



Original Research Article

Synthesis and characterization of new azo amino compounds and study of impact of aliphatic chain length on liquid crystalline behavior

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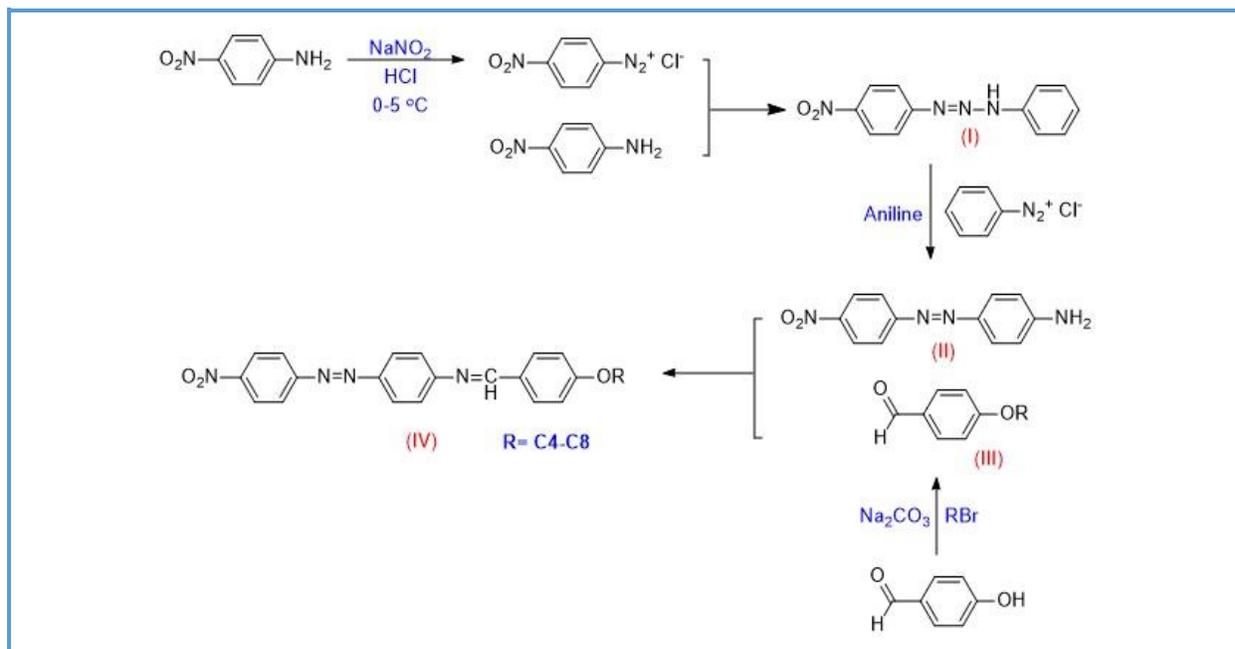
Nematic phase

ABSTRACT

Many novel mesogenic azo-Schiff base compounds have been produced successfully. An azo compound was obtained by a reaction of *p*-nitroaniline and hydrochloric acid with NaNO₂ to prepare diazonium salt, this was followed by a coupling reaction with aniline to produce the final azo dye (II). While alkoxybenzaldehyde was prepared by reacting benzaldehyde with an alkyl halide (III). Finally, azo-Schiff bases were prepared by reacting azo dye with alkoxybenzaldehyde. The prepared compounds were diagnosed using FT-IR and ¹H NMR spectrometers. A polarizing optical microscope (POM) and a differential scanning calorimeter (DSC) were used to study liquid crystalline properties. It was observed that the thermal stability of the liquid crystalline phases of the prepared compounds increased with the length of the aliphatic chain. In addition, most of the compounds gave liquid crystalline properties and more than one transition, and the reason for this is the molecular structure of the compounds. Likewise, increasing the length of the terminal groups decreased the melting points of the products.

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Graphical Abstract



Introduction

Several organic compounds, as are widely known, can exhibit not only gas, liquid, and solid phases but also intermediate phases between liquid and solid, known as mesophases [1]. So, liquid crystals are intermediate states between solid crystalline and isotropic phases [2, 3].

Due to its unique properties, it has been used in many medical and industrial fields. Therefore, lately, LC has been employed in self-assembly transistors and organic photovoltaic cells [4, 5], and optical sensors for imaging trypsin activity [6], light polarization [7], and Elastomers were generated by weakly cross-linking thermotropic liquid crystal phase with reactive mesogens to create artificial muscles. [8]. Aromatic azo groups are highly colored and frequently used as dyes [9].

Azo compounds contain the $\text{R}_1\text{-N=N-R}_2$ group, When the R groups in aromatic azo compounds are Arene rings, the structures are more stable than when the R groups are alkyl groups [10, 11].

A coupling reaction between a diazonium salt and a coupling agent produces aromatic azo compounds [12]. When a diazonium salt reacts with aryl amines, a yellow color is frequently produced. So, many different azo compounds can be formed by coupling different diazonium salts with aryl amines [13, 14].

Because their availability, good photo-fatigue resistance, and the significant shift of their molecular structure during E-to-Z photoisomerization, azo-dyes liquid crystals have lately gained a lot of attention for optical storage applications [15, 16]. Azo-dye have a good dichroic ratio, making them ideal for the efficient liquid crystal devices with low power consumption [17]. The main objective of the research is to prepare new amino dyes and study their liquid crystal behavior, as well as study the effect of the length of aliphatic chains on the thermal stability of liquid crystal phases.

Experimental

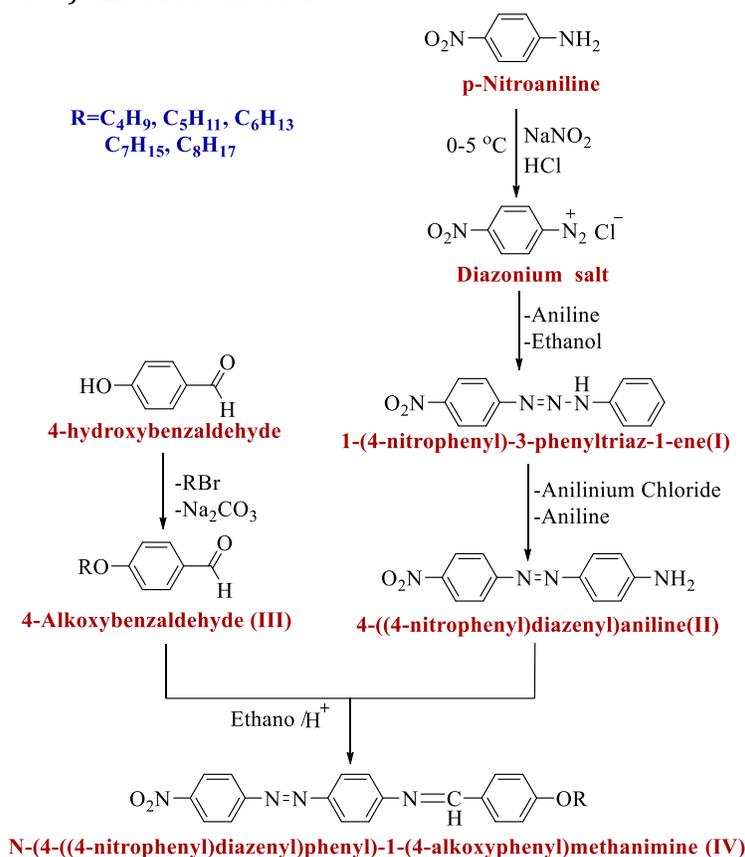
Materials and methods

4-Nitro aniline (Merck), Sodium nitrite (Fluka), Aniline (Merck), 1-Bromobutane (Fluka), 1-Bromopentane (Fluka), 1-Bromohexane (Fluka), 1-Bromoheptane (Fluka), 1-Bromooctane (Fluka), Sodium carbonate (Aldrich), 4-Hydroxy benzaldehyde (Aldrich), Sodium acetate (Merck), Hydrochloric acid (Fluka), and Ethanol Absolute (Merck). The IR spectrum was recorded using a Shimadzu FT-IR 8400S (KBr) scale Fourier transform infrared spectrometer (4000-400). An Ultra Shield 400

MHz Bruker 2003 was used to record a ¹H NMR spectra. A Differential Scanning Calorimeter (DSC-60) Shimadzu, polarizing optical microscope (POM) type (Optike) was used to analyze the liquid crystalline characteristics.

General procedure

All compounds were prepared according to the [Scheme 1](#).



Scheme 1. Synthesis pathway of the prepared compounds

Synthesis of 1-(4-nitrophenyl)-3-phenyltriaz-1-ene (I) [18]

0.03 mol (3.09 mL) of HCl was dissolved in 20 mL of water and 0.02 mol (2.76 g) of *p*-nitro aniline was added to it (A). Stir the mixture until the amine dissolves (The solution was cooled by an ice bath (0-5 °C)). After that, 0.02 mol (1.38

g) of NaNO₂ dissolved in the least amount of water is added. Then, the reaction mixture was stirred for half an hour. In another beaker (B), 0.02 mol (1.86 g) of aniline was dissolved in 20 mL of ethanol. Solution (B) was progressively added to the solution (A) and stirring continued for an hour. The suction filtration is used to filter the mixture with a small amount of cold

water and wash the solid product off the Buchner funnel, and recrystallized from 60-80 °C petroleum ether. Yield=90%, orange powder, m.p.=139-141 °C, IR (KBr): 3402 cm⁻¹ (NH), 3032 cm⁻¹ (C-H aromatic); (1493/1577) cm⁻¹ (C=C aromatic); 1448 cm⁻¹ (N=N). 1308 cm⁻¹, 1647 cm⁻¹ (NO₂) [19].

Synthesis of 4-(4-nitrophenyl)diazenyl)aniline (II)

After dissolving 0.02 mol (4.84 g) of azo dye in the least amount of aniline, 0.01 mol (1.295 g) of anilinium chloride was added to it. The reaction mixture was refluxed for one hour in a water bath at 40-45 °C. Then, drop by drop, added the mixture to a solution of glacial acetic acid diluted with an equal amount of distilling water. The resulting product was filtered, washed in cold water, and recrystallized from CCl₄. Yield=88%, orange powder, m.p.= 236-238 °C, IR (KBr): (Asym. 3364, sym. 3402) cm⁻¹ (NH₂), 3009 cm⁻¹ (C-H aromatic); (1507/1586)

cm⁻¹ (C=C aromatic); 1422 cm⁻¹ (N=N). 1319 cm⁻¹, 1651 cm⁻¹ (NO₂).

Synthesis of 4-alkoxybenzaldehyde (III) [20]

0.02 mol (2.76 g) of 4-hydroxy benzaldehyde was dissolved in 30 mL of DMF in a round flask and 0.02 mol (0.8 g) of sodium hydroxide was added to it. After 20 minutes of refluxing, 0.025 moles of alkyl halide was added to the mixture. The reflux was kept at 130 °C for 6 hours in an oil bath. The mixture is cooled and added drop by drop to ice water, then the product was extracted. Table 1 shows some properties of the prepared compounds.

All the FT-IR spectra of the prepared compounds indicated the disappearance of the peak at 3276 cm⁻¹ for the OH bond of the hydroxyl group, while the carbonyl group of aldehydes remained within the range 1687-1694 cm⁻¹. Also, the infrared spectrum of the prepared compounds showed other spectroscopic, as show Table 2.

Table 1. Shows some properties of 4-alkoxybenzaldehyde (C4-C8) (III)

Comp. NO.	R	bp. °C	Color	Yield%	Density g/mL
1	C4	283-285	yellow	79	1.035
2	C5	144-146	Light yellow	73	1.022
3	C6	150-152	yellow	75	0.993
4	C7	152-154	yellow	72	0.98
5	C8	138-140	yellow	70	0.979

Table 2. Shows some infrared spectra of the prepared compounds (C4-C8) (III)

Comp. NO.	R	FT-IR, ν (cm ⁻¹)					
		ν C-H Arom.	ν C-H Aliph. Asym, sym.	ν C=O Aldehy.	ν C=C Arom.	C-H Aldehy.	ν C-O ether
1	C4	3018	2932 2846	1691	1599 1509	1722	1158
2	C5	3022	2933 2859	1687	1597 1510	1718	1158
3	C6	3019	2930 2823	1689	1600 1509	1739	1158
4	C7	3020	2926 2841	1693	1599 1508	1752	1158
5	C8	3018	2925 2862	1694	1600 1508	1742	1158

Synthesis of N-(4-((4-nitrophenyl)diazanyl)phenyl)-1-(4-alkoxyphenyl)methanimine (IV)

0.01 mol of 4-alkoxybenzaldehyde (III) was dissolved in 20 mL of absolute ethanol and drops of glacial acetic acid were added. The mixture was then treated with 0.01 mol of 4-((4-nitrophenyl) diazenyl) aniline (II) under reflux for 3–4 hours. The product was cooled, filtered, and recrystallized from the ethanol. **Table 3**, shows some properties of prepared compounds (IV).

The FT-IR spectra of the Schiff bases were studied, and it was observed that the peak of the symmetric and asymmetric stretching of the amino group at (Asym. 3364, sym. 3402) cm^{-1} had disappeared, as well as the disappearance of the peak of the carbonyl group within the range 1687–1694 cm^{-1} , as the disappearance of these peak is an indication of the occurrence of

the interaction. Also, A new peak to azomethene group (C=N) in FT-IR spectrum was appeared at range (1629–1659) cm^{-1} , **Table 4**: shows the FT-IR absorption values for the prepared series compounds.

The structural formulas of the prepared compounds were confirmed using $^1\text{H-NMR}$ and using the solvent [DMSO- d_6], which gave further evidence of the correctness of the product composition.

$^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ to the (C6) Compound: 0.89 (t, 3H, $^3J_{\text{HH}}=8.0$ Hz, CH_3), 1.24–1.44 (m, 6H, 3 CH_2), 1.74 (m, 2H, CH_2), 4.04 (t, 2H, CH_2), 6.88–8.50 (m, 12H, aromatic benzene), 8.64 (s, 1H, $\text{CH}=\text{N}$), as displayed in **Figure 1** [21].

$^1\text{H NMR}$ (300 MHz, DMSO- d_6) δ to the (C8) Compound: 0.90 (t, 3H, $^3J_{\text{HH}}=8.2$ Hz, CH_3), 1.22–1.46 (m, 10H, 5 CH_2), 1.74 (m, 2H, CH_2), 4.03 (t, 2H, CH_2) 7.04–8.0 (m, 12H, aromatic benzene), 8.66 (s, 1H, $\text{CH}=\text{N}$), as displayed in **Figure 2**.

Table 3. Shows some infrared spectra of the prepared compounds (C4 – C8) (IV)



Comp. NO.	R	mp. °C	Colour	Yield (%)
1	C4	198-200	Orange	83
2	C5	189-190	Yellow	79
3	C6	162-164	Orange	75
4	C7	155-156	Orange	81
5	C8	149-151	Yellow	82

Table 4. shows the FT-IR absorption values for the Schiff bases compounds

Comp. NO.	R	N=N	NO ₂ Asym.	C≡C Ar.	I.R.-KBr, ν (cm^{-1})		C-H Ar.	C=N
					C-H Aldehyde	C-H Alf. (Asym. Sym.)		
1	C4	1460	1618	1643	2798	2849	3059	1640
					2766	2817		
2	C5	1413	1642	1621	2708	2892	3083	1659
					2786	2867		
3	C6	1429	1623	1653	2757	2901	3028	1634
					2788	2859		
4	C7	1428	1637	1637	2702	2856	3067	1629
					2776	2823		
5	C8	1443	1632	1667	2779	2885	3039	1651
					2759	2837		

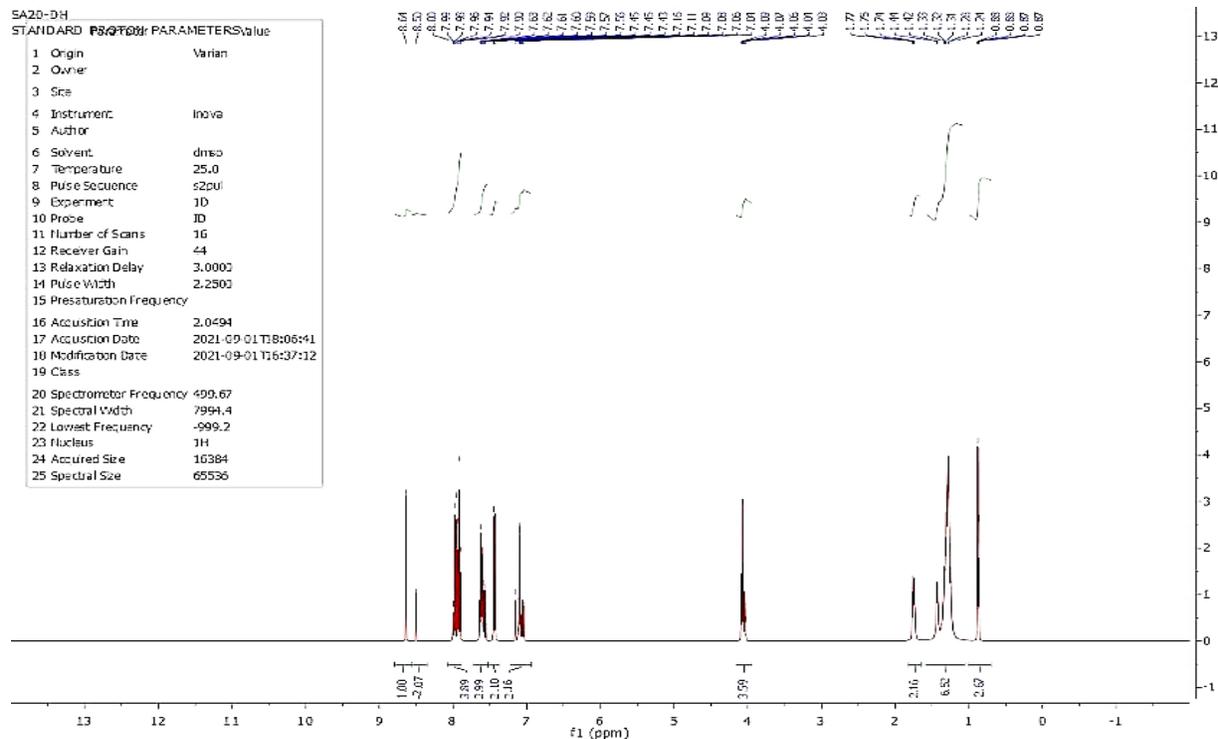


Figure 1. The ¹H NMR spectrum of the compound C6

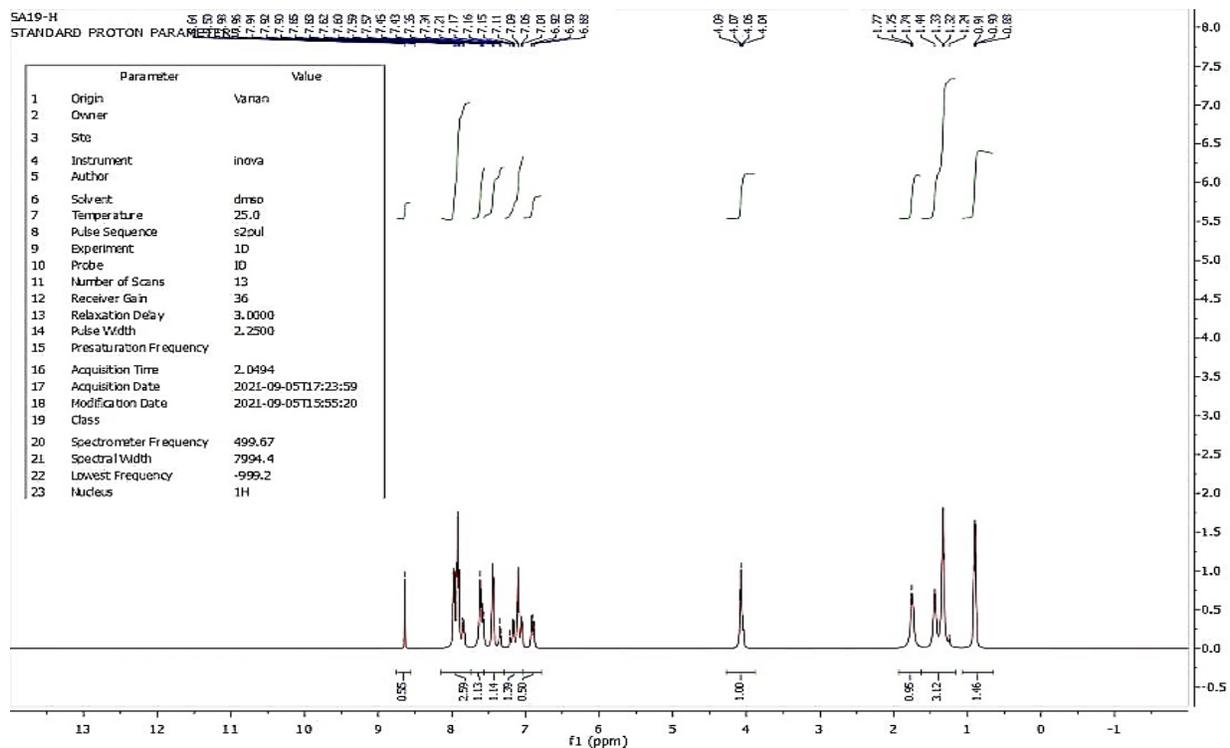


Figure 2. The ¹H NMR spectrum of the compound C8

Results and Discussion

Discussion of liquid crystalline behavior (General concepts)

As shown in the above scheme, a new series of azo-Schiff bases was produced by coupling the reaction of the diazonium salt with aniline, then the output was reacted with an aldehyde to obtain the final product.

The liquid crystalline behavior was determined for most of the prepared compounds by using polarizing the optical microscope POM and Differential Scanning Calorimetry (DSC) techniques. It has been taken roughly (2–3) mg of dry matter and heated it in an inert environment of N₂ [22-25].

DSC was used to identify thermal transitions in liquid crystal compounds, as show in Figure 3 and 4, also determined the nature and type of thermal liquid crystalline behavior with the use of POM. Figures 5-12 shows the results of texture of liquid crystalline phases.

Most of the compounds are mesomorphic, with a variety of SmA, SmC, and N phases, based on the findings. Most of the prepared compounds indicated liquid crystal phases with a high-temperature range, and the reason for this is the presence of three aromatic rings

linked by bonds that increase the electronic conjugated along the axis of the molecule, as well as the presence of the aliphatic terminal groups.

The nematic phase of some of the prepared compounds revealed the schlieren texture [26, 27], as well as, the marble texture [28].

As shown in Table 5, the reason for the appearance of liquid crystalline phases in most of the prepared compounds was the construction of a mesogenic unit consisting of three aromatic rings linked by bond that increase the electronic conjugated, in addition to the presence of aliphatic terminal groups that increase the flexibility of the molecule at the ends.

All the above effects were the main reason for the liquid crystal behavior of the prepared compounds.

POM was used to determine the types of liquid crystal phases [29, 30]. All the compounds were monotropic and it was only in heating.

This study showed that the thermal range of the liquid crystalline phases exhibited by compounds was affected by the length of the aliphatic chain.

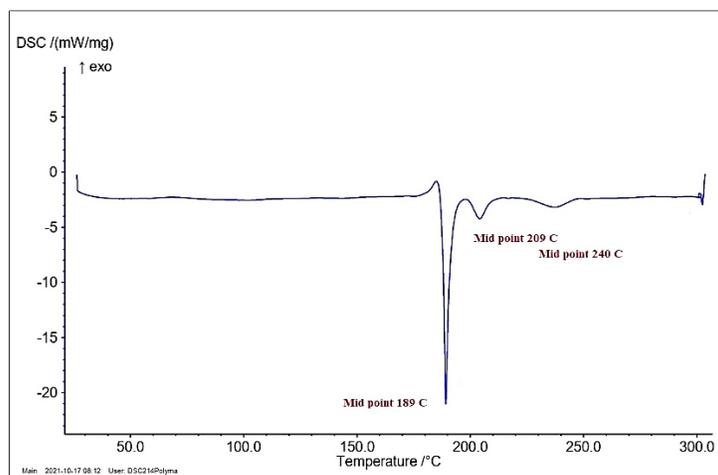


Figure 3. DSC analysis of the compound C5

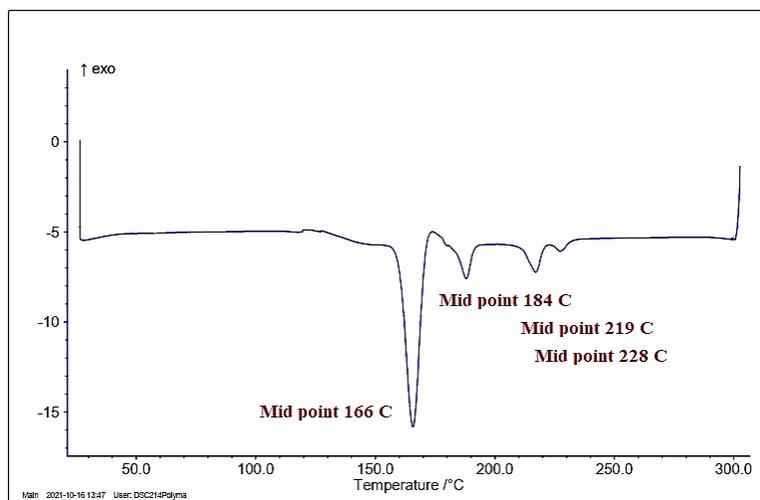


Figure 4. DSC analysis of the compound C6



Figure 5. SA comp. C4

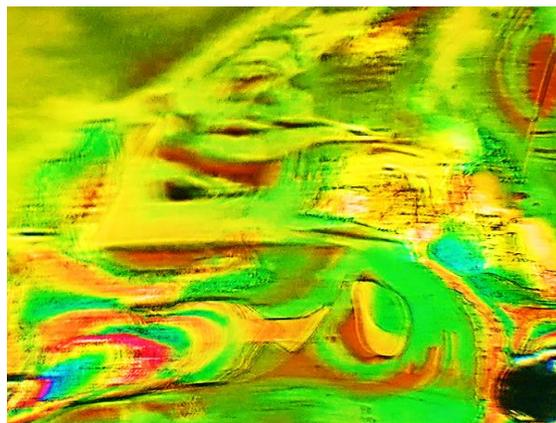


Figure 6. SA comp. C6

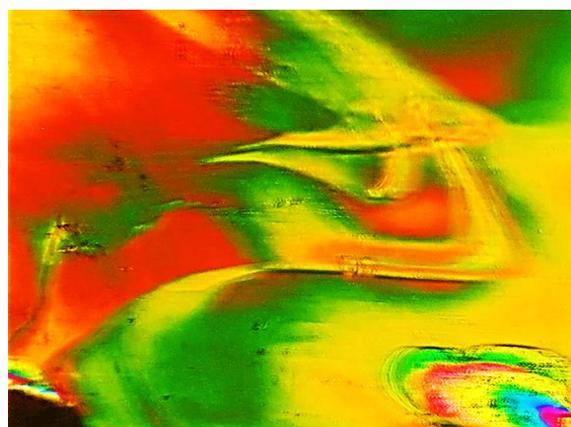


Figure 7. N comp. C6

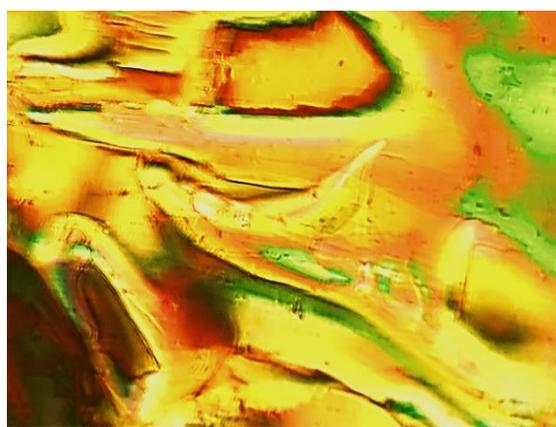


Figure 8. SC comp. C6

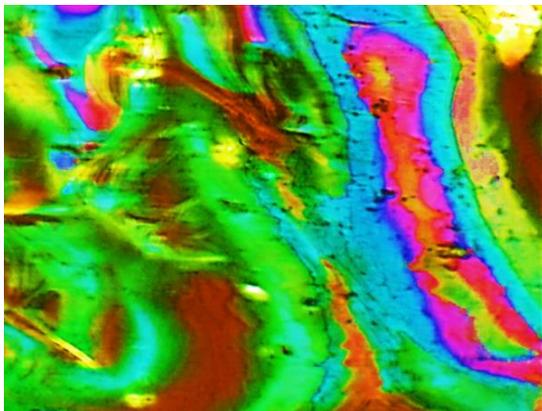


Figure 9. SC comp. C8

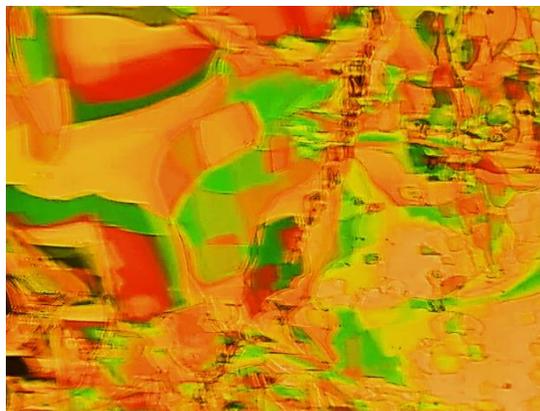


Figure 10. N comp. C5



Figure 11. N comp. C4



Figure 12. N comp. C8

Table 5. Liquid crystal phase transitions in a differential scanning calorimeter (DSC) and a polarizing optical microscope (POM) for prepared substances

App.	R	Cr	S _A	S _C	N	ΔT _{SA}	ΔT _{SC}	ΔT _N	Structure
DSC		201	221		232	20		11	
POM	C4	203	221		233	18		12	
DSC		189	209		240	18		31	
POM	C5	192	209		241	17		32	
DSC		166	184	219	228	18	35	9	
POM	C6	166	185	221	230	19	36	9	
DSC		-							
POM	C7	156							
DSC		-							
POM	C8	152		173	209		21	36	

Conclusions

From the practical results which were obtained and discussed, the conclusions can be summarized as follow:

- The prepared compounds were of high purity, and this was confirmed by various spectroscopic tests.
- Raising the number of aromatic rings led to an increase in the hardness of the molecules,

which in turn caused an increase in their melting points.

- There is no odd-even effect on the liquid crystalline properties of the series compounds.
- Most of the prepared compounds revealed liquid crystal phases with a high-temperature range due to the presence of three aromatic rings in the center of the molecule linked by bonds increase the electronic conjugated, as well as the presence of aliphatic terminal groups that increase the flexibility of the molecule.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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