flocculants, and the development of biomaterials.<sup>34,35</sup> However, acrylamide itself is not typically known for exhibiting mesogenic (liquid crystal) properties. In the present study, we are introducing acrylamide groups in the molecular systems and further studied the effect on the liquid crystalline behavior. By introducing a long alkyl spacer into the molecular structure of a compound, the flexibility and freedom of movement between the mesogenic groups can be increased. This increased flexibility tends to reduce the intermolecular interactions and hinder the formation of well-ordered liquid crystalline phases. As a result, the transition temperature of the compound is generally shifted to higher values. The phase behavior of the synthesized two-phenyl system-based LCs is shown in Fig. 1.

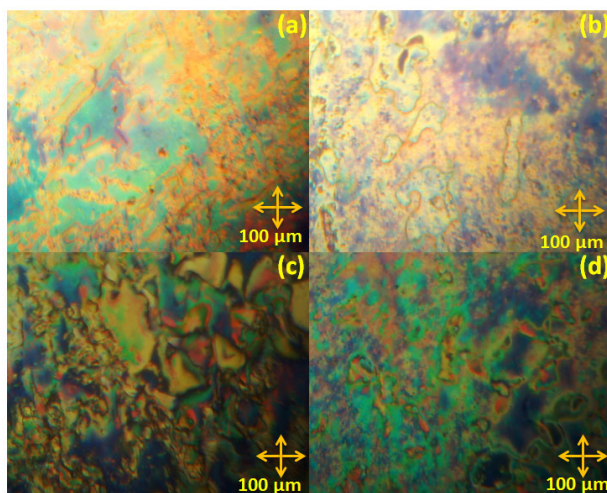


**Fig. 1.** Phase behavior of the synthesized acrylamide LCs (**C<sub>1</sub>-C<sub>4</sub>**).

The phase behavior in liquid crystals refers to the different structural arrangements and physical states that liquid crystal materials can exhibit under specific conditions. Liquid crystals can exist in several distinct phases, each characterized by a particular molecular organization and ordering pattern. As we go from lower to higher members, both the observed phase transitions (Cr-N & N-I) show the descending tendency. Further, it is common to observe the trends in phase transitions as certain molecular parameters are changed. These trends can provide insights into the relationship between molecular structure and phase behavior. When considering the Cr-N transition in all four single linking unit-based LCs, where the material transitions from a crystalline phase to a nematic phase, a descending tendency indicates that as the size or molecular weight of the compounds increases, the transition temperature decreases. This behavior suggests that larger or bulkier molecules have a lower tendency to order into a crystalline phase, leading to a decrease in the transition temperature. In the N-I transition of all compounds, where the material shifts from a nematic phase to an isotropic phase, a descending trend indicates that with increasing size or molecular weight, the transition temperature from the nematic phase to the isotropic phase decreases. This implies that larger or more complex molecules have a reduced tendency to maintain nematic order at higher temperatures, leading to a lower transition temperature.

### 3.2 Texture study

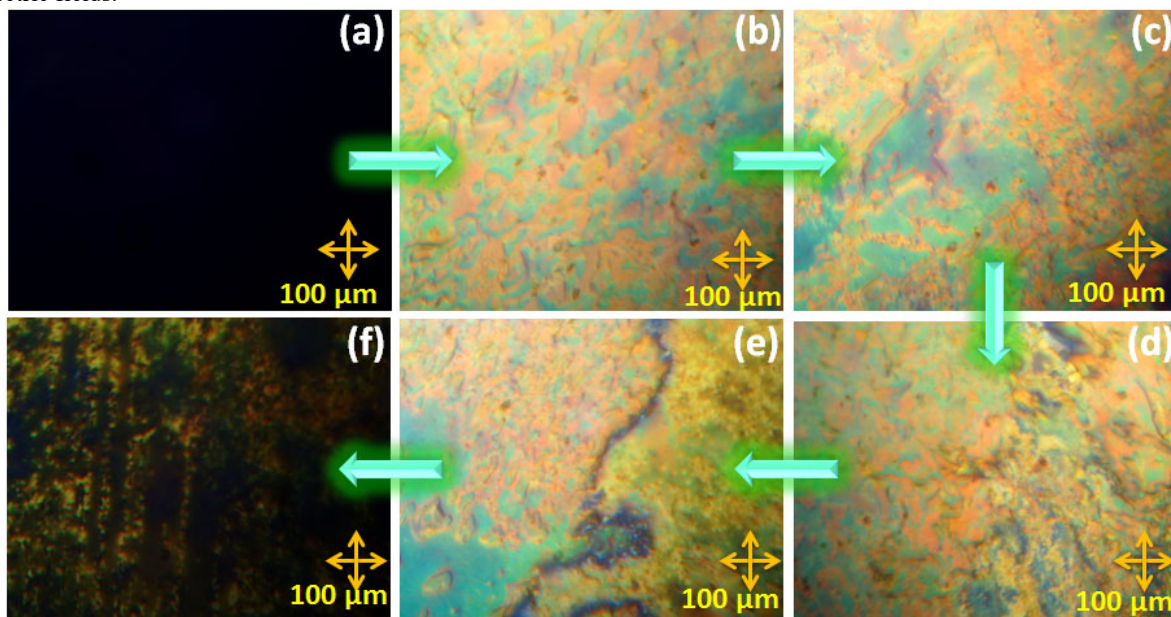
The observation of a mesophase texture by cooling a glass slide from an isotropic state to a mesomorphic state with a cooling rate of 2.0 °C/min suggests the presence of a temperature-dependent phase transition in the material. Experimental techniques such as polarized light microscopy can be used to observe and characterize the mesophase textures in liquid crystal materials. These techniques allow for the visualization and analysis of the molecular ordering and texture patterns in the material. The POM texture image of all four materials is shown in **Fig. 2**.



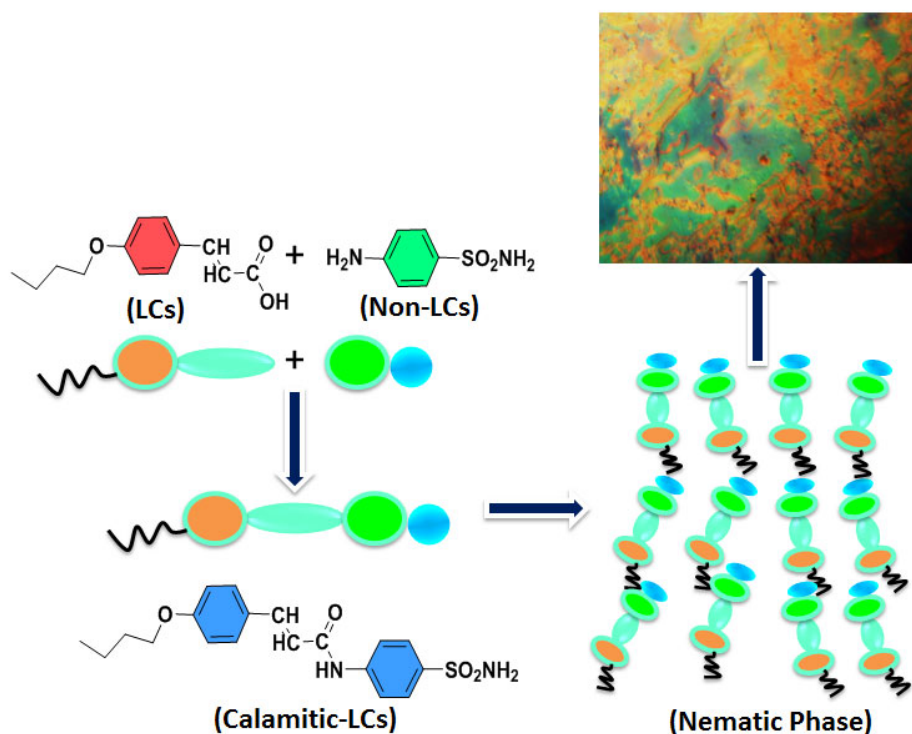
**Fig. 2.** Optical photomicrographs on cooling condition; (a) nematic phase at 132.0 °C for comp. C<sub>1</sub>; (b) nematic phase at 127.0 °C for comp. C<sub>2</sub>; (c) nematic phase at 110.0 °C for comp. C<sub>3</sub>; (d) nematic phase at 108.0 °C for comp. C<sub>4</sub>.

The microphotograph texture images of the compounds were captured during the cooling process. Compound C<sub>1</sub> with butyloxy chain shows marble type texture pattern of nematic phase at 132.0 °C respectively. Similarly, compound C<sub>2</sub> with hexyloxy tail group shows a threaded type of texture pattern of nematic phase at 127.0 °C respectively. Likewise, compound C<sub>3</sub> with octyloxy tail exhibited schlieren type texture pattern of the nematic phase at 110.0 °C and transformed into isotropic phase at 138.0 °C respectively. Furthermore, compound C<sub>4</sub> with decyloxy tail displayed threaded type texture pattern nematic phase at 108.0 °C respectively. Addition to this, all four materials show a similar type of texture pattern in the heating cycle as well. To enhance our understanding of the mesophase behavior, we conducted measurements to determine the phase sequence of the selected compound (C<sub>1</sub>) under different temperature conditions (**Fig. 3**). By examining the changes in the observed textures as the temperature is varied, we can identify and characterize the different phases present in the material. This analysis helps us understand how the molecular arrangement and ordering within the liquid crystal evolve with temperature, providing insights into the thermotropic behavior of the compound. The schematic molecular arrangement of the small molecular system-based LCs with nematic mesophase is depicted in **Fig. 4**. The generation of the nematic mesophase is primarily influenced by the molecular shape and the intermolecular interactions between the molecules. Small molecular systems with a single linking unit often possess elongated or rod-like molecular structures, promoting the alignment of the molecules along a common axis.<sup>36</sup> This alignment arises from the balance between attractive and repulsive forces between the molecules, such as van der Waals interactions and dipole-dipole interactions.<sup>37</sup> The presence of the -SO<sub>2</sub>NH<sub>2</sub> group can affect the liquid crystalline properties by introducing polarity and increasing the polarizability of the molecule. As a result, the molecule containing the -SO<sub>2</sub>NH<sub>2</sub> group tends to have a higher dipole moment compared to other linking group.<sup>38</sup> The presence of the -SO<sub>2</sub>NH<sub>2</sub> group introduces electronegative atoms (oxygen and nitrogen) into the molecule, leading to increased polarity. These electronegative atoms can withdraw electron density,

creating a polarized region within the molecule. The presence of the sulfonamide group at terminal position can enhance the molecular polarizability towards the molecular system, allowing the molecule to respond more readily to external electric fields.<sup>39</sup>



**Fig. 3.** Phase sequence of compound C<sub>1</sub> on cooling condition; (a) isotropic liquid at 152.0 °C (a); nematic droplets at 130.0 °C (b); nematic droplets at 125.0 °C (c); nematic droplets at 121.0 °C (d); nematic droplets at 114.0 °C (e); solid crystal at 107.0 °C (f).



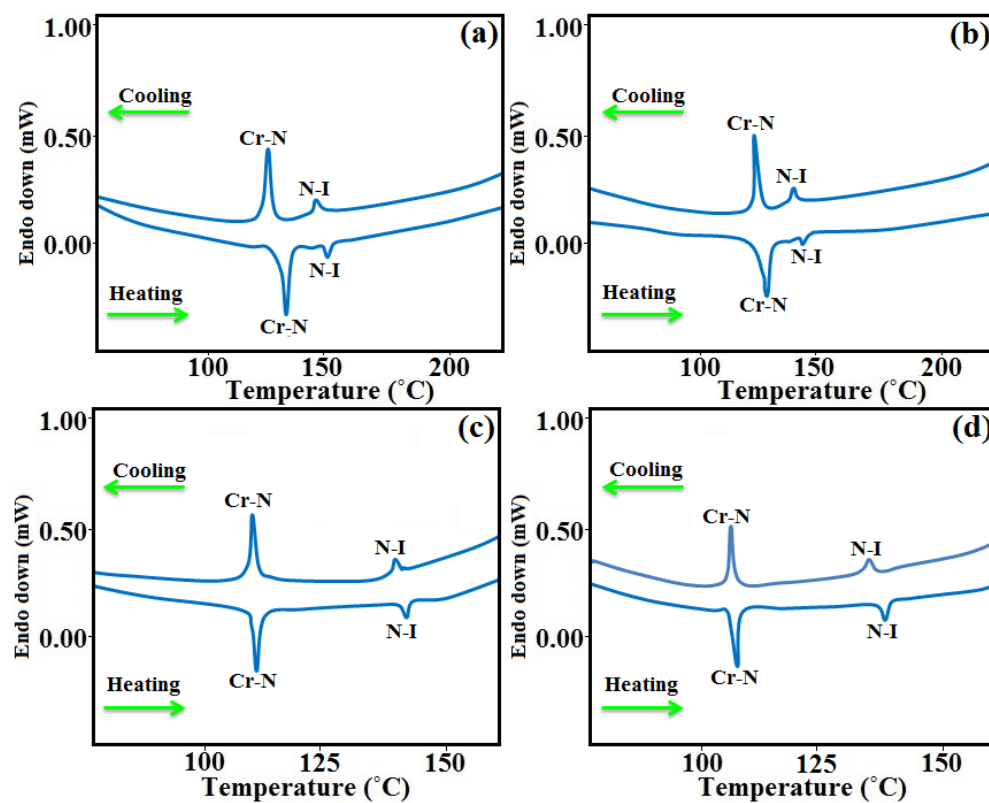
**Fig. 4.** Schematic arrangement pattern of molecules in the formation of nematic mesophase.

### 3.2 DSC investigation

Differential Scanning Calorimetry (DSC) is indeed a valuable tool for the identification and analysis of phase transitions, including the determination of phase transition temperatures in liquid crystal systems. DSC measures the heat flow associated with thermal events in a sample, allowing for the detection of changes in enthalpy (heat content) that occur during phase transitions. The DSC thermogram of all four derivatives (C<sub>1</sub>-C<sub>4</sub>) is shown in **Fig. 5**. During a DSC experiment, the sample is subjected to a controlled temperature program, typically from a lower temperature to a higher temperature. As the sample undergoes phase transitions, the heat flow into or out of the sample is recorded, resulting in characteristic peaks in



the DSC curve. The position and shape of these peaks can provide information about the nature and temperature of the phase transition. The phase transition temperatures along with the enthalpy change values are supplied in **Table 1**. It is observed that two endothermic peaks corresponding to the transition from the solid phase to the nematic phase (Cr-N) and from the nematic phase to the isotropic phase (N-I) are evident in both the heating and cooling cycles. The presence of these two endothermic peaks during heating indicates the transformation from a solid state to a nematic phase, which is a liquid-like phase characterized by orientational order but not positional order. The heat flow recorded during this transition manifests as an endothermic peak in the DSC curve. As the temperature continues to rise, the second endothermic peak occurs, indicating the transition from the nematic phase to the isotropic phase. The isotropic phase is a disordered liquid phase where both orientational and positional orders are lost. Once again, the heat flow associated with this transition is detected as an endothermic peak in the DSC curve. Further, the associated enthalpy value for both transition temperatures signify the presence of liquid crystalline properties in all four single linking unit based calamitic LCs. Furthermore, the transition temperatures obtained from the DSC analysis can be further correlated with the microscopic temperatures observed using POM study. This correlation helps in establishing a comprehensive understanding of the phase transitions and provides additional insights into the material's thermal properties. Compound C<sub>1</sub> with butyloxy group, displays two endothermic peaks at 131.7 °C and 149.2 °C, confirming the existence of transitions from the solid phase to the mesophase and from the mesophase to the isotropic liquid phase, respectively. Similarly, compound C<sub>2</sub> containing a hexyloxy group exhibits two endothermic peaks at 126.8 °C and 149.1 °C, indicating the presence of a mesophase in the compound.



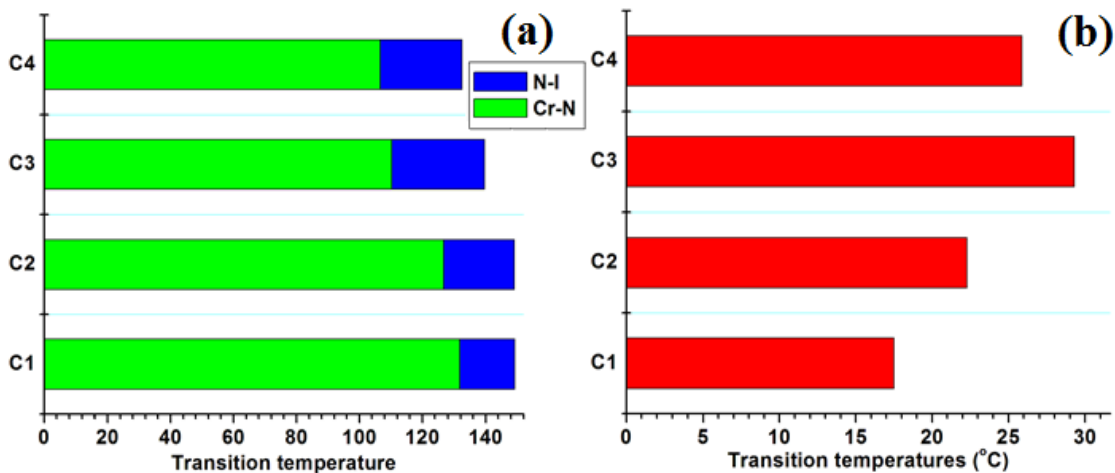
**Fig. 5.** DSC thermogram of compound C<sub>1</sub> (a); compound C<sub>2</sub> (b); compound C<sub>3</sub> (c); compound C<sub>4</sub> (d) on the second heating and cooling cycle.

**Table 2.** Transition temperature (°C), enthalpy (J g<sup>-1</sup>), of the compounds (C<sub>1</sub>-C<sub>4</sub>) by DSC measurement.

Comp.	Transition	Heating scan(°C)	Cooling scan(°C)	ΔH (Jg <sup>-1</sup> )	ΔH (Jg <sup>-1</sup> )
C <sub>1</sub>	Cr-N	131.7	128.1	10.4	12.86
	N-I	149.2	148.6	4.41	5.34
C <sub>2</sub>	Cr-N	126.8	126.7	9.8	10.8
	N-I	149.1	146.2	2.73	3.32
C <sub>3</sub>	Cr-N	110.3	109.8	11.9	10.6
	N-I	139.6	138.1	3.97	6.05
C <sub>4</sub>	Cr-N	106.6	104.2	9.65	10.6
	N-I	132.5	130.6	5.06	6.48

(Cr = solid crystal, N = nematic phase, I = isotropic phase).

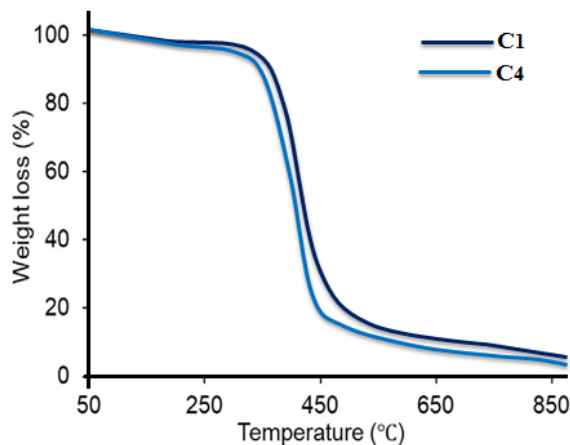
On the other hand, compound **C**<sub>3</sub>, which features an octyloxy tail group, displays two endothermic peaks at 110.3 °C and 139.6 °C, indicating the presence of phase transitions from crystalline (Cr) to nematic (N) phase and from nematic (N) to isotropic (I) phase, respectively. In addition, compound **C**<sub>4</sub> with decyloxy chain showed two endothermic peaks at 106.6 °C and 132.6 °C, this is due to the formation of the nematic phase from solid crystal and further transform into isotropic liquid. Apart from this, all four compounds displayed two endothermic peaks at similar temperatures on cooling condition which confirm the enantiotropical type behavior of the present synthesized acrylamide-based LCs. It is evident that higher alkyl chain groups result in the promotion of mesogenic properties at lower temperatures, including the clearing temperature, compared to lower alkyl chain functionalized compounds. This can be attributed to the increased rigidity of the molecules, facilitated by acrylamide linking units supported by left side-substituted alkyl arms with a range of chain lengths extending from the lower to higher members at the terminal side position.<sup>40</sup> Additionally, the presence of higher alkyl chain groups in a compound can favor lower melting points. This can be attributed to the increased flexibility and molecular mobility provided by the longer alkyl chains. The presence of these flexible alkyl chains disrupts the packing and ordering of the molecules, making it easier for the compound to undergo the phase transition from a solid to a liquid crystalline state at lower temperatures.<sup>41</sup> The bar graph represents the thermal behavior of all four derivatives in heating conditions (**Fig. 6a**). Addition to this, the mesophase temperature range of all four acrylamide mesogens (**C**<sub>1</sub>-**C**<sub>4</sub>) is shown in **Fig. 6b**.



**Fig. 6.** Thermal behavior of the compounds (**C**<sub>1</sub>-**C**<sub>4</sub>) (a); mesophase temperature range (b) upon heating condition.

### 3.3 TGA analysis

Thermogravimetric analysis is a technique used to study the thermal stability of the liquid crystalline sulfonamide derivatives. It measures the weight change of a sample as it is heated or cooled under controlled conditions. The thermal stability of azo-cinnamate based liquid crystalline compounds can be assessed by subjecting them to TGA analysis (**Fig. 7**).



In the present study, we have specifically chosen two compounds with lower alkyl and higher alkyl chain groups to investigate the influence of alkyl side arms on the thermal stability of the materials. This approach allows for a comparative analysis to understand how different alkyl side arms impact the thermal behavior of the sulfonamide-based LCs. The obtained data in your study indicates that the selected two derivatives of acrylamide based liquid crystalline compounds exhibited good thermal stability up to 330 °C. This suggests that these compounds can withstand relatively high

temperatures without undergoing significant weight loss or decomposition. However, beyond the 330 °C mark, the TGA spectra showed that the compounds underwent complete degradation over the temperature range of 420 °C to 450 °C. This indicates that the compounds experienced a rapid weight loss or decomposition process within this temperature range, resulting in their eventual breakdown. One can see that the compound with a higher alkyl chain displayed slightly higher weight loss as compared to the lower chain substituted material. The specific reasons for this difference in weight loss can vary and depend on various factors, including the molecular structure, intermolecular interactions, and packing arrangements of the compounds. The presence of a longer alkyl chain can potentially affect the stability of the compound by influencing its molecular mobility, intermolecular forces, or even the accessibility of certain functional groups during thermal decomposition.<sup>42</sup>

### 3.4 Structure property relationship

In molecular systems exhibiting liquid crystalline properties, the relationship between molecular structure and properties, particularly the left terminal end, central linking group, and right terminal end, plays a crucial role in determining their behavior. The molecular structure, encompassing the nature and arrangement of the molecules, significantly influences several key properties of liquid crystals, including their phase behavior, transition temperatures, stability, and optical properties. In this current study, we have compared the phase transition temperature, mesophase stability, and the onset of the mesophase with homologous series previously reported, which share a similar molecular structure based on a single chalcone linking unit<sup>8,9</sup>. The molecular structure of present synthesized acrylamide-based materials and previously reported homologous series-1 and series-2 is depicted in Fig. 8. All three series share a commonality in the left terminal group and the two-phenyl-based molecular system but differ in the central linking unit and the right terminal end. The acrylamide-based molecular system synthesized in this study, which features a sulfonamide terminal end, demonstrates a higher thermal stability in the nematic mesophase compared to the other two series. Furthermore, the mesophase temperature range of the acrylamide-based materials is broader when compared to the chalcone-based homologous series. This suggests that the incorporation of the sulfonamide terminal end in the acrylamide-based system contributes to enhanced stability and a wider temperature range for the nematic mesophase. The specific chemical interactions and structural characteristics of the acrylamide-based materials likely play a role in these improved thermal properties.

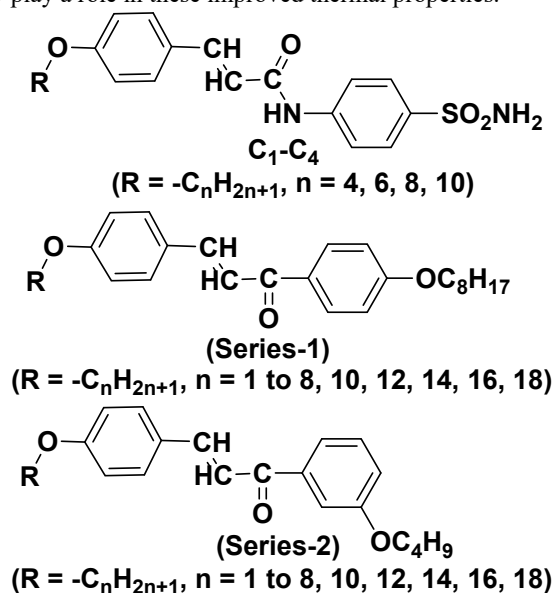


Fig. 8. Structurally similar analogous series.

Furthermore, the present sulfonamide compounds showed N-I thermal stability at about 142.2 °C (C<sub>1</sub> to C<sub>4</sub>) which is higher as compared series-1 (96.5 °C) and series-2 (86.2 °C) respectively. This may be due to the presence of sulfonamide at the right terminal group which can further influence the overall polarity, thermal stability, and intermolecular forces within the molecular system supported by acrylamide group to induce thermally stable nematogenic mesomorphism. The more flexibility towards both terminal ends (series-1, series-2) leads to favor mesomorphism at lower temperature and less thermal stability as compared to -SO<sub>2</sub>NH<sub>2</sub> substituted materials. Additionally, the shape, size, polarity, dipole moment, and flexibility of the terminal groups can affect the molecular arrangement, packing efficiency, and ultimately, the phase behavior of the material.

## 4. Conclusions

The synthesis protocol developed for sulfanilamide functionalized acrylamide compounds with flexible arms was designed to be efficient and systematic. It likely involved a series of well-defined steps and reactions to ensure the successful



formation of the desired target compounds. Further, we have investigated the liquid crystalline properties in all derivatives. All four acrylamide linked sulfonamide materials (**C1-C4**) with variable alkyl chain displayed enantiotropic nematic mesophase with good temperature range and stability. These findings provide valuable insights into the structure-property relationship of liquid crystals and demonstrate the potential advantages of using acrylamide-based small molecular system with sulfonamide terminal ends in terms of enhanced stability of mesophase and thermal behavior. Additionally, this type of nematic liquid crystals (LCs) with a small molecular systems can be easily synthesized using a single-step synthesis method. This streamlined synthesis approach allows for efficient and cost-effective manufacturing, making it more feasible for industrial applications and potential commercial use.

## 5. Synthesis and characterization of target compounds (**C1-C4**)

### 5.1 Preparation of 4-n-alkoxy benzaldehyde (**A1-A4**)

4-n-alkoxy benzaldehyde is prepared by the previously reported method.<sup>29</sup>

### 5.2 Preparation of 4-n-alkoxy cinnamic acid (**B1-B4**)

4-n-alkoxy cinnamic acid is prepared by the previously reported method.<sup>30</sup>

### 5.3 Synthesis of acrylamide-based target compounds (**C1-C4**)

Finally, the targeted compounds have been prepared by esterification of sulfanilamide (1 mmol) with 4-n-alkoxy cinnamic acid derivatives (**B1-B4**) (1.2 mmol) in presence of DCC (2.2 mmol) and DMAP (0.05 mmol) using dichloromethane (30 ml) as a solvent.<sup>31</sup> The white precipitate of DCU is obtained which was isolated by filtration and discarded, while the filtrate was evaporated to dryness. The obtained crude product was further recrystallized by ethanol to get pure product. The synthetic route of the target compounds is shown in **Scheme 1**.

### 5.4 Selected data of synthesized compounds (**C1-C4**)

**Compound C1:** 72 % yield, light yellow color, FT-IR (KBr) in  $\text{cm}^{-1}$ : 2980-3030 (-C-H- str in  $\text{CH}_3$ ), 1450 (-NH), 1640 ( $>\text{C}=\text{O}$  str), 930 (*trans*, vinyl group), 834 (aliphatic alkyl chain), 807 (*para*-disubstituted aromatic ring), 1240 ( $-\text{SO}_2$  group).  $^1\text{H}$  NMR:  $\delta\text{H}$  ( $\text{CDCl}_3$ , 400 MHz): 0.90 (t, 3H,  $-\text{OC}_4\text{H}_9$ ), 1.46 (m, 2H,  $-\text{OC}_4\text{H}_9$ ), 1.74 (m, 2H,  $-\text{OC}_4\text{H}_9$ ), 4.06 (t, 2H,  $-\text{OC}_4\text{H}_9$ ), 7.32 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.56 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.02 & 7.67 (d, 4H, first phenyl ring), 7.61 & 7.79 (d, 4H, second phenyl ring), 6.62 (s, 2H,  $-\text{SO}_2\text{NH}_2$  group), 8.81 (s, 1H, amide);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  ppm 19.0 ( $\text{CH}_3$  of  $-\text{OC}_4\text{H}_9$  chain), 31.3 ( $-\text{CH}_2$  aliphatic chain), 68.6 ( $-\text{OCH}_2$ ), 114.2, 129.3, 130.2, 120.4, 140.6, 135.1, 158.2 (Ar-C), 119.6 ( $\alpha$  carbon of  $-\text{CO}-\text{CH}=\text{CH}$ ), 141.3 ( $\beta$  carbon of  $\text{CO}-\text{CH}=\text{CH}$ ), 162.7 ( $-\text{C}=\text{O}$  group of amide).

**Compound C2:** 74 % yield, yellow color, FT-IR (KBr) in  $\text{cm}^{-1}$ : 2882 (-C-H- str in  $-\text{CH}_3$ ), 1460 (-NH), 1640 ( $>\text{C}=\text{O}$  str), 1240 ( $-\text{SO}_2$ ), 930 (*trans*, vinyl group), 820 (*para*-disubstituted aromatic ring), 801 (aliphatic alkyl chain).  $^1\text{H}$  NMR:  $\delta\text{H}$  ( $\text{CDCl}_3$ , 400 MHz): 0.88 (t, 3H,  $-\text{OC}_6\text{H}_{13}$ ), 1.46 (m, 2H,  $-\text{OC}_6\text{H}_{13}$ ), 1.76 (m, 2H,  $-\text{OC}_6\text{H}_{13}$ ), 4.06 (t, 2H,  $-\text{OC}_6\text{H}_{13}$ ), 7.32 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.84 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.10 & 7.46 (d, 4H, first phenyl ring), 7.53 & 8.01 (d, 4H, second phenyl ring), 6.46 (s, 2H,  $-\text{SO}_2\text{NH}_2$  group), 8.83 (s, 1H, amide);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  ppm 14.1, 19.2 ( $\text{CH}_3$  of  $-\text{OC}_6\text{H}_{13}$  chain), 31.6 ( $-\text{CH}_2$  aliphatic chain), 68.6 ( $-\text{OCH}_2$ ), 114.2, 129.3, 130.2, 120.4, 140.6, 135.1, 158.2 (Ar-C), 118.3 ( $\alpha$  carbon of  $-\text{CO}-\text{CH}=\text{CH}$ ), 140.9 ( $\beta$  carbon of  $\text{CO}-\text{CH}=\text{CH}$ ), 161.8 ( $-\text{C}=\text{O}$  group of amide).

**Compound C3:** 73 % yield, off white color, FT-IR (KBr) in  $\text{cm}^{-1}$ : 2986 (-C-H- str in  $-\text{CH}_3$ ), 1440 (-NH), 1610 ( $>\text{C}=\text{O}$  str), 1240 ( $-\text{SO}_2$ ), 930 (*trans*, vinyl group), 801 (*para*-disubstituted aromatic ring), 788 (aliphatic alkyl chain).  $^1\text{H}$  NMR:  $\delta$  ppm ( $\text{CDCl}_3$ , 400 MHz): 0.90 (t, 3H,  $-\text{OC}_8\text{H}_{17}$ ), 1.46 (m, 8H,  $-\text{OC}_8\text{H}_{17}$ ), 1.76 (m, 2H,  $-\text{OC}_8\text{H}_{17}$ ), 4.01 (t, 2H,  $-\text{OC}_8\text{H}_{17}$ ), 7.57 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.86 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.01 & 7.34 (d, 4H, first phenyl ring), 6.68 & 8.01 (d, 4H, second phenyl ring), 6.67 (s, 2H,  $-\text{SO}_2\text{NH}_2$  group), 8.54 (s, 1H, amide);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  ppm 14.2, 19.3, ( $\text{CH}_3$  of  $-\text{OC}_8\text{H}_{17}$  chain), 31.3 ( $-\text{CH}_2$  aliphatic chain), 68.6 ( $-\text{OCH}_2$ ), 114.2, 129.2, 130.2, 120.4, 140.4, 135.1, 158.2 (Ar-C), 119.4 ( $\alpha$  carbon of  $-\text{CO}-\text{CH}=\text{CH}$ ), 141.56 ( $\beta$  carbon of  $\text{CO}-\text{CH}=\text{CH}$ ), 160.74 ( $-\text{C}=\text{O}$  group of amide).

**Compound C4:** 76 % yield, light yellow color, FT-IR (KBr) in  $\text{cm}^{-1}$ : 2978 (-C-H- str in  $-\text{CH}_3$ ), 1420 (-NH), 1680 ( $>\text{C}=\text{O}$  str), 1240 ( $-\text{SO}_2$ ), 932 (*trans*, vinyl group), 806 (*para*-disubstituted aromatic ring), 723 (aliphatic alkyl chain).  $^1\text{H}$  NMR:  $\delta$  ppm ( $\text{CDCl}_3$ , 400 MHz): 0.88-0.90 (t, 3H,  $-\text{OC}_{10}\text{H}_{21}$ ), 1.28-1.32 (m, 12H,  $-\text{OC}_{10}\text{H}_{21}$ ), 1.47 (m, 2H,  $-\text{OC}_{10}\text{H}_{21}$ ), 1.76 (m, 2H,  $-\text{OC}_{10}\text{H}_{21}$ ), 4.08 (t, 2H,  $-\text{OC}_{10}\text{H}_{21}$ ), 7.67 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 8.12 (d, 1H,  $-\text{CO}-\text{CH}=\text{CH}-$ ), 7.12 & 7.69 (d, 4H, first phenyl ring), 7.79 & 6.87 (d, 4H, second phenyl ring), 6.47 (s, 2H,  $-\text{SO}_2\text{NH}_2$  group), 8.67 (s, 1H, amide);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  ppm 19.2 ( $\text{CH}_3$  of  $-\text{OC}_{10}\text{H}_{21}$  chain), 31.4 ( $-\text{CH}_2$  aliphatic chain), 68.6 ( $-\text{OCH}_2$ ), 114.3, 129.2, 130.2, 120.4, 140.6, 135.1, 158.2 (Ar-C), 114.4 ( $\alpha$  carbon of  $-\text{CO}-\text{CH}=\text{CH}$ ), 140.2 ( $\beta$  carbon of  $\text{CO}-\text{CH}=\text{CH}$ ), 161.7 ( $-\text{C}=\text{O}$  group of amide).

## Acknowledgments

LM and JYS acknowledge thanks to Department of Chemistry, Faculty of Basic and Applied Science, Madhav University for providing research lab facility. Authors are also thankful to the Department of Chemistry, School of Science, Gujarat University for POM analysis study. The authors are also thanks to IIT Indore Centre for providing spectral services.

Vinay S. Sharma gratefully acknowledges Human Resource Development Group-Council of Scientific & Industrial Research (CSIR), New Delhi for Research Associate Fellowship (File No: 09/070(0075)/2020-EMR-I).

## References

1. Bisoyi, H. K., and Li, Q. (2021) Liquid crystals: versatile self-organized smart soft materials. *Chem. Rev.*, 122 (5) 4887-4926.
2. Ghosh, T., and Lehmann, M. (2017) Recent advances in heterocycle-based metal-free calamitics. *J. Mater. Chem. C.*, 5 (47) 12308-12337.
3. Koh, T. M., Ha, S. T., Lee, T. L., Lee, S. L., Yeap, G. Y., Lin, H. C., and Subramaniam, R. T. (2011) Synthesis and mesomorphic evaluation of new calamitic liquid crystals containing benzothiazole core. *Chin. Chem. Lett.*, 22 (5) 619-622.
4. Madsen, L. A., Dingemans, T. J., Nakata, M., and Samulski, E. T. (2004) Thermotropic biaxial nematic liquid crystals. *Phys. Rev. Lett.*, 92 (14), 145505.
5. Patel, R. B., Patel, V. R., and Doshi, A. V. (2012) Synthesis and mesomorphism of novel liquid-crystalline isobutyl-p-(p'-n-alkoxy cinnamoyloxy) cinnamates. *Mol. Cryst. Liq. Cryst.*, 552 (1) 3-9.
6. Woltman, S. J., Jay, G. D. and Crawford, G. P. (2007) Liquid-crystal materials find a new order in biomedical applications. *Nat. Mater.*, 6 (12) 929-938.
7. Sharma, V. S. and Patel, R. B. (2017) Synthesis and study of mesomorphic properties in rod-like chalconyl compounds. *Mol. Cryst. Liq. Cryst.*, 643 (1) 52-61.
8. Sharma, V. S., Vekariya, R. H., Sharma, A. S. and Patel, R. B. (2017) Mesomorphic properties of liquid crystalline compounds with chalconyl central linkage in two phenyl rings. *Liq. Cryst. Today*, 26 (3) 46-54.
9. Matsukizono, H., Iwamatsu, K., Endo, S., Okumura, Y., Anan, S. and Kikuchi, H. (2023) Synthesis of liquid crystals bearing 1, 3-dioxane structures and characterization of their ferroelectricity in the nematic phase. *J. Mater. Chem. C*, 11 (18) 6183-6190.
10. Sato, M., Nagano, S. and Seki, T. (2009) A photoresponsive liquid crystal based on (1-cyclohexenyl) phenyldiazene as a close analogue of azobenzene. *Chem. Comm.*, (25) 3792-3794.
11. Gan, S. M., Yuvaraj, A. R., Lutfor, M. R., Mashitah, M. Y. and Gurumurthy, H. (2015) Synthesis, liquid crystal characterization and photo-switching studies on fluorine substituted azobenzene based esters. *RSC adv.*, 5 (9) 6279-6285.
12. Rahman, M.S., Wolter, T., Tripathi, A., Abbott, N.L., Mavrikakis, M. and Twieg, R.J. (2022) Investigation of the mesogenic behavior of alkoxy and fluorine tail terminated alkoxy nitrobiphenyls for chemoresponsive liquid crystals. *Liq. Cryst.*, 49 (15) 2082-2094.
13. Bisoyi, H.K. and Kumar, S. (2010) Discotic nematic liquid crystals: science and technology. *Chem. Soc. Rev.*, 39 (1) 264-285.
14. Viney, C., Twieg, R. J., Russell, T. P. and Depero, L. E. (1989) The structural basis of transitions between highly ordered smectic phases in semifluorinated alkanes. *Liq. Cryst.*, 5 (6) 1783-1788.
15. Foo, K. L., Ha, S. T. and Yeap, G. Y. (2022) Synthesis and phase transition behavior of calamitic liquid crystals containing heterocyclic core and lateral ethoxy substituent. *Ph. Transit.*, 95 (2) 178-192.
16. Desai, V., Sharma, V. S., Shah, R. R., Meena, L., Mali, H. and Patel, R. B. (2022) Synthesis and characterization of newly syringaldehyde based chalcone liquid crystals. *Mol. Cryst. Liq. Cryst.*, 745 (1) 1-15.
17. Desai, V., Sharma, V. S. and Patel, R. B. (2018) Synthesis and study of novel biological active chalconyl-ester based bent-core LCs: Effect of tail/lateral group. *Mol. Cryst. Liq. Cryst.*, 668 (1) 29-47.
18. Srinivasa, H.T. and Kumar, S. (2017) Synthesis and characterization of some new chalcone liquid crystals. *Liq. Cryst.*, 44 (10) 1506-1514.
19. Sasidharan, A.K., Mathew, J., Achalkumar, A.S. and Mathews, M. (2022) Synthesis and Liquid Crystalline Properties of Low Molecular Weight Bis-Chalcone Compounds. *Curr. Org. Synth.*, 19 (3) 463-475.
20. Nakum, K.J., Katariya, K.D., Hagar, M. and Jadeja, R.N. (2022) The influence of lateral hydroxyl group and molecular flexibility on the mesogenic behaviour of a new homologous series based on thiophene-chalcone: Synthesis, characterization, crystal structure and DFT study. *J. Mol. Str.*, (1261) 132891.
21. Thaker, B. T., Patel, P. H., Vansadiya, A. D. and Kanojjiya, J. B. (2009) Substitution effects on the liquid crystalline properties of thermotropic liquid crystals containing Schiff base chalcone linkages. *Mol. Cryst. Liq. Cryst.*, 515 (1) 135-147.
22. Chaudhari, M., Sharma, V.S., Ganga, V.S.R., Sharma, A.S., Mali, H. and Shrivastav, P.S., (2022) Room temperature imidazolium linked chalcone based ionic LCs: Role of terminal position on mesomorphism. *J. Mol. Str.*, (1270) 133834.
23. Yang, X., Jin, X., Zhao, T. and Duan, P. (2021) Circularly polarized luminescence in chiral nematic liquid crystals: generation and amplification. *Mater. Chem. Front.*, 5 (13) 4821-4832.
24. d'Alessandro, A. and Asquini, R. (2021) Light propagation in confined nematic liquid crystals and device applications. *Appl. Sci.*, 11 (18) 8713.
25. Tripathi, P. K., Singh, D. P., Yadav, T., Singh, V., Srivastava, A. K., and Negi, Y. S. (2023) Enhancement of birefringence for liquid crystal with the doping of ferric oxide nanoparticles. *Opt. Mater.*, (135) 113298.

26. Apaydin, S., and Török, M. (2019) Sulfonamide derivatives as multi-target agents for complex diseases. *Bioorganic Med. Chem. Lett.*, 29 (16) 2042-2050.
27. Shim, W. S., Kim, S. W., and Lee, D. S. (2006) Sulfonamide-based pH-and temperature-sensitive biodegradable block copolymer hydrogels. *Biomacromolecules*, 7 (6) 1935-1941.
28. Supuran, C. T. (2003) Indisulam: an anticancer sulfonamide in clinical development. *Expert Opin. Investig. Drugs.*, 12 (2) 283-287.
29. Kashyap, D., Patel, S., Prajapat, V., Sharma, V., and Vasava, D. (2019) Effect of the linking unit on the calamitic-shaped liquid crystal: a comparative study of two homologous series of benzoate and cinnamate linked compounds. *Mol. Cryst. Liq. Cryst.*, 681 (1) 58-70.
30. Desai, V., Sharma, V. S., and Patel, R. B. (2018) Synthesis and study of novel biological active chalconyl-ester based bent-core LCs: Effect of tail/lateral group. *Mol. Cryst. Liq. Cryst.*, 668 (1) 29-47.
31. Thakor, A., Dwivedi, D. J., Desai, V., Jadeja, U. H., Sharma, V. S., and Patel, R. B. (2022) Synthesis and characterization of biphenyl-based azo liquid crystals and its optical properties: effect of lateral and tail group. *Mol. Cryst. Liq. Cryst.*, 726 (1) 8-26.
32. Gao, M., Ma, L., and Luo, J. (2016) Effect of alkyl chain length on the orientational behavior of liquid crystals nano-film. *Tribol. Lett.*, (62) 1-7.
33. Sharma, V. S., and Patel, R. B. (2017) Effect of alkyl chain in the terminal ester group on mesomorphic properties of new rod like homologous series: Synthesis and characterization. *Mol. Cryst. Liq. Cryst.*, 643 (1) 62-75.
34. Wang, S., Zhang, C., & Chang, Q. (2017). Synthesis of magnetic crosslinked starch-graft-poly (acrylamide)-co-sodium xanthate and its application in removing heavy metal ions. *J. Exp. Nano sci.*, 12 (1) 270-284.
35. Mani, B., and Kathavarayan, S. (2016) Studies on photocrosslinking and flame-retardant properties of chalcone-based polyacrylamides. *Polym. Adv. Technol.*, 27 (4) 466-476.
36. Imrie, C. T., and Taylor, L. (1989) The preparation and properties of low molar mass liquid crystals possessing lateral alkyl chains. *Liq. Cryst.*, 6(1), 1-10.
37. Bisoyi, H. K., and Li, Q. (2021) Liquid crystals: versatile self-organized smart soft materials. *Chem. Rev.*, 122 (5) 4887-4926.
38. Jafari Ozumchelouei, E., Hamidian, A. H., Zhang, Y., and Yang, M. (2020) Physicochemical properties of antibiotics: A review with an emphasis on detection in the aquatic environment. *Water Environ. Res.*, 92 (2) 177-188.
39. Arshad, M. N., Faidallah, H. M., Asiri, A. M., Kosar, N., & Mahmood, T. (2020). Structural, spectroscopic and nonlinear optical properties of sulfonamide derivatives; experimental and theoretical study. *J. Mol. Str.*, (1202) 127393.
40. Suthar, D. M., Doshi, A. A., and Doshi, A. V. (2013) Study of liquid crystalline state and evaluation of its properties through a novel Homologous series. *Mol. Cryst. Liq. Cryst.*, 582 (1) 79-87.
41. Patari, S., Chakraborty, S., and Nath, A. (2016) The optical anisotropy and orientational order parameter of two mesogens having slightly different flexible side chain—a comparative study. *Liq. Cryst.*, 43 (8) 1017-1027.
42. Niemczak, M., Rzemieniecki, T., Sobiech, Ł., Skrzypczak, G., Praczyk, T., and Pernak, J. (2019) Influence of the alkyl chain length on the physicochemical properties and biological activity in a homologous series of dichlorprop-based herbicidal ionic liquids. *J. Mol. Liq.*, 276, 431-440.



© 2024 by the authors; licensee Growing Science, Canada. This is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).