

Mesomorphic Studies on a Series of Nickel (II) Centered Aromatic Complexes Displaying Liquid Crystalline Phases

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Abstract

Two new series (A & B) of three materials each based on the aroyl hydrazinato-nickel (II) complex were synthesized and characterized. The core molecule in these series consists of two 4-benzoyloxy benzylidene moieties and two benzene rings attached at the azomethine moiety. These latter benzene rings have one or two alkoxy chains comprised of either 10, 12, 16 or 18 carbon atoms. The characterization of these two series by polarized optical microscopy and differential scanning calorimetry is described herein. Upon cooling from the Isotropic phase, three of the six materials display a monophasic columnar phase and the other three possess a biphasic nematic and columnar phases. Upon heating, all six materials have a clearance point at high temperatures without displaying mesomorphic behavior. In series B mesogens, it was observed that the longer the hydrocarbon tail length, the lower the clearance point.

Keywords

Columnar, Mesomorphic, Nematic, Discotic, Metallomesogens, Polarized Optical Microscopy, Differential Scanning Calorimetry

1. Introduction

The fourth state of matter, commonly known as the liquid crystal state was first discovered by the Austrian scientist Friedrich Reinitzer in 1888. The original liquid crystalline type discovered by Reinitzer from natural sources is of the rod-like or calamitic type whereby the molecular length is far greater than the

width. The rod-like liquid crystalline materials are behind much of the LC display industry exceeding 100 billion dollars a year. The second liquid crystalline type discovered in 1977 by Sivaramakrishna Chandrasekhar is the disk-like or discotic type. Discotic mesogenic materials are typically comprised of a rigid aromatic core and flexible peripheral chains. These discotic materials have been attracting attention due to their fundamental importance as model systems for the study of charge and energy transport and due to the possibilities of their application in organic electronic devices [1] [2] [3]. Discotic mesogens are being researched and considered as a novel generation of organic semiconductors as well as mesophase semiconductors due to their remarkable performance in electronic and optoelectronic devices [4].

Heterocyclic rings incorporated as core centers in the design and synthesis of mesogenic materials have been widely investigated for four decades in discotic liquid crystal research [5] [6] [7]. Five or six membered heterocyclic rings have been studied extensively in liquid crystals research due to their structural variety and well known chemistry. Good mesomorphic behavior often resulted from such structures which can be attributed to their electronic properties and polarizability [7].

Congruent to the use of heterocyclic rings, metal containing liquid crystals, (metallomesogens) have received considerable attention for more than three decades now [8] [9] [10] [11]. Numerous transition metal complexes with varying molecular structures were synthesized and their mesomorphic properties investigated. Mesomorphism can sometimes be induced in nonmesogenic organic ligands upon coordination with the proper metal ion. In such cases, a metallomesogen displays the unique properties of a liquid crystal anisotropic fluid combined with the electronic and optical properties of a metal complex [12].

A dominant factor in molecular organization at the molecular and supra-molecular levels is molecular shape. Fine tuning of mesomorphic behavior can be adjusted by choosing a particular metal ion and positioning substituents on the ligand aromatic rings [13].

When phenyl based organic structures possessing long peripheral hydrocarbon chains are coordinated with the proper metal atom, the resulting complexes are often columnar liquid crystalline products capable of self-organization and assembling into supramolecular structures. These supramolecular structures often display notable and desirable properties such as gelation, thermochromism and solvatochromism [14]. The number and length of the peripheral hydrocarbon chains attached to the phenyl rings have their marked effects on the mesomorphism of columnar liquid crystals [15]. As such, liquid crystalline materials whose supramolecular structures can be altered by varying the number and length of the peripheral hydrocarbon chains are potentially very important in the design and development of functional mesogens which are industrially important.

Certain metallomesogens have played a very important role in the design of switchable nonlinear optical materials. This is due to their peculiar structural

geometry, paramagnetism, polarizability and birefringence [16]. Some among these types of materials are those that are capable of exhibiting light emission and/or charge transport abilities rendering such functional materials extremely important in industrial applications such as Imaging and visual displays as well as in solar cells. Mesogenic materials possessing luminescence are of great industrial importance and are potential candidates for use as organic light emitting diodes (OLED) [17].

Schiff bases, named after their discoverer, German scientist Hugo Schiff are organic compounds containing an imine or an azomethine group. They result from the condensation of a primary amine with a carbonyl compound, either an aldehyde or a ketone [18].

Metal complexes prepared from Schiff bases are well known for their biological and medicinal activities [19] [20] [21] and are among the best known metallomesogens since they have the potential of adding to liquid crystallinity such properties as magnetism, dielectric anisotropy, birefringence, color, redox behavior and coordination geometry [22].

Numerous metallomesomorphic materials with varying branched chain lengths (ethers or esters) attached to the rigid core were prepared and characterized over the years [14] [23]. We embarked on our research presented in this paper in order to compare with work we and others have done on bis(hydrazinato)-nickel (II) complexes [23] [24] [25]. It seemed interesting for us to gain an insight into the role that the hydrocarbon tail lengths, their multiplicity and position on the benzene ring play in determining if the outcome is a mono or poly mesomorphic phase(s) and on how tail length affects the mesophase temperature range. We also wanted to find out if these newly synthesized molecules are stable for a prolonged period of time in the mesophase and Isotropic phase. Synthesis of these novel mesogens is straightforward with a high yield and purification ease.

Chung *et al.* reported that their mesogens which are relatively similar to ours exhibited columnar disordered phases with a crossover from rectangular to hexagonal phases [24]. Our mesogens reported here are highly ordered and very stable at high temperatures. In another study, similar aroyl hydrazinato-nickel (II) complexes exhibited a smectic C phase and a nematic phase [25].

This study is an investigation of the formation of liquid crystal phases (nematic and columnar) in a series of six molecules based on the aroyl hydrazinato-nickel (II) complex. This study also correlates the number of chains bonded to the benzene ring and chain length to mesomorphic behavior. The general schematic diagram for three (RZN 7, 8 & 9) of the six molecules in this series is given in **Figure 1** while the general schematic diagram for the other three (RZN 11, 12 & 13) is provided in **Figure 2**.

2. Materials and Methods

The materials' phase sequences were determined by polarized optical microscopy

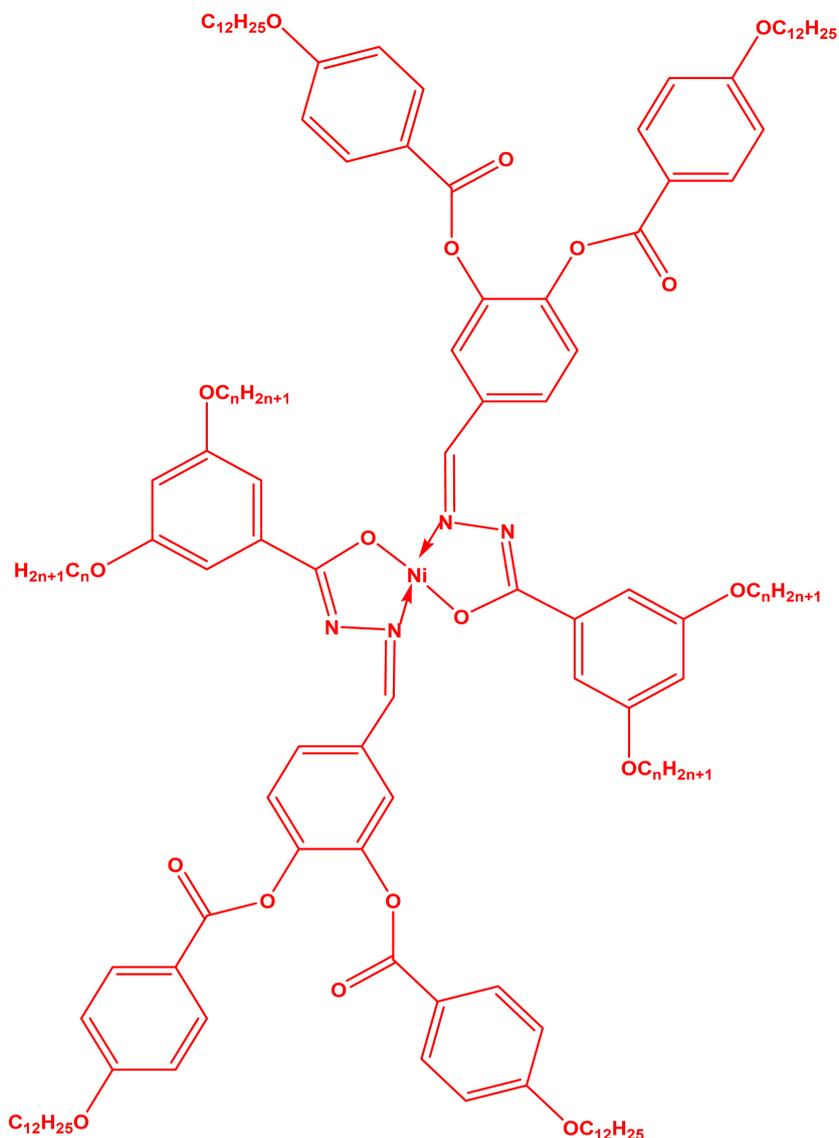


Figure 1. General Structure of series A: RZN-7 ($n = 12$), RZN-8 ($n = 16$) & RZN-9 ($n = 18$).

(POM) and differential scanning calorimetry (DSC). For polarized optical microscopy observations, an Olympus BH2 polarizing microscope equipped with a graduated rotation stage was used. The specimens were contained in 5 μm gap commercial glass cells treated for planar alignment and coated on the inside with a thin layer of indium tin oxide (ITO). The specimen temperature was varied and controlled to $\pm 0.1^\circ\text{C}$ using a heating/freezing stage temperature controller from Linkam (TMS 94).

The endothermic or exothermic energy with respect to temperature can be measured using DSC studies. Generally, when the LC complex is cooled, exothermic peaks are recorded; the area under the peaks along with the weight of the sample provides the energy possessed by the respective mesogenic phase. Similarly, when the liquid crystal is heated the endothermic peaks are observed.

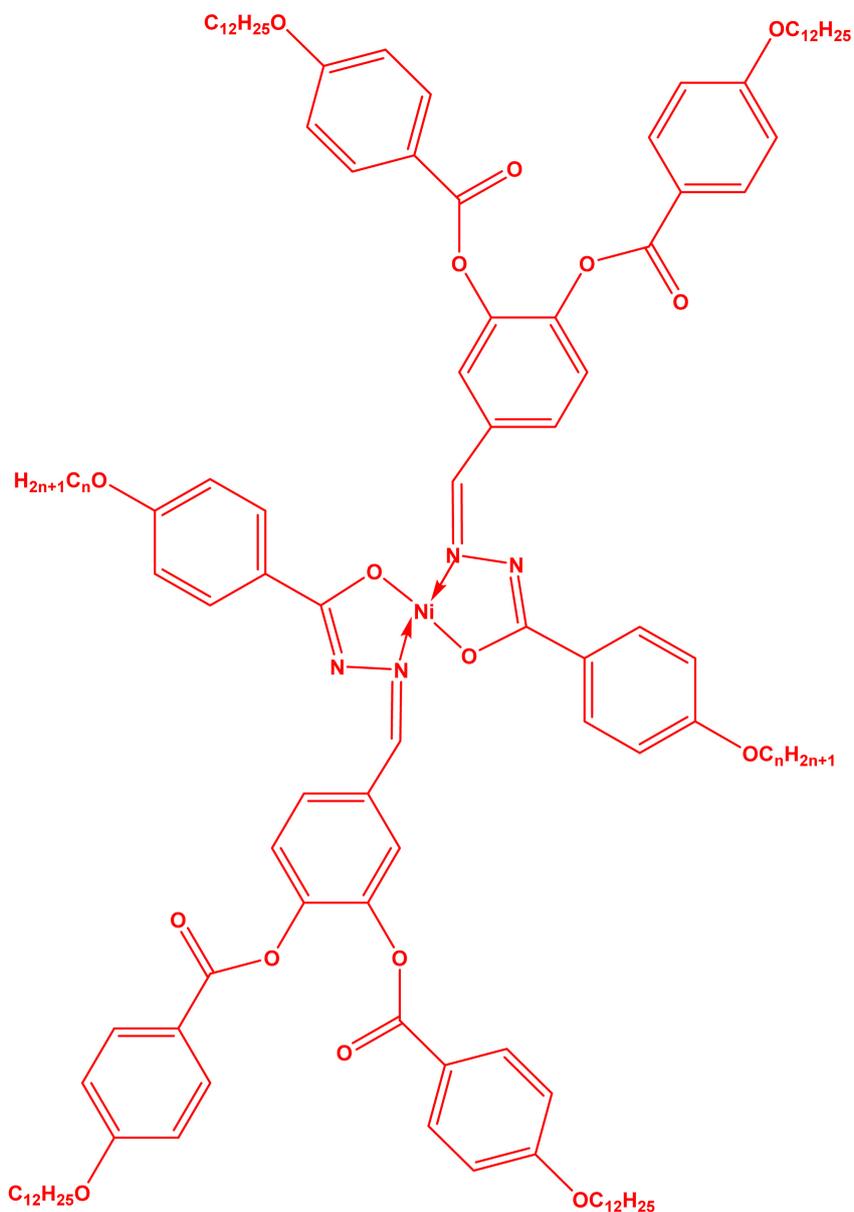


Figure 2. General structure of series B: RZN-11 ($n = 10$), RZN-12 ($n = 16$) & RZN-13 ($n = 18$).

DSC measurements were acquired on a TA DSC Q20 model with a temperature range of $-40^{\circ}C$ to $400^{\circ}C$. A heating/cooling rate of $3.00^{\circ}C/min$ was used throughout the scanning procedure.

3. Results

The materials' molecular structures are provided in **Figure 1** and **Figure 2** for series A and B respectively. The code names, POM transition temperatures (heating/cooling) as well as DSC heating/cooling data together are provided in **Table 1** and **Table 2** for series A and B respectively. A sample DSC thermogram for one of the samples is presented in **Figure 3**. The transition temperatures

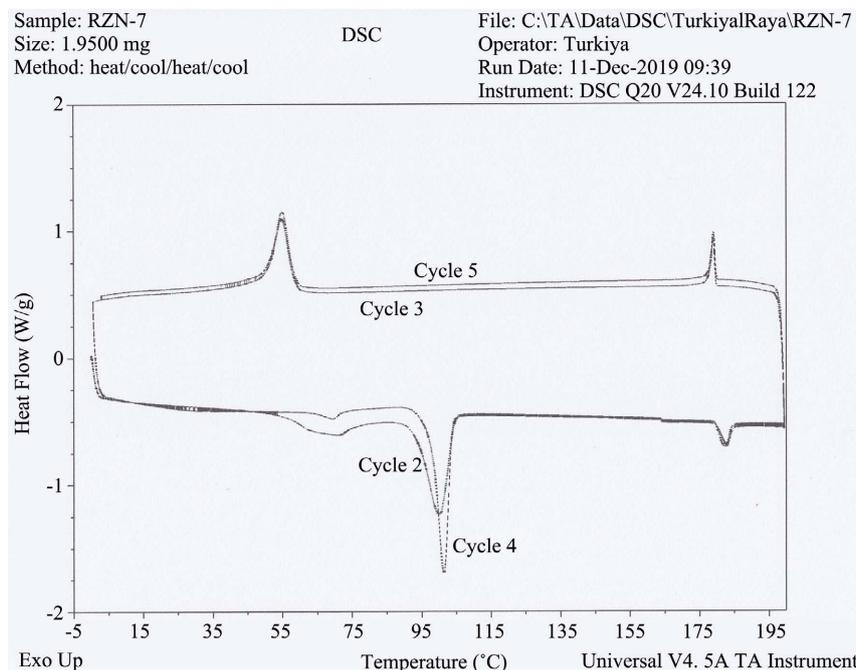


Figure 3. DSC thermogram of the mesogen RZN-7 displaying both the heating and cooling stages.

Table 1. POM and DSC observations for series (A) members, temperatures are in °C; the numbers in parenthesis indicate the transition enthalpy in units of J/g.

Code	n	POM Cooling	POM Heating	DSC Cooling	DSC Heating
RZN-7	12	¹⁰³ I ↔ Col → ⁷⁰ K	¹⁸⁰ K → I	¹⁰² ⁷² I ↔ Col → K (1.20) (77.8)	¹⁸² K → I (91.4)
RZN-8	16	⁹⁴ I ↔ Col → ⁶⁷ K	¹⁹⁴ K → I	⁹⁵ ⁶⁵ I ↔ Col → K (1.52) (49.2)	¹⁹³ K → I (86.9)
RZN-9	18	⁹⁵ I ↔ Col → ⁷⁷ K	¹⁹⁰ K → I	⁹⁵ ⁷⁶ I ↔ Col → K (0.85) (38.6)	¹⁸⁸ K → I (60.7)

Table 2. POM and DSC observations for series (B) members, temperatures are in °C; the numbers in parenthesis indicate the transition enthalpy in units of J/g.

Code	n	POM Cooling	POM Heating	DSC Cooling	DSC Heating
RZN-11	10	¹²⁰ ¹⁰⁶ ⁷⁵ I ↔ N ↔ Col → K	¹⁸⁶ K → I	¹²⁰ ¹⁰⁵ ⁷⁴ I ↔ N ↔ Col → K (1.20) (1.52) (77.8)	¹⁸⁵ K → I (81.3)
RZN-12	16	¹¹⁴ ¹⁰¹ ⁸¹ I ↔ N ↔ Col → K	¹⁶² K → I	¹¹³ ¹⁰⁰ ⁸³ I ↔ N ↔ Col → K (1.51) (1.18) (29.2)	¹⁵⁹ K → I (86.9)
RZN-13	18	⁹¹ ⁷⁷ ⁶⁸ I ↔ N ↔ Col → K	¹⁴⁰ K → I	⁹³ ⁷⁵ ⁶⁶ I ↔ N ↔ Col → K (0.85) (0.93) (23.6)	¹³⁸ K → I (63.4)

observed by polarized optical microscopy agree within $\pm 2^\circ\text{C}$ with the DSC recordings. The mesophases are observed upon cooling with two mesophases observed upon cooling in series B.

The mesophase in series A compounds is observed upon cooling from the isotropic. All 3 series A members display a columnar phase as discerned from POM observations.

The mesophases in series B compounds are observed upon cooling from the isotropic. All 3 series B members display a nematic phase first and upon further cooling, a columnar phase appears as discerned from POM observations.

4. Discussion

It is evident from the data in **Table 1**, that in Series A mesogens, the shorter the hydrocarbon tail comprising the 3,5-bis (alkoxy)phenyl group, the wider the mesogenic temperature range. For RZN-7, where the hydrocarbon tail length is made up of 12 carbons, (n is 12) the columnar mesophase appears over a wider temperature range than in RZN-8 (n is 16) and the latter has its columnar phase displayed over a wider temperature range than RZN-9 where n is 18. The aforementioned observations are evident upon cooling from the isotropic in both DSC and POM measurements. Only one mesophase, a columnar phase is observed in series A mesogens. The presence of longer hydrocarbon tails at positions 3 and 5 of the phenyl ring does not lower the clearance point temperature in series A mesogens contrary to what was observed in series B mesogens.

Figure 4 below shows the POM photo for the mesogen RZN-9 upon cooling from the isotropic phase. Columnar phase crystals start forming at below 95°C .

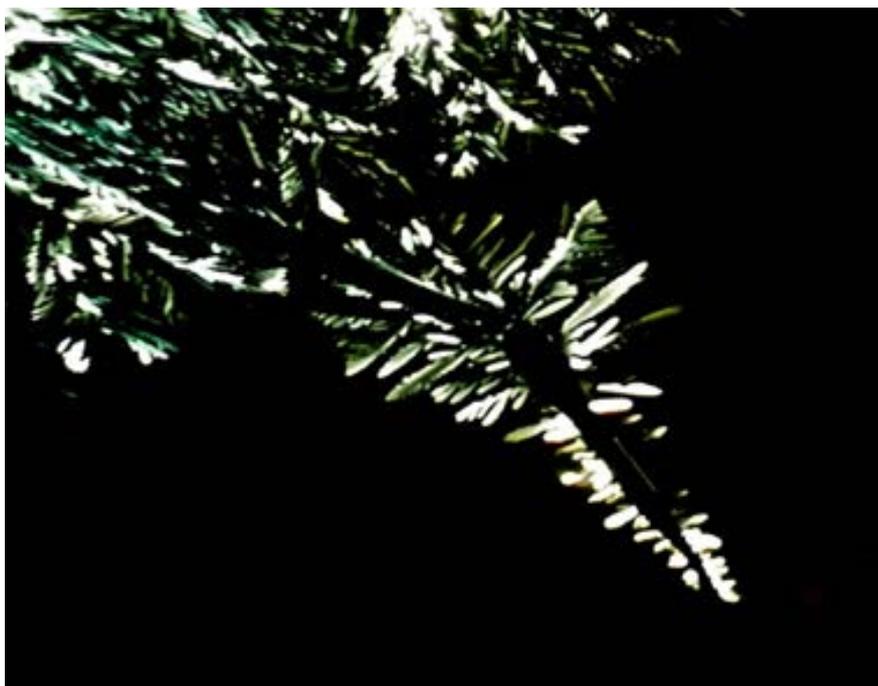


Figure 4. POM photo for RZN-9 upon cooling, 94°C .

The same general trend is observed in series B mesogens (**Table 2**) whereby the shorter the single hydrocarbon tail constituting the 4-(alkoxy)phenyl group, the wider the transition phase temperature window. In RZN-11 with a hydrocarbon tail made up of 10 carbons ($n = 10$), the mesophase range is wider than in RZN-12 ($n = 16$) and the latter has a wider mesophase temperature range than RZN-13 ($n = 18$). In series B mesogens however, the longer the hydrocarbon tail length, the lower the clearance point temperature. Going from RZN-11 to RZN-12 to RZN-13, the clearance point falls from 186°C to 162°C to 140°C respectively.

All 3 mesogens in series B displayed biphasic mesomorphic behavior observed upon cooling from the isotropic phase. A nematic phase is observed first which upon further cooling transforms into a more ordered columnar phase.

The individual IUPAC names for each of the six mesogens presented in this study are:

RZN-7: bis((Z)-(((Z)-3,4-bis((4-(dodecyloxy)benzoyl)oxy)benzylidene)hydrazineylidene)(3,5-bis(dodecyloxy)phenyl)methoxy)nickel

RZN-8: bis((Z)-(((Z)-3,4-bis((4-(dodecyloxy)benzoyl)oxy)benzylidene)hydrazineylidene)(3,5-bis(hexadecyloxy)phenyl)methoxy)nickel

RZN-9: bis((Z)-(((Z)-3,4-bis((4-(dodecyloxy)benzoyl)oxy)benzylidene)hydrazineylidene)(3,5-bis(octadecyloxy)phenyl)methoxy)nickel

RZN-11: bis((Z)-(((Z)-3,4-bis((4-(dodecyloxy)benzoyl)oxy)benzylidene)hydrazineylidene)(4-(decyloxy)phenyl)methoxy)nickel

RZN-12: bis((Z)-(((Z)-3,4-bis((4-(dodecyloxy)benzoyl)oxy)benzylidene)hydrazineylidene)(4-(hexadecyloxy)phenyl)methoxy)nickel

RZN-13: bis((Z)-(((Z)-3,4-bis((4-(dodecyloxy)benzoyl)oxy)benzylidene)hydrazineylidene)(4-(octadecyloxy)phenyl)methoxy)nickel

Figure 5 below shows the POM photos of RZN-11 upon cooling from the isotropic. Both nematic and columnar phases are observed.

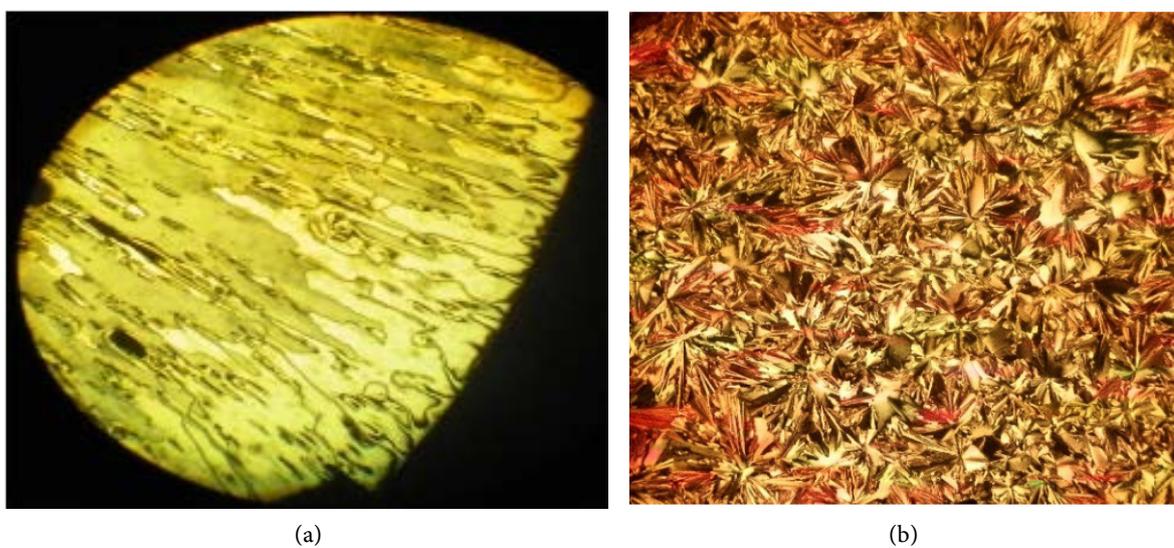


Figure 5. POM photo for RZN-11 upon cooling, (a) nematic phase at 115°C and (b) columnar phase at 70°C .

5. Conclusions

Two novel series (A & B) of mesogenic materials made up of three members each were synthesized and characterized using polarized optical microscopy and differential scanning calorimetry.

Series A members (RZN-7, RZN-8 and RZN-9) displayed monophasic columnar liquid crystalline behavior upon cooling from the isotropic phase. It was evident from both POM and DSC measurements that the shorter the hydrocarbon chain length, the wider the mesogenic temperature range window.

Series B members (RZN-11, RZN-12 and RZN-13) displayed biphasic nematic and columnar liquid crystalline behavior upon cooling from the isotropic phase. Similar to observations in series A members, It was evident from both POM and DSC measurements that the shorter the hydrocarbon chain length, the wider the mesogenic temperature range window.

It was also observed that with the presence of only one hydrocarbon tail at position 4 of the phenyl ring (series B mesogens), a biphasic liquid crystalline nematic followed by columnar phases appeared. Whereas when two hydrocarbon tails at positions 3 and 5 of the phenyl ring are present (series A mesogens), a monophasic columnar phase is exhibited.

No mesogenic behavior was observed in both series A and B upon heating from the solid crystalline phase to the Isotropic phase. However in series B mesogens it was observed that the longer the single hydrocarbon tail, the lower the clearance point. In series A mesogens, no such correlation was evident. Members of both series are stable for prolonged periods of time at high temperatures even in the isotropic phase.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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