

Synthesis and Liquid Crystalline Properties of Triazole-Based Azo-Schiff Base Derivatives for Optoelectronic Applications

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Abstract: A new series of 1,2,4-triazole-based heterocyclic Schiff base derivatives were prepared via a multi-stage synthetic pathway. This pathway begins with the base compound 2-((4-hydroxybenzylidene)amino)acetic acid, which reacts with thiocarbonylhydrazide to produce the required intermediates. These compounds were subsequently subjected to condensation, isomerization, and structural modification to yield the final derivatives. The chemical structure of the prepared compounds was confirmed using a range of advanced spectroscopic techniques. Fourier transform infrared (FT-IR) spectra revealed the characteristic extensions and vibrations of the imine ($-C=N-$) and azo ($-N=N-$) groups. In addition to the signals of the hydroxyl ($-OH$) and thiol ($-SH$) groups, both the 1H -NMR and ^{13}C -NMR spectra supported the validity of the proposed structure by showing chemical shifts consistent with the heterocyclic structure and the triazole nucleus. The structural study showed that the molecular shape of 3-phenylthiazolidine-2-one compounds replaced by pentyloxy and octyloxy chains has a spatial distribution and morphological regularity that gives it remarkable mesogenic behavior, indicating the possibility of its use in crystalline liquid material applications or thermally responsive functional materials. According to POM, the birefringent textures and typical upon heating textures patterns of the samples confirm the presence of thermotropic liquid crystalline phases nematic (N) and smectic (SC). The synthesized triazole-based azo-Schiff base derivatives have been found to possess conjugated π -systems and anisotropic molecular order, thus suggesting their potential application in LCD and optoelectronic materials.

1 INTRODUCTION

Aromatic heterocycles are planar rings of atoms containing at least one non-carbon atom (N, S, O) [1]-[4]. A large portion of natural products are heterocyclic compounds, and some are being utilised as pharmaceuticals, agrochemicals, etc [5]-[6]. One of its most important interactions is that Azo-Schiff base compounds represent a novel category of. These organic compounds are notable for possessing two functional groups in their structures: ($CH=N$) and ($N=N$) [7]-[9]. Schiff bases are Compounds that are formed as a result of the nucleophilic addition reaction of aldehydes and ketones with primary amines, and which have carbon-nitrogen double bonds ($-C=N-$) in their structure [10]-[11]. Azo dyes, being the largest class of synthetic dyes carrying the ($-N=N-$) group, which are categorised based on their elemental composition and use, are the main focus of colour chemistry [12]. Azo-Schiff base ligands and their metal complexes have been extensively studied

over the past few decades. It has been found that azo Schiff base compounds have a wide range of applications in liquid crystals [13]. Liquid crystals (LCs) are imperative middle phases that exhibit properties of both the fluid and solid states [14]-[18]. The liquid crystal technological revolution is intriguing because it exhibits characteristics of both liquids and solid crystals. They exhibit fluidic behavior, although their molecular arrangement remains fixed, similar to that of a crystal [19].

2 EXPERIMENTAL

2.1 Synthesis of 2-((4-hydroxybenzylidene)amino)acetic acid[A]

Initially, (0.5g) of glycine was dissolved in (10 mL) of absolute ethanol in a round-bottom flask.

Similarly, p-hydroxybenzaldehyde (0.8g) was dissolved in (10 mL) of absolute ethanol in a separate container. Then, three drops of concentrated sulfuric acid were added to the mixture of glycine and p-hydroxybenzaldehyde as a catalyst for the reaction to form a Schiff base. Then, the reaction mixture was heated in a water bath at 55-60°C for 8 hours. (TLC) was used to monitor the reaction's progress. The mixture was allowed to cool to room temperature. The solid product was then separated from the liquid phase by filtration. After filtration, the precipitate was washed with distilled water [20].

2.2 Synthesis of Thiocarbonohydrazid [B]

The mixture hydrazine hydrate (24.5ml) was placed, which was equipped with a thermometer, an efficient agitator, and a reflux condenser. The temperature was lowered to 10 °C, and (6.2ml) of carbon disulfide was added dropwise into the flask while maintaining the temperature below 15 °C. The temperature was raised gradually to 85 °C for two hours. TLC checked the reaction completion and the compound's purity. The Reaction mixture was cooled to 10 °C, and the precipitate was filtered and washed with distilled water [21].

2.3 Synthesis of 4-(4-amino-5-mercapto-4H-1,2,4-triazol-3-yl)methyl)imino)methyl)phenol [C]

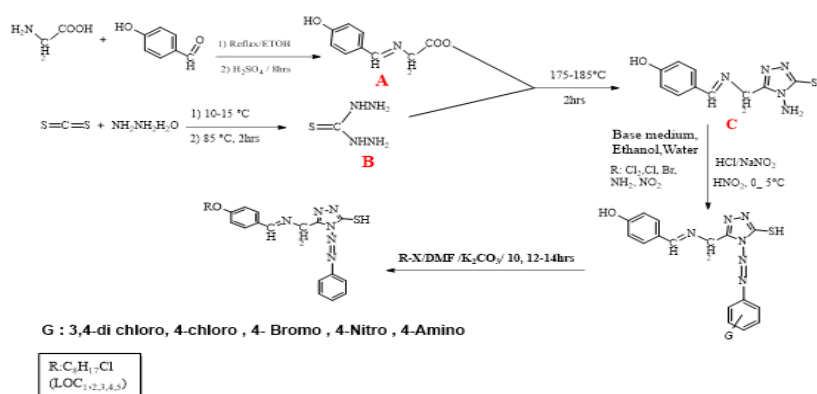
The 2-((4-hydroxybenzylidene)amino)acetic acid (1.79 g) and thiocarbonohydrazide (1.59 g) was ground thoroughly with a mortar to create a homogenous mixture. After being put in a Pyrex fusion tube, the mixture was heated for two hours at 175-185°C in an oil bath. The product was then rinsed with a cold solution of sodium bicarbonate and distilled water (5 g, 25 ml) to remove any last traces of acidic impurities. The washing process produced effervescence, which indicates that the acidic byproducts were neutralised. After that, the substance was filtered and thoroughly cleaned with cold distilled water.

2.4 Synthesis of 4-(5-mercapto-4-(4-substituted-phenyl)diazonyl)-4H-1,2,4-triazol-3-yl)methyl)imino)methyl)phenol [C1-C5]

The mixture (1g) of the substance was dissolved in a solution composed of (2 g in 10 ml) of HCl in distilled water and stirred until completely dissolved. The solution was chilled in an ice bath, maintaining a temperature range of 0-5°C. A preposition solution was obtained by dissolving 2g of sodium nitrite (NaNO₂) in 5 mL of distilled water, which was also cooled in the same ice bath. The sodium nitrite solution was added dropwise to the produced starting material solution, while continuously stirring and cooling. Subsequently, (0.89g) of chlorobenzene, bromobenzene, aniline, nitrobenzene, and dichlorobenzene were solubilised in appropriate solvents. This was checked using pH papers until the solution reached a neutral level, forming a diazonium dye precipitate [22].

2.5 Synthesis of 4-(4-Substituted)diazonyl)-5-(E)-(4(octyloxy)benzylidene)amino)methyl)-4H-1,2,4-triazole-3-thiol of L[OC1-OC5]

A round-bottom 50 mL flask with a reflux condenser was used. (0.3 g) of a mixed diazonium salt [C1-C5], synthesised earlier, was dissolved in 5 mL of DMF. The media was adjusted for reaction conditions by adding 0.1 g of K₂CO₃. 5 mL of DMF was used to dissolve 0.11 mL of 1-chloro-octanone in another container. After that, this solution was gradually added to the initial mixture while being constantly stirred. The resultant mixture was heated in an oil bath for 12-14 hrs at a temperature between 120 and 130 °C. The progress of the reaction was monitored using TLC. The reaction mixture was then allowed to cool gradually to room temperature, thoroughly washed with distilled water to remove any inorganic salts and impurities, and subsequently dried in an oven at a low temperature between 40 and 50°C [23].



Scheme 1: Synthesis of the compounds (C₁-C₅)(LOC₁-LOC₅)(LPC₁-LPC₅).

3 RESULTS AND DISCUSSION

3.1 Characterization by FTIR

3.1.1 FTIR Spectrum of 2-((4-hydroxybenzylidene)amino)acetic acid[A]

FT-IR spectrum exhibits a broad band at 3167 (O–H), 2879 cm⁻¹ (C–H) stretching, 1667 cm⁻¹ (C=O) (carboxylic group), 1598 cm⁻¹ (C=N) stretching (hydrazone), 1519,1546 cm⁻¹ (C=C) Aromatic, 1386–1315 cm⁻¹ (C–N) stretching (hydrazine) and (C–O) stretching (C–O) bending (phenol and carboxyl), 1160 cm⁻¹.

3.1.2 FTIR Spectrum Thiocarbonohydrazid[B]

The band at 3271 and 3209 cm⁻¹, symmetric and asymmetric group (NH₂), 2858 cm⁻¹ (C–H) Aromatic, 1609.8 cm⁻¹ to (C=N) imine, 1511.9, 1445.3 cm⁻¹

(C=C), while those at 1261.3 and 1171.2 cm⁻¹ represent (C–N) bending.

3.1.3 FTIR Spectrum of 4-(5-mercapto-4-(4-substituted-phenyl)diazenyl)-4H-1,2,4-triazol-3-yl)methyl)imino)methyl)phenol [C1-C5]

The main bands were shown in Table 1.

3.1.4 FTIR Spectrum of 4-(4-Substituted)diazenyl)-5-(E)-4(octyloxy)benzylidene) amino)methyl)-4H-1,2,4-triazole-3-thiol of L[OC1-OC5]

FTIR LOC1 2929.8, 2860.4 cm⁻¹ (C–H) Stretching (aliphatic & aromatic), 1604.7 cm⁻¹ (C=N) Stretching (imine / azomethine group), 1506 cm⁻¹ (N=N), 1456 cm⁻¹ (C=C) stretching (aromatic ring), 1252 cm⁻¹ (C–O) Stretching (phenolic / alkoxy group), 1170 cm⁻¹ (C–N) Stretching (triazole ring) [24], (Fig. 1). The main bands were shown in Table 2, Figures 2 - 5.

Table 1: FT-IR Vibrational bands of synthesized compounds [C₁-C₅].

Comp.Symb.	ν (cm) ⁻¹ , IR						
	(O–H)	(C–H) Ar.	(C–H) Aliph.	(C=N)	(C=C)	(N=N)	(C–N)
C	3310 3197	3083	2854	1607	1512	1443	1169 1242
C1	3196	3090	2810 2936	1609	1511	1440	1172 1235
C2	3334 3154	3010	2809	1605	1511	1445	1167 1261
C3	3164	3048	2801	1605	1511	1441	1171 1237
C4	3329 3166	3096	2817	1609	1511	1441	1171 1241
C5	3188	3075	2895	1609	1515	1440	1168 1237

Table 2: FT-IR Vibrational bands of synthesized compounds L[OC₁-OC₅].

Com. Symb.	ν (cm ⁻¹), IR					
	C-H Arom.	C-H Aliph.	C=N	C=C	N=N	C-N
LOC1	2929	2860	1604	1506	1456	1170 1252
LOC2	2928	2858	1606	1508	1458	1170 1251
LOC3	2926	2856	1606	1508	1458	1171 1249
LOC4	2926	2828	1602	1510	1448	1251
LOC5	2928	2929	1602	1509	1454	1168

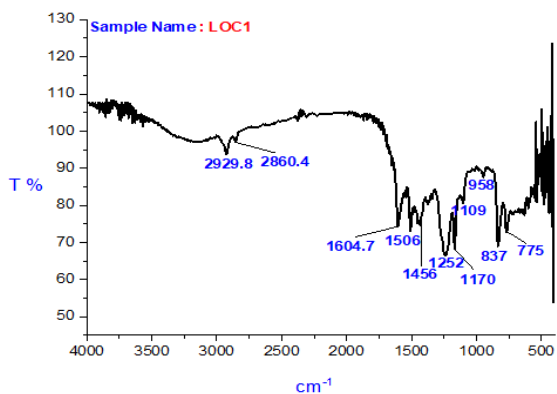


Figure 1: FTIR spectrum of LOC1.

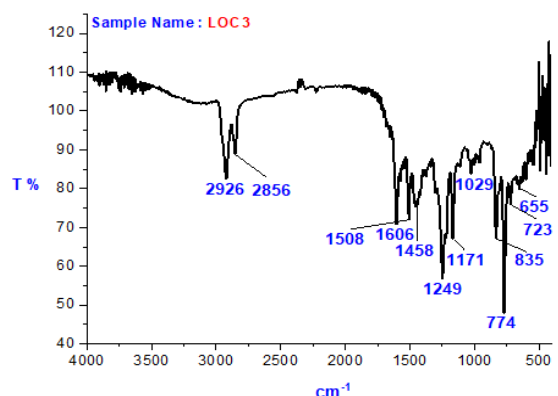


Figure 3: FTIR spectrum of LOC3.

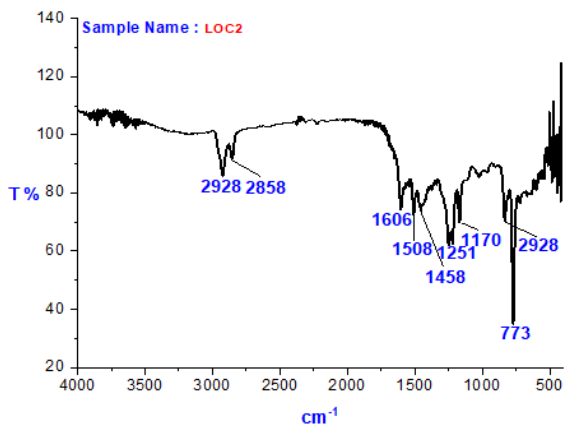


Figure 2: FTIR spectrum of LOC2.

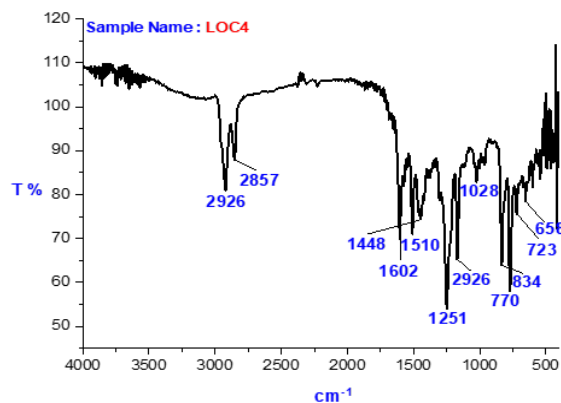


Figure 4: FTIR spectrum of LOC4.

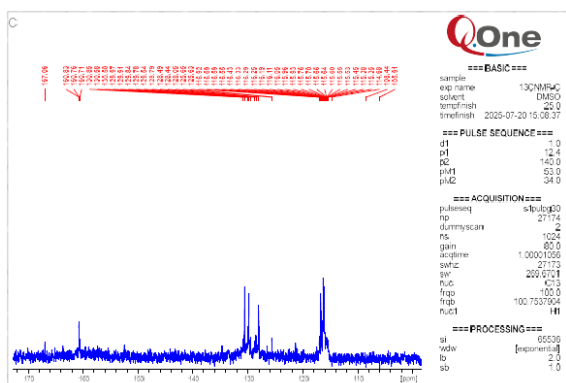


Figure 9: ¹³C-NMR Spectrum of C.

3.2.3 NMR Spectrum of 4-(5-mercapto-4-(4-substituted-phenyl)diazonyl)-4H-1,2,4-triazol-3-yl)methyl)imino)methyl)phenol [C1-C5]

¹H-NMR δ 9.93,9.81 ppm (s, (N-H), δ 8.57ppm (s, 1H, Imine. H) (=CH=N-), δ 7.80–7.00ppm (m (6–7H) arom. H) (phenolic + di chloropyridine rings), δ 6.80–6.60ppm (m, phenolic ring), δ 5.40–5.50ppm (s, phenolic), 13.0–14.0ppm (s,(S-H) (triazole-thione, Hexchangeable), (Fig. 10). The ¹³C-NMR 108–133 ppm Aromatic carbons. Of both the phenolic and dichloro-pyridine rings, as well as the carbon attached to the azomethine (–CH=N) group (Fig. 11).

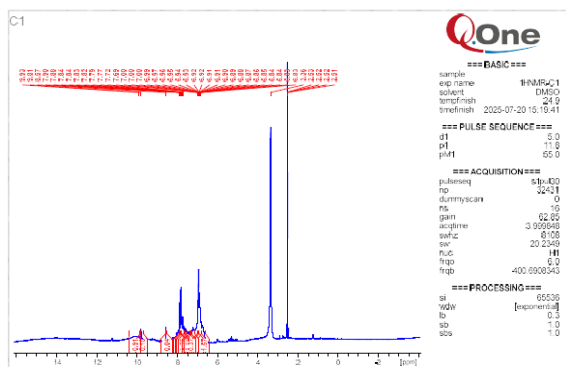


Figure 10: ¹H-NMR Spectrum of C1

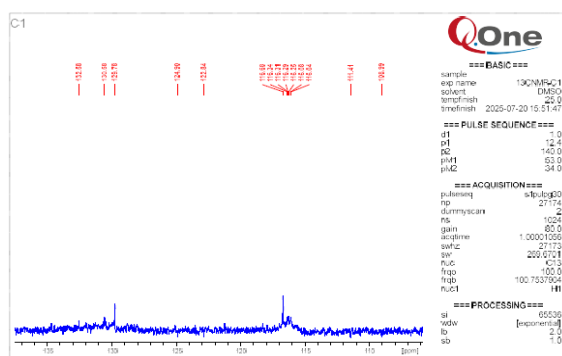


Figure 11: ¹³C-NMR Spectrum of C1

3.2.4 NMR of 4-(4-Substituted)diazonyl)-5-(E)-(4(octyloxy)benzylidene)amino)methyl)-4H-1,2,4-triazole-3-thiol of L [OC1-OC5]

¹H-NMR spectrum of LOC1. δ 9.89 ppm (s, ~1H, imine. H) (–CH=N–), δ 8.6 – 6.8 ppm (m, ~4–6H, arom. H), δ 4.66 ppm (s/weak t, ~2H, (–O–CH–). H), δ 3.37 ppm (m, ~2–4H, CH. H) Near hetero aromatic (N or S), δ 1.29 (br m / triplet, 3H, methyl. H) Long alkyl chain (Fig. 12).

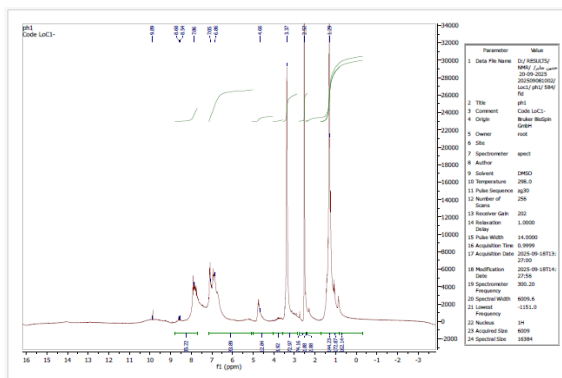


Figure 12: ¹H-NMR spectrum of [LOC1].

¹H-NMR spectrum of LPC5. δ 10.23 – 9.80 ppm (br s, ~1H amide. H), δ 8.24 – 6.86 ppm (m, ~4–6H, arom. H), δ 4.76 ppm (s or weak d, ~1H, C–H. H) near O/N (–CH–O– or –CH–N–), δ 3.73 – 3.11ppm (m ~4H, methylene. H) Near O/N (–CH–O– / –CH–N–), δ 2.29, 2.24 ppm (s to weak m, ~2–3H Aliph. H), Ar (–CH–C=O–, Ar–CH), δ 1.37, 1.24ppm (t/m, ~3–6H, Aliph. H) CH / CH (Fig. 13).

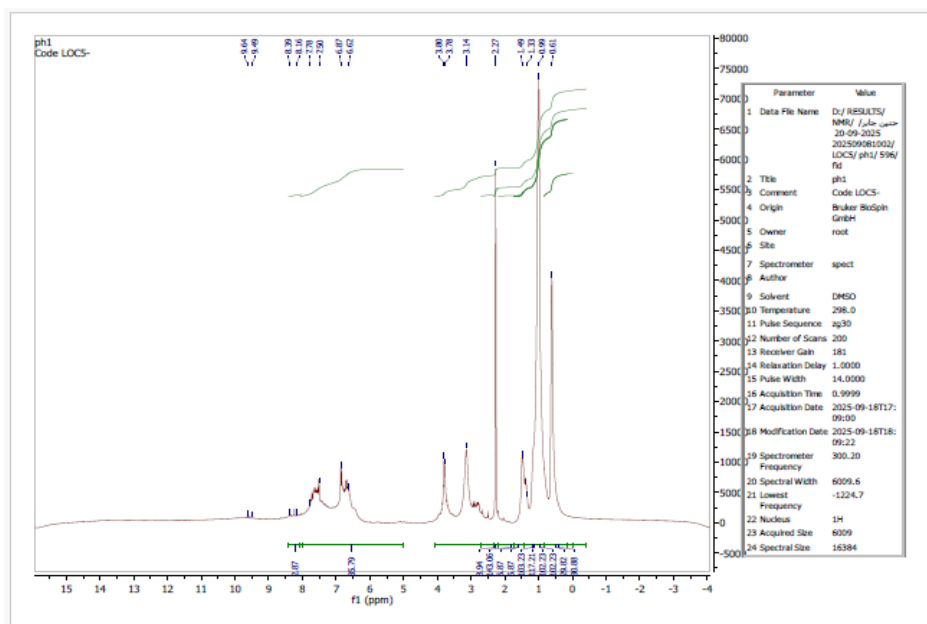


Figure 13: ¹H-NMR spectrum of [LPC5].

3.3 Characterization by (POM)

POM analysis confirmed that the synthesized triazole azo-Schiff base derivatives were thermotropic liquid crystalline. Rephrase More Undo Alkoxy substituent-containing compounds exhibited nematic (N) and smectic (SC) textures upon heating the thermal transitions of the prepared compounds were shown in Table 3, presumably because a rod-like aromatic structure with polar terminal groups could stabilize monotropic mesophases which were thermally more stable due to anisotropic molecules [25], (Fig. 14 - 16).

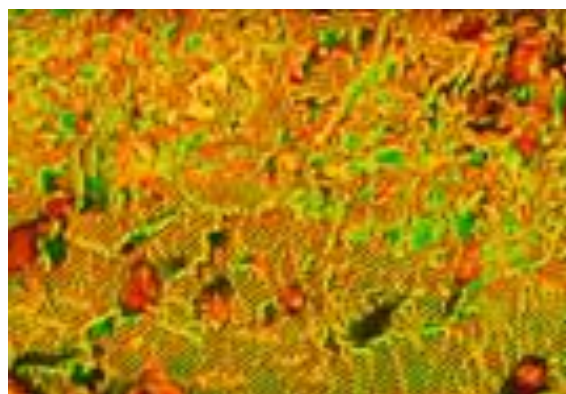


Figure 15: The Smectic phase of (LOC2).

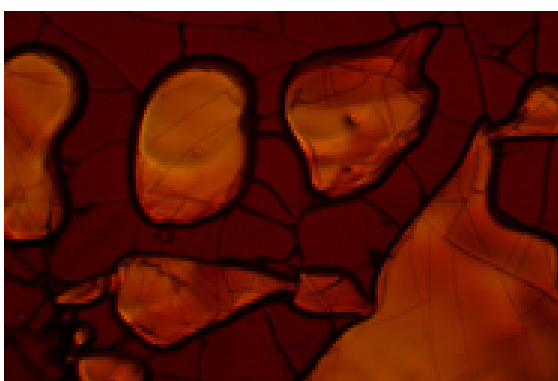


Figure 14: The nematic phase of (L-OC1).

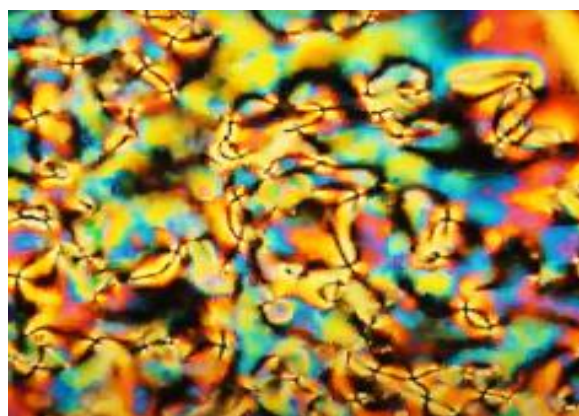


Figure 16: The Nematic phase of (LOC2).

Table 3: Thermal transitions and liquid crystalline phases of the prepared compounds.

Comp	Heat	Cr	SA	SC	N	ΔSC	ΔN
L-OC1	Heat	158		172		12	
	Cool						
Comp.	Heat	Cr	SA	SC	N	ΔSC	ΔN
L-OC2	Heat	166		179	193	13	14

4 CONCLUSIONS

The current study demonstrated the successful preparation of a new series of heterocyclic Schiff base derivatives based on the 1,2,4-triazole nucleus via a multi-stage synthetic pathway starting from the base compound 2-((4-hydroxybenzylidene) amino)acetic acid. This gradual approach has allowed control over the chemical structure of the final compounds through condensation, isomerization, and structural modification processes, resulting in the production of derivatives bearing long alkoxy chains of the pentyloxy and octyloxy types. The structural identity of these derivatives was verified using a comprehensive suite of advanced spectroscopic techniques FT-IR spectra confirmed the presence of key functional groups such as imine ($-C=N-$) and azo ($-N=N-$) in addition to signals from hydroxyl ($-OH$) and thiol ($-SH$) groups. The 1H -NMR and ^{13}C -NMR spectra also showed that the chemical shifts matched the expected arrangement of the heterocyclic structure and triazole nucleus, thus supporting the proposed structure of the prepared compounds. Through polarized light microscopy (POM) analysis, it was found that octyloxy and pentyloxy derivatives possess clear birefringence and exhibit a characteristic nematic or thickened texture, which is direct evidence of their stable mesogenic behavior. These compounds also exhibit a level of long-range organization resulting from the morphological symmetry and spatial distribution of the 3-phenylthiazolidine-2-one chain, reflecting the influence of the alkoxy chains on the phase response and optical properties. These results confirm that combining a triazole nucleus with azo-Schiff units and long alkoxy chains generates materials that combine thermal stability with a distinctive phase response, making this class of compounds promising candidates for the development of mesogeneous materials for optoelectronic applications and display technologies. In addition, they can be used in the design of advanced functional materials based on thermal or optical responses. Therefore, this study represents an important step towards expanding the

base of mesogenic compounds based on multifunctional heterocyclic systems.

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