Executive Summary

of the thesis entitled

Synthesis & characterization of some novel Schiff base derivatives, their metal complexes and study of their mesomorphic behavior

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Chapter-1

Introduction of Liquid Crystal

Liquid Crystals

The solid, liquid and gaseous states, the common states of matter differ primarily by the types and order found in the state. The molecule into crystalline solid, possessing high order has positional order and orientation order. When most solids melt at specific temperatures in an isotropic liquid, both orders are completely lost; the molecules move and tumbel randomly. Certain substances, however, have intermediate states having more order than in liquids, but less order than in typical crystals. These orderly fluids are termed liquid crystals. A liquid crystal substance in this state is highly anisotropic in some of its properties like birefringence associated with crystalline solids and yet has the flowing property like liquids. In the LC state, molecules tend to point to a common axis, named the director [1].

History of Liquid Crystals

In 1888, the Austrian botanist Friedrich Reinitzer noted the unusual melting behavior of cholesterol benzoate, exhibited two melting points on heating. The solid ester first melted at 145.5 ^{o}C to form a turbid liquid, which, when further heated to 178.5 ^{o}C, disappeared and became a clear isotropic liquid [2]. Reinitzer sent the material to Otto-Lehman. Lehmann observed the substance of Reinitzer with the help of the polarising microscope and confirmed the existence of the new physical state of matter [3]. He proposed the term "liquid crystal" for the new intermediate state between the crystalline solid and the isotropic liquid.

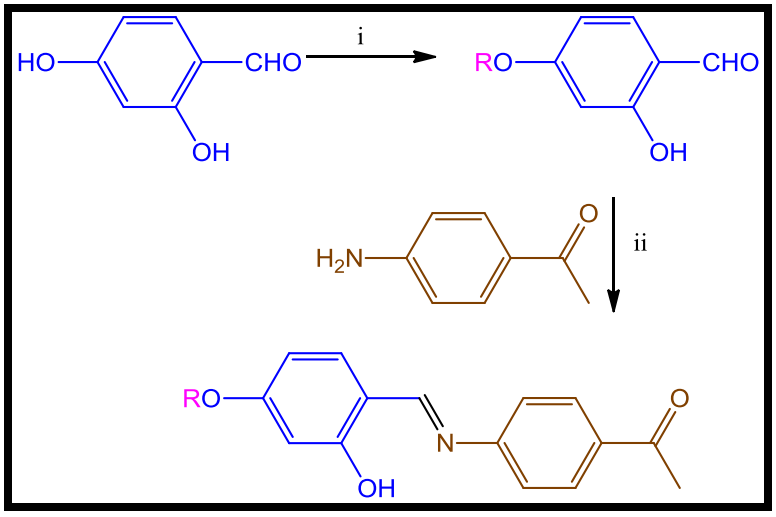
Chapter-2

Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone and their metal complexes: synthesis, characterization and mesomorphic behavior

2.1 Introduction

Metallometogens, a metal containing liquid crystals, the properties of various metallic coordinating complexes can be combined with the physical properties of liquid crystals**.** Metallomesogens have been extensively studied due to their unique geometric structure and the ability to combine the optical, electronic and magnetic properties of transition metal complexes with liquid crystal ligands [4-8]. In this work, we present the synthesis and liquid crystalline property of the new homologous series of the Schiff base of 4-*n*-alkoxy-2-hydroxybenzaldehyde with 4-amino acetophenone and their Cu(II) complexes.

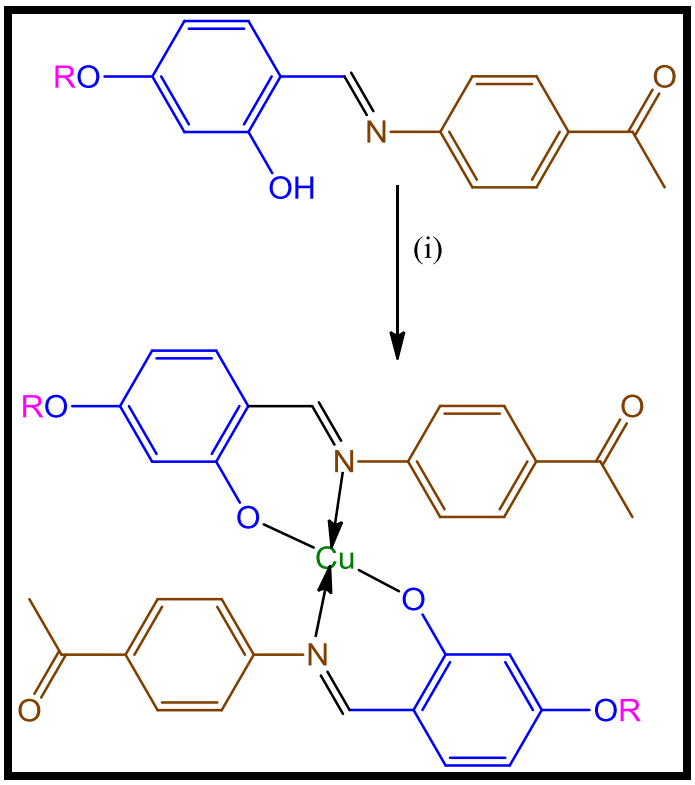
2.2 Synthesis Scheme



Where R = C_nH_{2n+1}; n = 2 to 8, 10, 12, 14, 16, 18.

Reagents and reaction conditions: i) RBr, $KHCO_3$, KI, dry acetone, reflux 24 hr, ii) glacial AcOH, absolute EtOH, reflux 4 hr.

Scheme 1.Synthesis protocol of series-A



Where R = C_nH_{2n+1}; n = 2 to 8, 10, 12, 14, 16, 18.

Reagents and reaction conditions: i) $Cu(COOCH_3)_2.H_2O$, absolute EtOH, reflux 3 hrs.

Scheme 2. Synthesis protocol of series-B

2.3 Results and discussion

In the POM observation of *n*-ethoxy derivative, it melted directly from the crystal into an isotropic liquid, and did not show a liquid crystal phase. The *n*-propoxy derivative is directly converted into an isotropic liquid when heated, but when cooled, it shows a fan-shaped optical texture of the smectic-A phase, indicating that it is monotropic. Then, all members of the series-A from *n*-butyloxy to n-octadecyloxy have an enantiotropic smectic-A phase **(Figure 1).**

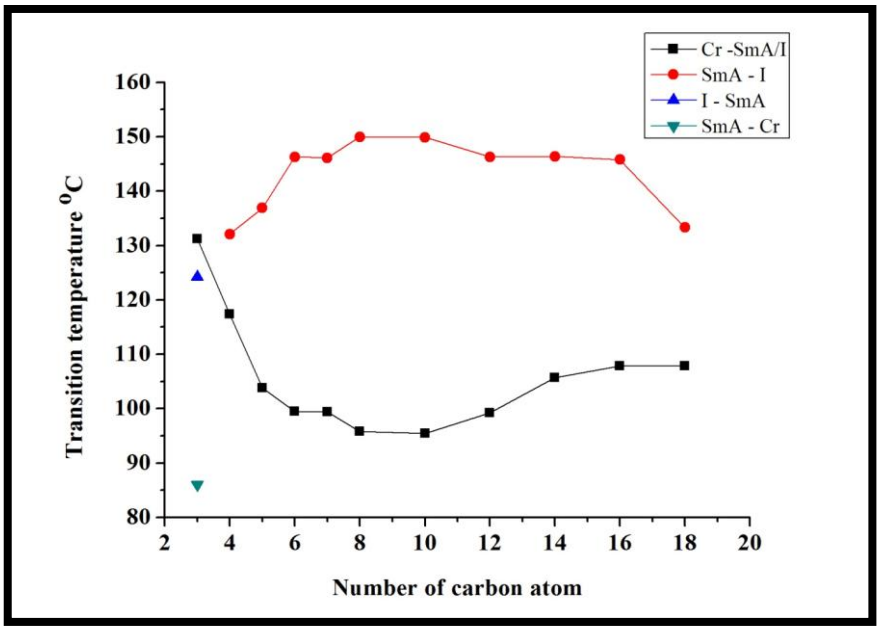


Figure 1. Dependence of transition temperatures on the increasing terminal alkoxy chain length for series-A

The thermal results of the series-B compounds show that *n*-ethoxy to *n*-butyloxy melted directly from the crystalline phase into an isotropic liquid. Compounds *n*-pentyloxy and *n*-hexyloxy become directly isotropic liquids when heated, but when cooled they show the typical fan-shaped optical texture of the SmA phase. Means monotropic, then all members of the series from *n*-heptyloxy to *n*-octadecyloxy exhibit the enantiotropic SmA phase **(Figure 2).** The POM images of series-A and series-B compound are given in **Figure 3** and **Figure 4** respectively.

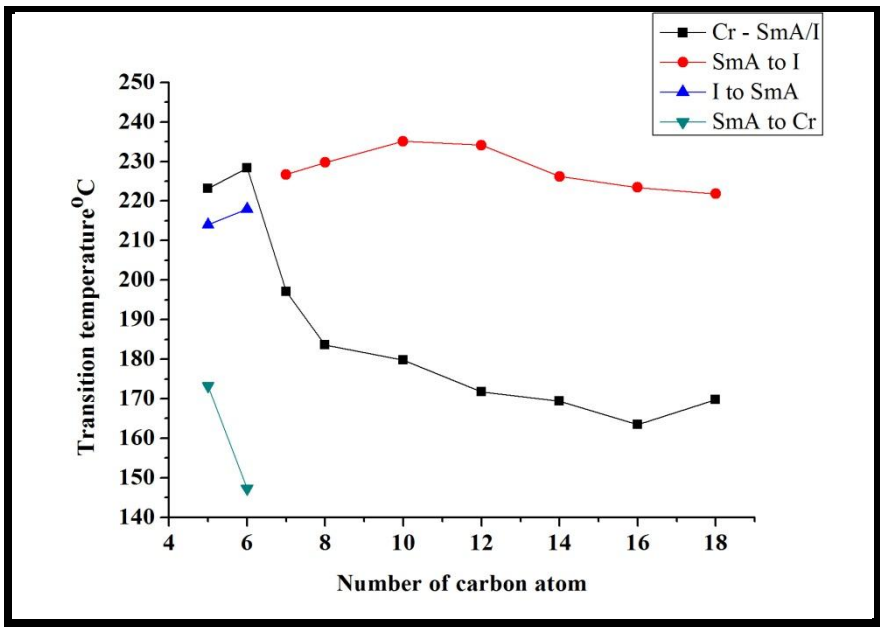


Figure 2. Dependence of transition temperatures on the increasing terminal alkoxy chain length for series-B

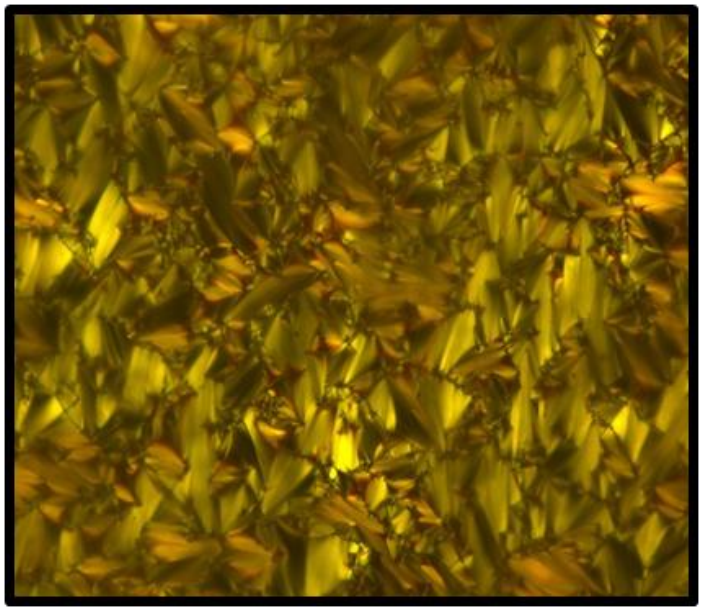


Figure 3. Fan-like texture of SmA phase of *n*-octylocy from series-A on cooling at 143.4 ^{o}C

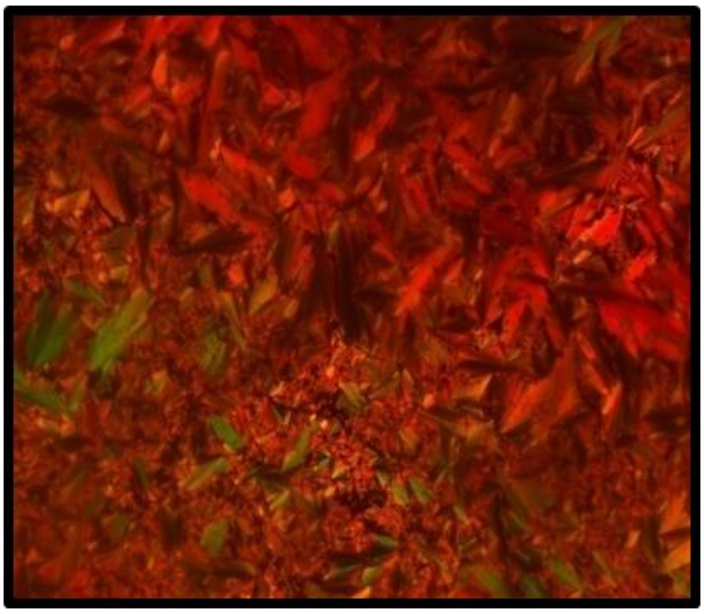


Figure 4. Fan-like texture of SmA phase of *n*-octylocy from series-B on cooling at 212.5 ^{o}C

2.4 Conclusion

- Two homologous series of ligand and Cu(II) complex were synthesized and characterized by FTIR, ^{1}HNMR, ^{13}CNMR and other analytical methods.
- The mesophase shown in the two series was studied by POM and confirmed by thermograms of DSC. Both series are purely smectogenic.
- In the homologous ligand series, the SmA intermediate phase starts with *n*-propoxy derivatives as monotropic, and then all members of the homologous ligand series show the enantiomeric behavior of SmA.
- In the Cu(II) metal complex series, the SmA mesophase starts with *n*-pentyloxy derivatives as monotropic, and *n*-hexyloxy derivatives also show monotropic nature.

- Meanwhile, the enantiotropic SmA mesophase exhibited from *n*-heptyloxy to *n*-octadecyloxy derivatives. A chain length of 8 shows the maximum temperature range of the SmA phase, in both series on cooling.
- Molecular flexibility and terminal end group difference can cause variations in mesomorphic behaviors of a substance.

Chapter-3

Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetanilide and their metal complexes: synthesis, characterization and mesomorphic behavior

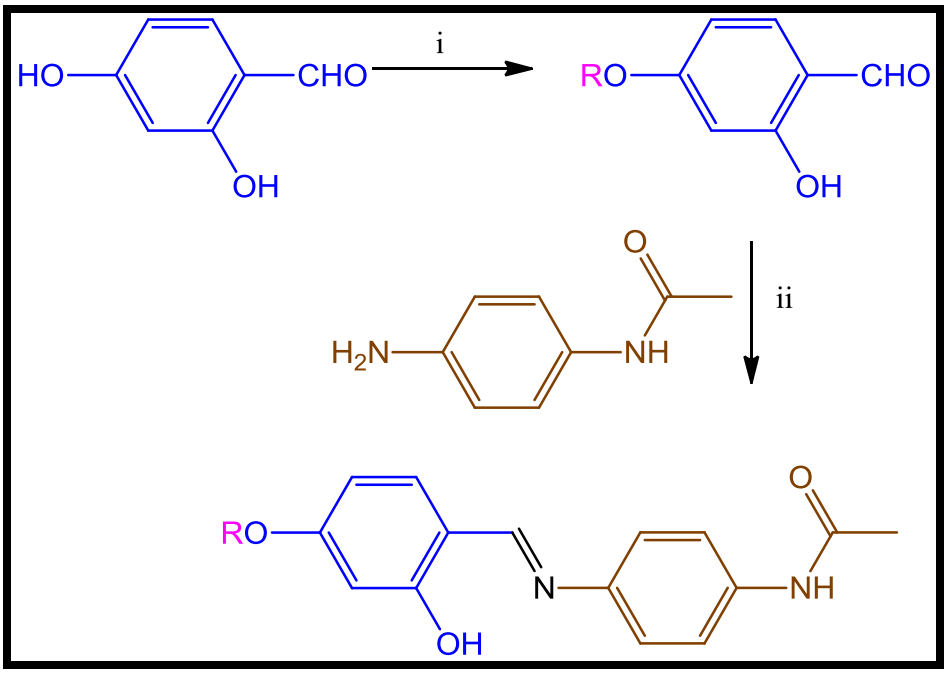
3.1 Introduction

Liquid crystal or mesogenic compounds due to their unique flow characteristics of liquid and the optical properties of crystals have a wide range of valuable scientific and technical applications, especially as display devices, organic light-emitting diodes, photoconductors, anisotropic networks, and semiconductors [9-13]. Schiff bases, imine functional groups (CH = N), are widely used as linking groups for rigid base fragments. It provides greater stability and promotes the formation of mesophases, though it produces a core staggered structure [14, 15]. Schiff's base, easy preparation and low cost make it the ideal choice for basic liquid crystal research. Several characteristic compounds with a variety of molecular shapes have been combined with Schiff base functional groups and have shown remarkable mesogenic properties [16-19]. Since the discovery of 4-methoxybenzylidene-4′-butyl aniline (MBBA), which exhibits a nematic mesophase at room temperature, Schiff bases have been frequently studied [20]. A review of the literature shows that liquid crystals with basic Schiff units have been extensively studied and used as linking groups for the production of various types of

liquid crystals [16-19, 21]. On the other hand, compounds that combine liquid crystal properties with metal ion properties are an important research goal today and have led to the development of many types of structures, including many metals [22]. They have both disk-like and rod-shaped liquid crystal properties [4]. In addition to the various complex geometries, variable oxidation states, magnetic properties, and redox behavior are further advantages of metallomesogens [23]. Complexation can also cause differences in the mesogenic properties of uncoordinated ligands [4]. The salicylaldimato metal complexes are known for their mesogenic properties, and due to the intramolecular H-bonding and their ability to form coordinate bonds with metal ions, the imine bond is stabilized. There has been considerable work on metallic mesogens [24]. Among other things, copper(II) complexes of Schiff bases are planar or nearly planar around copper atoms and lead to elongated planar compounds suitable for mesogenic properties [24-26]. Synthesized and studied copper (II) metal complexes, showing various smectic, nematic and columnar LC phases [27-31]. Due to the core properties of copper (II) paramagnetism, these metal isomers have amazing chemical and physical properties and have many potential applications [30].

In this study, new homologous series of Schiff base compounds were synthesized, characterized and their liquid crystal properties investigated. Moreover, using these Schiff bases, copper(II) containing metallomesogens were prepared and studied. The relationship between alkyl chain lengths and the behavior of liquid crystals was also examined.

3.2Synthesis Scheme

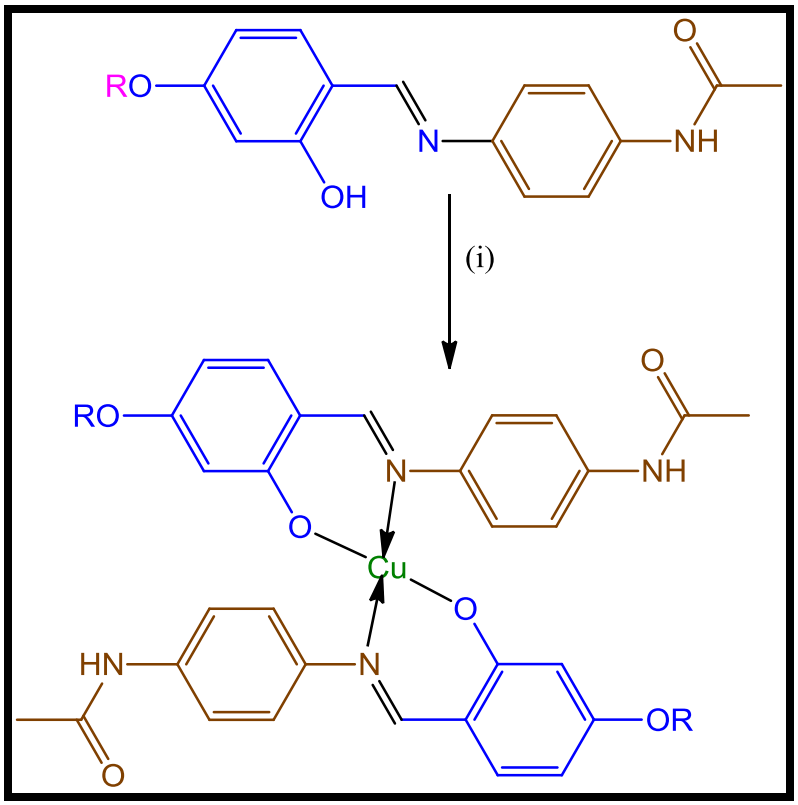


Where R = C_nH_{2n+1}; n = 2 to 8, 10, 12, 14, 16, 18.

i) RBr, $KHCO_3$, KI, dry acetone, reflux 24 hrs

ii) Glacial AcOH, absolute EtOH, reflux 4 hrs

Scheme 3. Synthesis protocol of series C



Where R = C_nH_{2n+1}; n = 2 to 8, 10, 12, 14, 16, 18.

i) $Cu(COOCH_3)_2.H_2O$, absolute EtOH, reflux 3 hrs.

Scheme 4. Synthetic protocol of series-D

3.3 Results and Discussion

The thermal results of series-C compounds show that up to *n*-pentyloxy derivatives are non-mesogenic. Then all the members of the series, from *n*-hexyloxy to *n*-octadecyl oxy, melt between 137-154 ^oC, depending on the length of the alkyl chain. Under the polarizing optical microscope the fluids display typical fan shape optical texture of SmA phase. They show mesomorphic behavior due to the resultant molecular rigidity and flexibility generates appropriate magnitudes of anisotropic forces of intermolecular end to end and lateral attractions. In the series, we observe that enthalpy changes for Cr in SmA is higher (ΔH= ~7-18 Jg^{-1}) than the SmA transition in I (ΔH= ~3-1 Jg^{-1}). The phase behavior of the series-C is depicted in **Figure 5.**

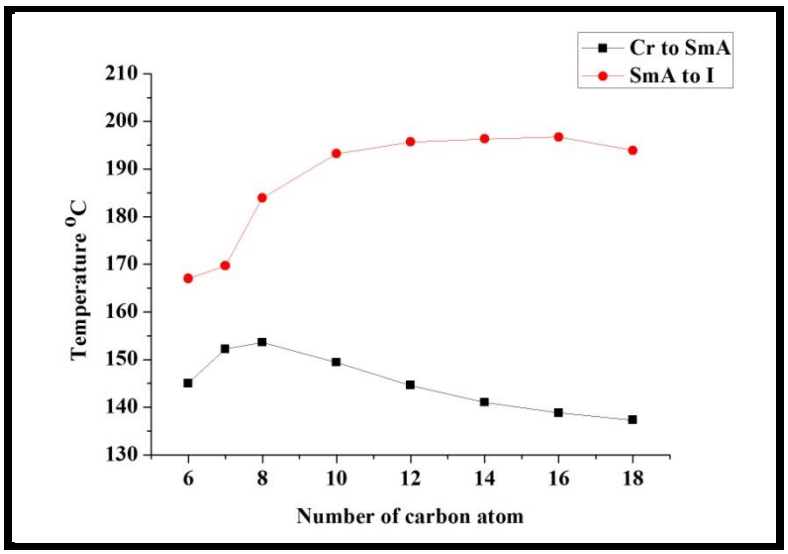


Figure 5. Dependence of transition temperatures on the increasing terminal alkoxy chain length

The thermal results of the series-D compounds show that from *n*-ethoxy to *n*-hexyloxy derivatives melts directly from the crystalline phase to the isotropic liquid without exhibiting an intermediate phase. While *n*-octyloxy to *n*-octadecyloxy shows an enantiotropic smectic-A phase behaviour **(Figure 6).** The POM images of series-C and series-D compound are given in **Figure 7** and **Figure 8** respectively.

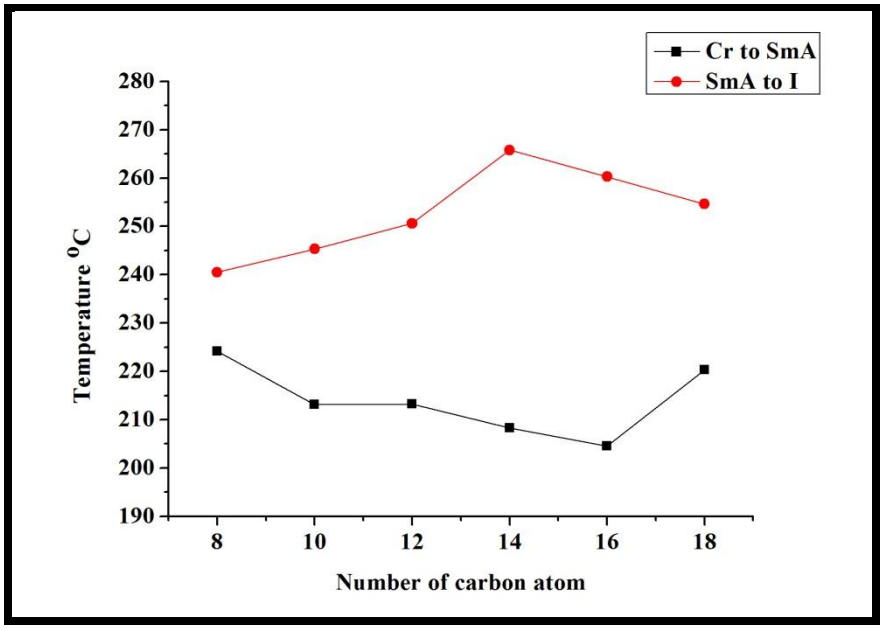
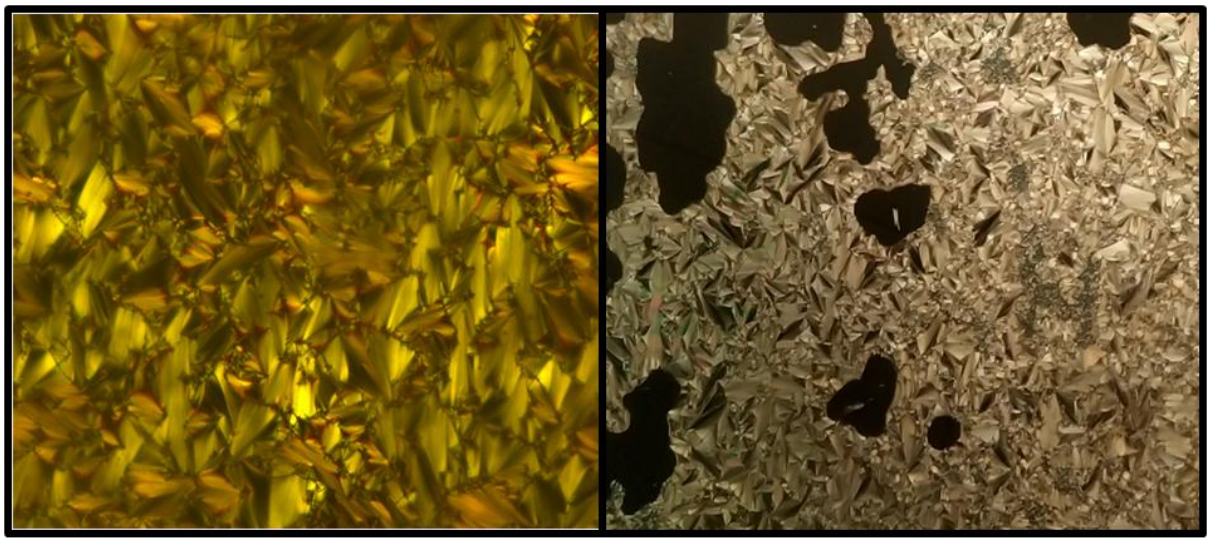
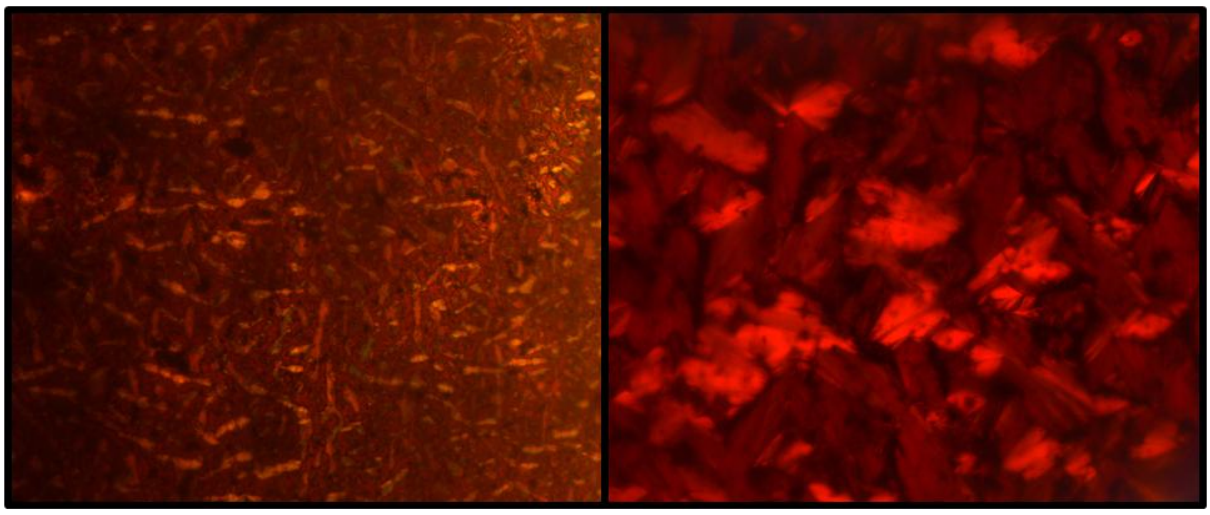


Figure 6. Dependence of transition temperatures on the increasing terminal alkoxy chain length



(a) (b)

Figure 7. Fan-like texture of SmA phase of series-C compounds (a) ***n*-heptyloxy** on cooling at 160.1 ^{o}C (b) ***n*-dodecyloxy** on heating at 192.6 ^{o}C



(a) (b)

Figure 8. Fan-like texture of SmA phase of series-D compounds (a) ***n*-octyloxy** on cooling at 230.3 ^{o}C (b) ***n*-octadecyloxy** on cooling at 235.7 ^{o}C

3.4 Conclusion

- In the present work, two homologues series of Schiff base ligand and corresponding Cu(II) complex have been synthesized and well characterized by FT-IR and ^{1}H-NMR measurements.

- All the mesophases observed were confirmed by the optical textural observation under POM and DSC thermogram studies.
- Both the series exhibited enantiotropic smectic A phase, in the homologues series of ligands and Cu(II) metal complexes mesomorphic property commence from n-hexyloxy(-OC_6H_{13}) terminal end group and n-octyloxy(-OC_8H_{17}) terminal end group respectively.
- The clearing temperatures of Cu(II) complexes are higher than the corresponding un co-ordinated ligands due to the presence of metal. It was also observed that mesomorphic behaviour and mesomorphic temperature range be governed by the terminal alkoxy chain length.

Chapter-4

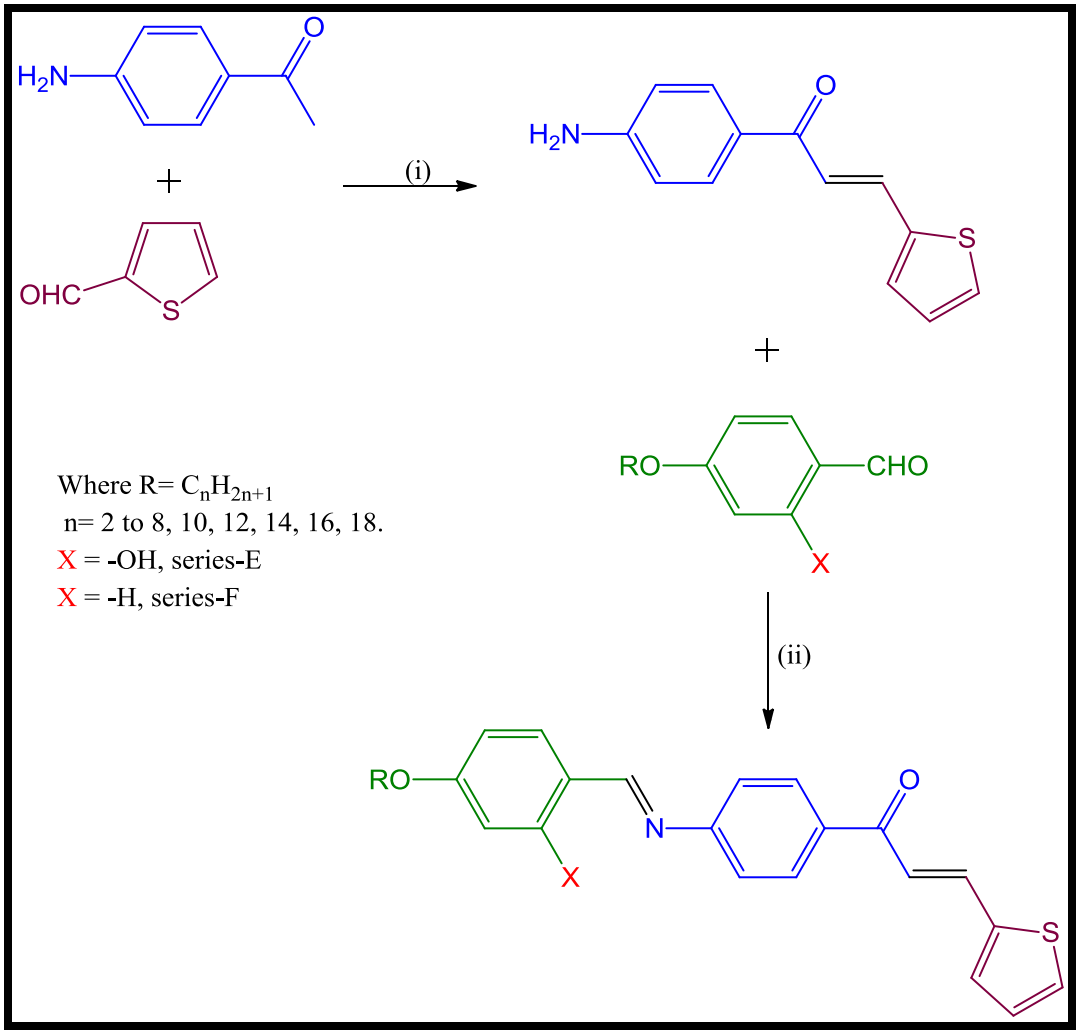
Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde and 4-n-alkoxy benzaldehyde with thiophene derivatives: synthesis, characterization and mesomorphic behavior

4.1Introduction

The research based on heterocyclic liquid crystals has attracted much more attention in recent years due to larger choices in the design and synthesis of novel heterocycles containing mesogenic compounds [32, 33]. It has been widely studied that the presence of heterocyclic moieties in core structures generates mesogenic materials [34, 35]. As the heterocyclic compounds having oxygen, nitrogen and sulphur atoms which are more polarisable than carbon, amalgamation of heterocyclic units as core moiety in liquid crystals results in variety of their mesogenic properties as well as physical properties. The presence of such electronegative atoms has often led to greater polar induction and reduced symmetry [36-38]. Polar induction by heteroatoms can be

responsible for developing and enriching the mesogenic properties of heterocyclic liquid crystals [37-39]. Numerous compounds containing heterocyclic moiety such as furan, thiophene, pyrrole, benzothiazole, pyridine, pyrimidine, oxadiazole have been reported to possess a variety of mesogenic properties [40, 41]. Pyrrole and thiophene based conducting polymers have been widely studied for their mesomorphic behavior [42-44].

4.2 Synthesis Scheme



i) Aq. NaOH, alcohol, stir 4 hr, ii) Few drops of glacial AcOH, absolute EtOH, reflux 4 hr

Scheme 5. Synthetic protocol of thiophene based homologous series E and F

4.3 Results and Discussion

The influence of molecular flexibility on the transition temperature and phase sequence of the corresponding compound is illustrated in **Figure 9.** The results show that the different types of mesophases appeared to depend on the flexibility of the molecule, the number of carbon atoms in the terminal alkoxy group. The enantiotropic nematic phase commences from *n*-heptyloxy derivative of the series **(E7)** and continues to *n*-tetradecyloxy derivative **(E12)**, while the smectic-A phase starts from *n*-tetradecyloxy derivative **(E14)** and continues until the last member of the series *n*-octadecyloxy **(E18)** derivative. The *n*-hexyloxy derivative **(E6)** of this series shows monotropic behavior and, exhibits a nematic phase. It is also observed that the clearing point decreases significantly as the chain length increases because of the increased flexibility. The POM images of series-E compounds given in **Figure 11.**

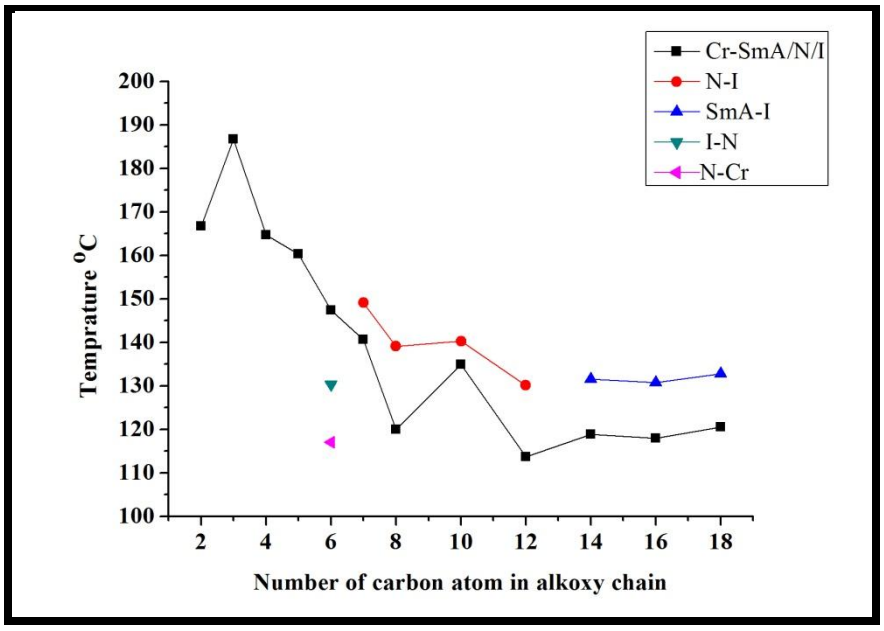


Figure 9. Dependence of transition temperatures on the increasing terminal alkoxy chain length on heating

The polarizing optical microscope and DSC analysis of the compounds revealed that *n*-ethoxy **F2** to *n*-hexyloxy **F6** derivatives were not mesogenic **(Figure 9).** They melt directly from the crystalline phase into the isotropic liquid and cool down; from the isotropic liquid directly into the crystalline phase, an intermediate phase does not exist. The derivatives, *n*-heptyloxy **F7** to *n*-tetradecyloxy **F14** has a monotropic nematic phase; they are directly converted into an isotropic liquid when heated, but show a typical marbled optical texture of a nematic phase when cooled. **Figure 12a** shows the nematic phase with a typical marble texture when the compound **F14** *n*-tetradecyloxy is cooled to 125.6 °C, and **Figure 12b** shows the transition from the nematic phase to the crystalline phase when the compound **F14** *n*-tetradecyloxy is further cooled to 94.5°C. The higher member of the homologous series, *n*-hexadecyloxy **F16** and *n*-octadecyloxy **F18** derivatives are also not mesogenic.

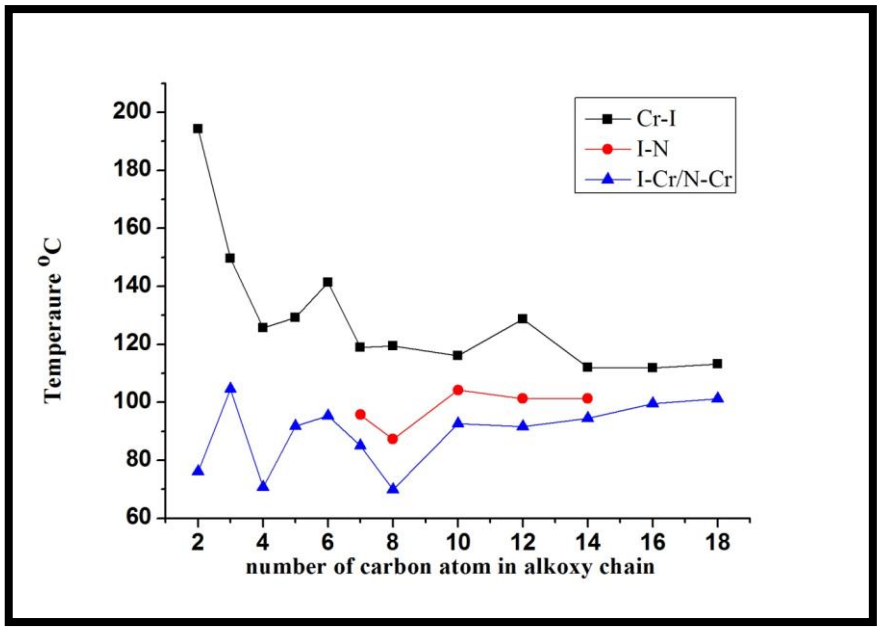


Figure 10. Dependence of transition temperatures on the increasing terminal alkoxy chain length

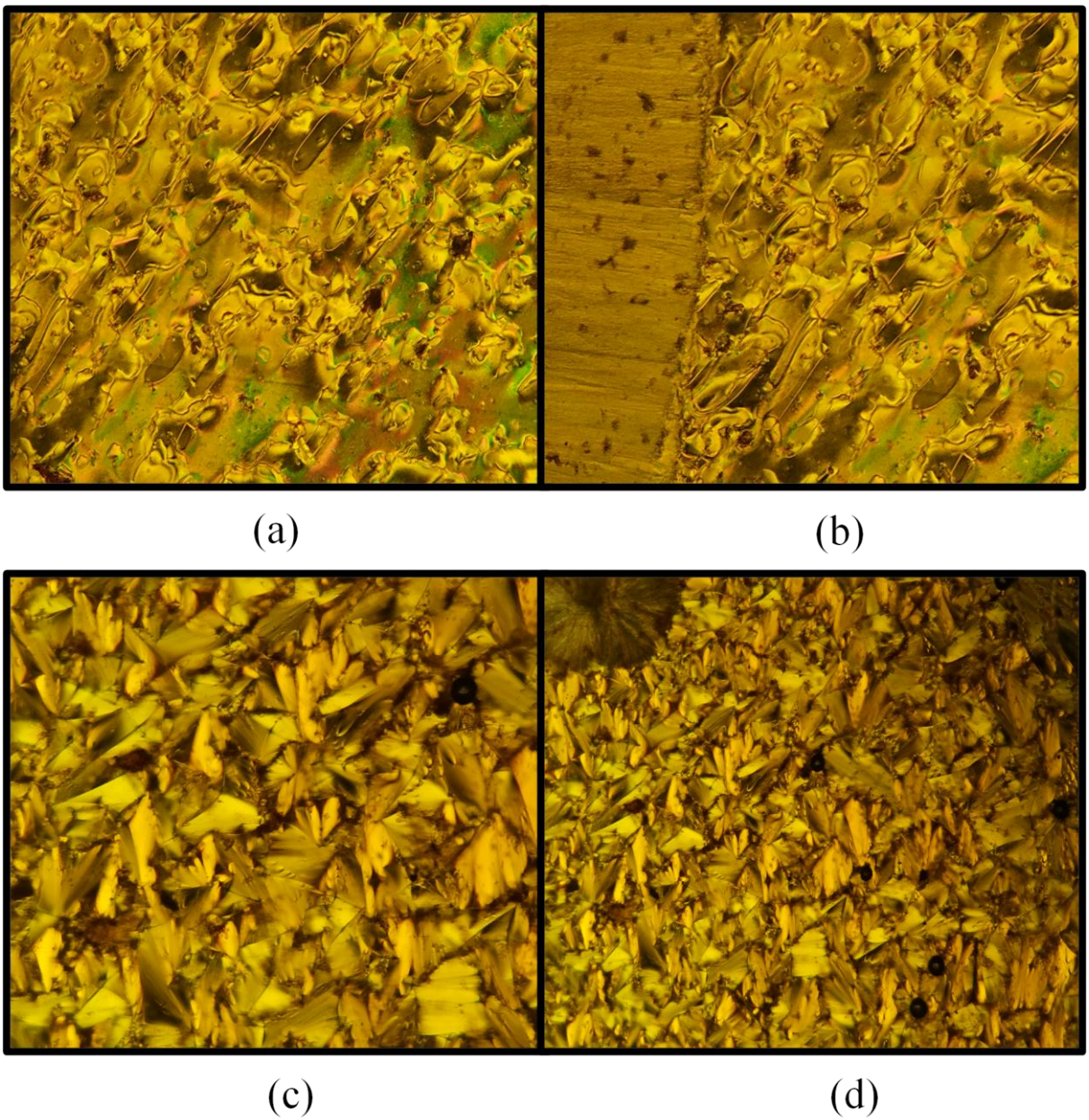
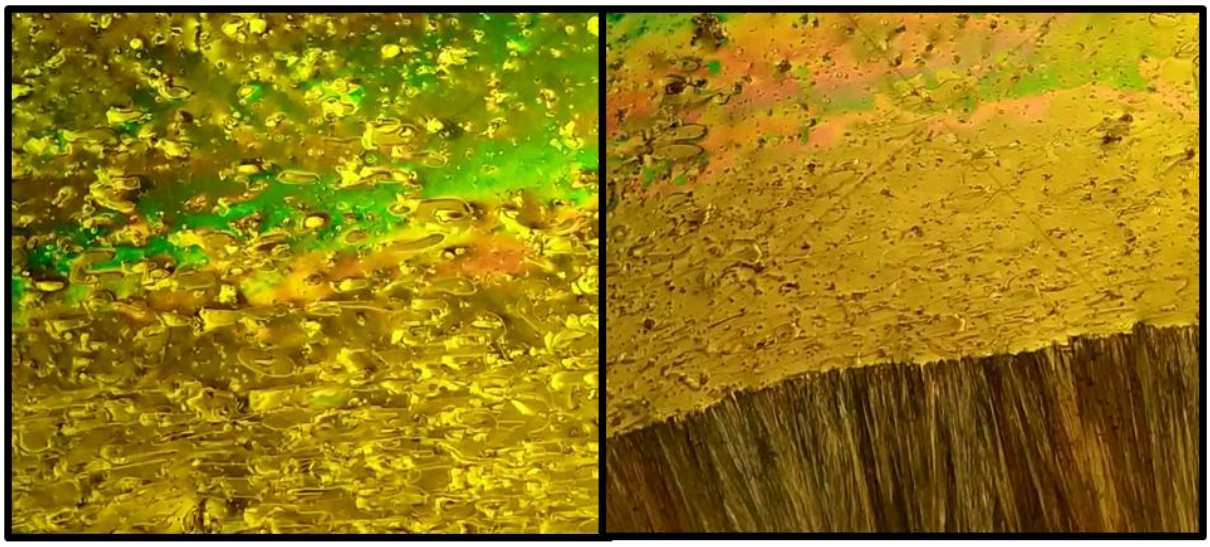


Figure 11. POM images of series-E compounds **a.** Marble texture of nematic phase of *n*-heptyloxy on cooling at 130 ^{o}C ; **b.** Nematic to crystal transition of *n*-heptyloxy on cooling at 123.8 ^{o}C; **c**. Fan shaped texture of Smectic-A of *n*-tetredecyloxy on cooling at 126.5 ^{o}C; **d.** Smectic-A to crystal transition of *n*-tetredecyloxy on cooling at 105.8 ^{o}C



(a) (b)

Figure 12. POM images of series-F compounds **a.** Marble texture of *n*-tetredecyloxy on cooling at 125.6 ^{o}C; **b.** Nematic to crystal transition of *n*-tetredecyloxy on cooling at 94.5 ^{o}C

4.4 Conclusion

- Two homologous series of Schiff base derivatives of (E)-1-(4-aminophenyl)-3-(thiophen-2-yl)prop-2-en-1-one with 2-hydroxy-4-*n*-alkoxybenzaldehyde and 4-*n*-alkoxybenzaldehyde were prepared by varying the terminal alkoxy groups from n=2 to 8, 10, 12, 14, 16, 18.
- The compounds have been characterized by ^{1}H and ^{13}C–NMR, ESI-MS, and IR spectroscopy. Single crystal X-ray diffraction studies of compound (E)-1-(4-((E)-(4-ethoxybenzylidene) amino) phenyl)-3-(thiophen-2-yl) prop-2-en-1-one has been reported.
- A homologous series-F is nematogenic, while series-E is nematogenic and smectogenic. In series-E lower members *n*-heptyloxy to *n*-dodecyloxy are

nematogenic and higher member *n*-tetredecyloxy to *n*-octadecyloxy are smectogenic.

- In series-F, the intermediate members *n*-heptyloxy to *n*-tetredecyloxy are mesomorphic while the remaining lower members *n*-ethoxy to *n*-hexyloxy and upper members *n*-hexadecyloxy and *n*-octadecyloxy of the series are non-mesogenic.
- The appearance of mesophase and the phase range depends on molecular flexibility.
- Intramolecular hydrogen bonding, significantly affects the mesomorphic behavior of studied homologous series.

Chapter-5

Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 1,3 phenylenediamine derivatives : synthesis, characterization and mesomorphic behaviour

5.1 Introduction

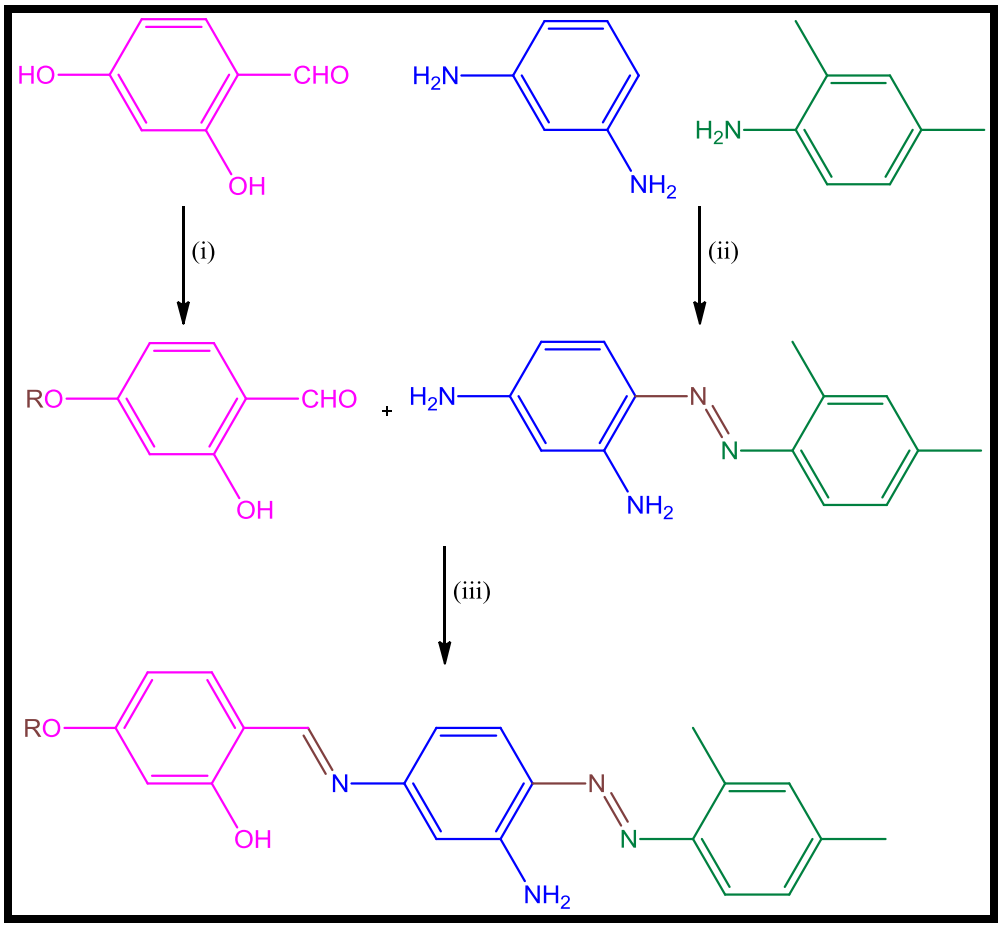
Liquid crystals have unique characteristics: their order is lower than crystalline solid but higher than liquid. Due to their scientific and technological value, liquid crystals are becoming a fascinating field of research. Azo dyes are the most important synthetic dyes, accounting for more than 60% of all commercial dyes, and have been extensively studied [45]. The advantage of the introduction of an azo linkage (-N=N-) into the LC compound is that the -N = N- bond has unique characteristics of cis-trans isomerization in the presence of ultraviolet light [46–52]. A more stable (trans) E configuration is converted to Z (cis) configuration on UV absorption (~ 365 nm). The reverse conversion, Z configuration (cis) to E configuration (trans) can be achieved,

either by illuminating it with ~ 450 nm light or keeping it in the dark, known as thermal back relaxation [46, 53, 54]. The azobenzene derivatives have certain application potential in the field of the optoelectronic field, such as dynamic holography [55, 56], optical computing, pattern recognition, LC dopant [57], optical data storage devices [58, 59], photo chromic switches[60, 61], and molecular logic gates [62]. The design of a liquid crystal compound containing azomethine an additional functional group in its molecular structure is particularly attractive [63]. The introduction of the azomethine linking group into the mesogenic structure increases the length of the molecular, molecular core polarizability and the stability of the mesophase [64]. Schiff bases derived from substituting salicylaldehyds called salicylaldimine derivatives are well recognized as liquid crystals because azomethine bonds are readily formed and stabilized by intramolecular hydrogen bonds [65, 66]. The intramolecular association in salicylaldimine derivatives causes a shielding effect due to the –OH group is less effective in broadening the molecule. Intramolecular hydrogen bonding may increase the rigidity of the molecule while significantly improving the chemical stability of the highly reactive unsubstituted Schiff base [66, 67].

Research papers are available on azo-azomethine liquid crystal compounds [63, 68-74]. Terminal substituents play an important role in the behavior of liquid crystal. Long alkoxy chains provide flexibility to the rigid core structure, which tends to have a lower melting point [75]. In the present study, we report the synthesis, characterization, photoisomerization, DFT calculation, and mesomorphic behavior of new liquid crystalline materials with three phenyl rings linked through–N=N–and –C=N– central bridges as rigid core and the rest of the molecular part –OH, $–CH_3$, $–NH_2$ as lateral substitution and –OR as a terminal end group. Consequently, the objective of this study is to understand and establish the effect of molecular flexibility on the properties of

liquid crystals. In addition, we used the DFT / B3LYP 631 + G (D, P) basis set to evaluate the molecular geometry, stability, frontier molecular orbital energy (FMO), dipole moment, and molecular electrostatic mapping of the compounds**.**

5.2 Synthesis Scheme



Where R= C_nH_{2n+2} and n= 2 to 8, 10, 12, 14, 16, 18.

i) RBr, $KHCO_3$, KI, dry acetone, reflux 24 hr.

ii) 0-5 ^oC ,HCl + $NaNO_2$,H_2O, CH_3COONa

iii) Few drops of glacial acetic acid, absolute ethanol, reflux 4 hr

Scheme 6. Synthetic protocol of series G

5.3 Results and discussion

All compounds of the synthetic series are mesogenic and have high thermal stability. In the homologous series, the lower derivatives from *n*-ethoxy **(G2)** to *n*-

heptoxy **(G7)** have an enantiotropic nematic phase **(Figure 13).** The POM image of the *n*-heptyloxy derivative **(G7)**, as shown in **Figure 14a**, shows the nematic droplet texture formed when the isotropic liquid is cooled to 162.8°C. After further cooling, the droplet texture of the nematic phase at 150.2 ^{o}C becomes the thred like texture of the nematic phase, as shown in **Figure 14b**. The middle derivatives of the homologous series, *n*-octyloxy **(G8)** and *n*-decyloxy **(G10)** are dimorphic; in addition to the enantiotropic nematic phase, they also exhibited the smectic-A. The POM image of the *n*-decyloxy derivative **(G10)** as shown in **Figure 14c** indicates the transition from the threaded texture of a nematic phase to the focal-conic fan-shaped texture of smectic-A phase when cooled to 150.3^{o}C. In the higher homologous of the series from *n*-dodecyloxy **(G12)** to *n*-octadecyloxy **(G18)** nematic phase disappeared and exhibited only enantiotropic smectic-A phase. The POM image of *n*-tetradecyloxy derivative **(G14)** is depicted in **Figure 14d**, indicating a focal- conic fan-shaped texture of the smectic-A phase on cooling at 151.9 ^{o}C.

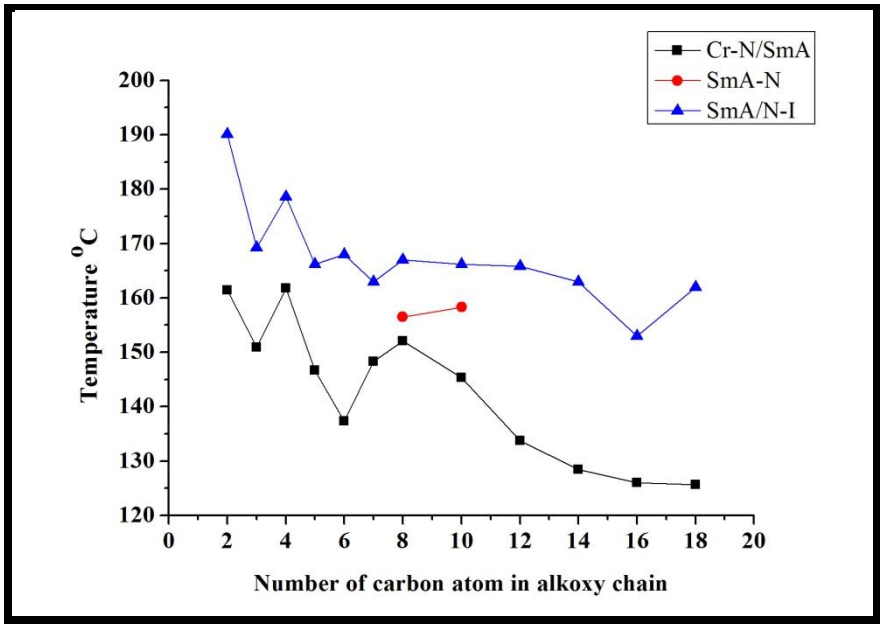


Figure 13. On heating phase behavior of homologous series G

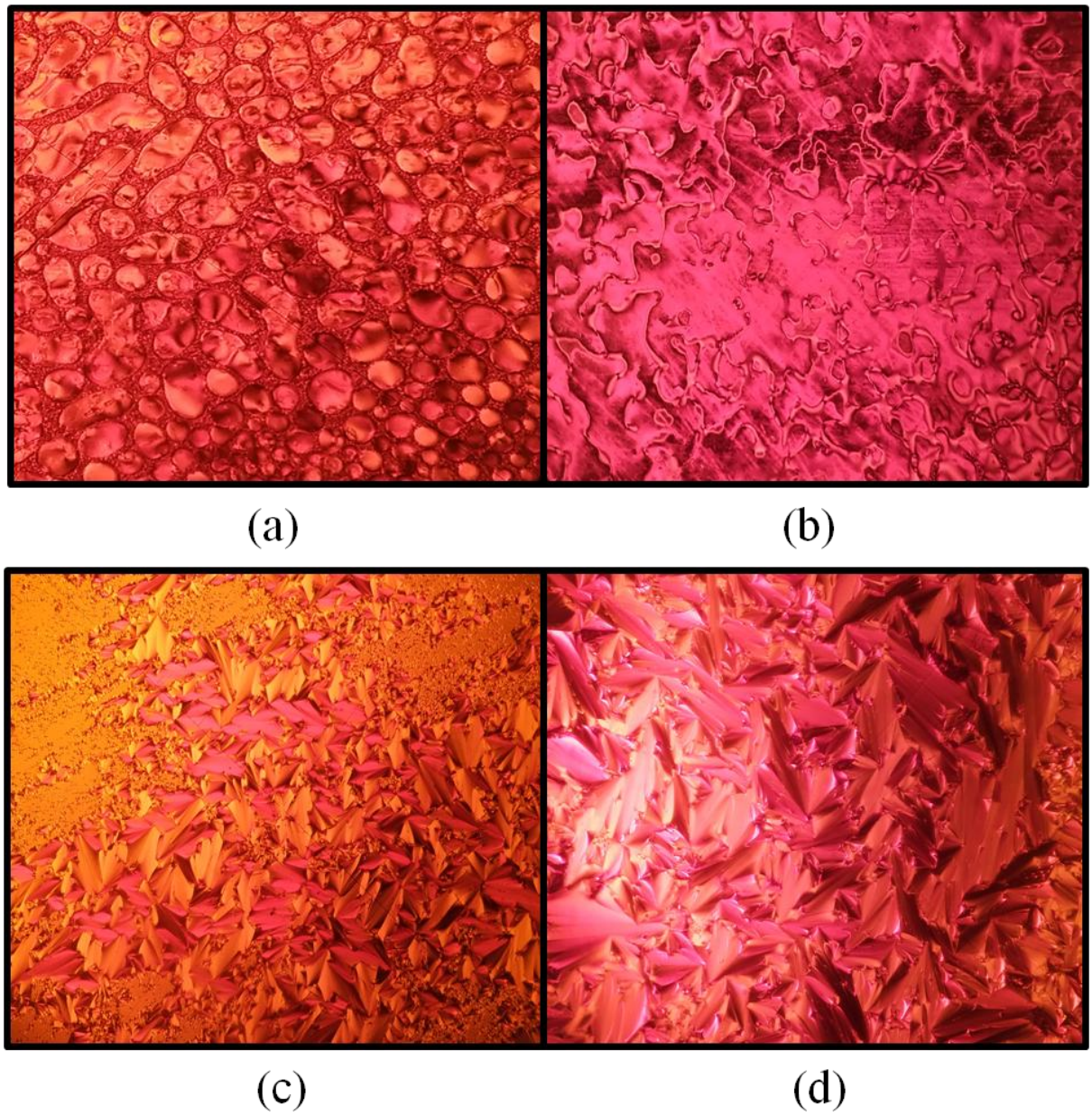


Figure 14. Polarising optical microscopic images of series-G compounds (a) The droplet texture of nematic phase of *n*-heptyloxy **G7** on cooling at 162.2 ^{o}C (b) The threaded texture of nematic phase of *n*-heptyloxy **G7** on cooling at 150.2 ^{o}C (c) The nematic phase converted to Sm-A phase of *n*-decyloxy **G10** on cooling at 150.3 ^{o}C (d) The focal-conic fan shaped texture of Sm-A phase of *n*-tetradecyloxy **G14** on cooling at 151.9 ^{o}C

5.4 Conclusion

- New azo-azomethine-based homologous series have been synthesized, characterized by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy and mesomorphic behavior studied using Differential Scanning Calorimeter (DSC) and Polarizing Optical Microscope (POM).
- The synthesized homologous series of azo-azomethine is smectogenic and nematogenic. All the compounds are mesogenic and exhibited various phases depending on their molecular flexibility.
- The lower members are nematic; the medium members are both nematic as well as smectic, and the higher members are smectic only. It is found that as the length of the terminal alkoxy chain increases, the stability of the smectic phase increases, while the stability of the nematic phase decreases.
- In the present series, the obtained mesophase type is nematic/smectic or both; the phase stability of the obtained mesophase; its mesophase range depends largely on the flexibility of the molecule.
- The mesomorphic result indicates that the mesophase range in the cooling scan is wider than the heating scan.
- The results of the DFT calculation show that the calculated polarization, dipole moment, and stability increase with the increase of chain length.

References

[1] Collings PJ, Hird M. Introduction to Liquid Crystals: Chemistry and Physics. 1st Ed.CRC Press, 1997, London.

[2] Reinitzer F. Wiener Monatsh.Chem.1888; 9: 421–441.

[3] Lehmann O. Z. Phys. Chem.1889; 4: 462–472.

[4] Giroud-Godquin A-M, Maitlis PM. Metallomesogens: Metal Complexes in Organized Fluid Phases. Angew. Chemie Int. Ed. English. 1991;30:375–402.

[5] Espinet P, Esteruelas MA, Oro LA, et al. Transition metal liquid crystals: advanced materials within the reach of the coordination chemist. Coord. Chem. Rev. 1992; 117: 215–274.

[6] Hudson SA, Maitlis PM. Calamitic metallomesogens: metal-containing liquid crystals with rodlike shapes. Chem. Rev.1993;93:861–885.

[7] Neve F. Metallomesogens. Synthesis, properties, and applications. Edited by J. L. Serrano, VCH, Weinheim 1996, xvii, 498 pp., hardcover, DM 298.00, ISBN 3-527-29296-9. Adv. Mater. 1996;8:864–866.

[8] Collinson SR, Bruce DW. Metallomesogens—Supramolecular Organization of Metal Complexes in Fluid Phases Perspect. Supramol. Chem. 1999. p. 285–369.

[9] Hikmet RAM, Broer DJ. Dynamic mechanical properties of anisotropic networks formed by liquid crystalline acrylates. Polymer. 1991;32:1627–1632.

[10] Chen H-W, Lee J-H, Lin B-Y, et al. Liquid crystal display and organic light-emitting diode display: present status and future perspectives. Light Sci. Appl. 2018;7:17168.

[11] Zhulai D, Koval'chuk A, Bugaychuk S, et al. Photoconductivity of ionic thermotropic liquid crystal with semiconductor nanoparticles. J. Mol. Liq. 2018;267:406–410.

[12] Han MJ, Wei D, Kim YH, et al. Highly oriented liquid crystal semiconductor for organic field-effect transistors. ACS Cent. Sci. 2018;4:1495–1502.

[13] Melnyk O, Garbovskiy Y, Glushchenko A. Science and technology of stressed liquid crystals: display and non-display applications. Phase Transitions. 2017;90:773–779.

[14] Jber N, M. Shukur M, Al Ahmed A. Schiff base liquid crystals with terminal alkoxy group synthesis and thermotropic properties. J. Al-Nahrain Univ. Sci. 2014;17 (2):46-22.

[15] Hagar M, Ahmed HA, Saad GR. Mesophase stability of new Schiff base ester liquid crystals with different polar substituents. Liq. Cryst. 2018;45:1324–1332.

[16] Ha S-T, Koh T-M, Yeap G-Y, et al. Mesogenic Schiff base esters with benzothiazole core: synthesis and phase transition studies. Phase Transitions. 2010;83:195–204.

[17] Ha S-T, Ong L-K, Wong JP-W, et al. Mesogenic Schiff's base ether with dimethylamino end group. Phase Transitions. 2009;82:387–397.

[18] Kala ALA, Harohally N V., Naveen S, et al. o-Hydroxy Schiff bases derived from 2-hydroxy-4-methoxy benzaldehyde: synthesis, x-ray studies and hydrogen bonding attributes. Mol. Cryst. Liq. Cryst. 2016;629:146–157.

[19] Sharma VS, Patel RB. Design and investigation of calamatic liquid crystals: Schiff base (–CH=N), chalcone (–CO–CH=CH–), and ester (–COO–) linkage group contain rigid rod shape with various terminal parts. Mol. Cryst. Liq. Cryst. 2017;643:141–158.

[20] Hagar M, Ahmed HA, Alhaddad OA. New azobenzene-based natural fatty acid liquid crystals with low melting point: synthesis, DFT calculations and binary mixtures. Liq. Cryst. 2019;46:2223-2234.

[21] Tandel RC, Patel NK. Synthesis and study of liquid crystalline properties of schiff's bases having 1,3,4-thiadiazole moiety. Liq. Cryst. 2014;41:495–502.

[22] Date RW, Bruce DW. Discotic salicylaldimato metal complexes exhibiting columnar mesophases and their mixtures with rod-like salicylaldimato complexes. Liq. Cryst. 2004;31:1435–1444.

[23] Marcos M, Omenat A, Barberá J, et al. Structural study of metallomesogens derived from tris-[2-(salicylideneamino)ethyl]amine. A molecular meccano. J. Mater. Chem. 2004;14:3321–3327.

[24] Hoshino N. Liquid crystal properties of metal–salicylaldimine complexes.: Chemical modifications towards lower symmetry. Coord. Chem. Rev. 1998;174:77–108.

[25] Datta C, Chakrabarty R, Das G, et al. Influence of spacer group substituent on mesomorphism in copper complexes of 'salen' type Schiff bases bearing long alkoxy arm. Liq. Cryst. 2014;41:541–551.

[26] Nejati K, Rezvani Z, Alizadeh E, et al. Synthesis and mesomorphic properties of symmetric tetradentate Schiff bases based on azo-containing salicylaldimines and their copper(II) complexes. J. Coord. Chem. 2011;64:1859–1870.

[27] Caruso U, Roviello A, Sirigu A. Nematic and smectic mesophases in a new series of Cu(II) organometallic complexes. Liq. Cryst. 1990;7:421–430.

[28] Heng BT, Yeap GY, Mahmood WAK, et al. New heterocyclic metallomesogens: synthesis, mesomorphic and thermal behaviours of Cu(II) complexes with 1,2,3-triazole-based Schiff bases ligands. Liq. Cryst. 2015;42:204–215.

[29] Cretu C, Cseh L, Tang BJ, et al. Mononuclear Cu(II) complexes of novel salicylidene Schiff bases: synthesis and mesogenic properties. Liq. Cryst. 2015;42:1139–1147.

[30] Thaker BT, Solanki DB, Patel BS, et al. Synthesis, characterisation and liquid crystalline properties of some Schiff base and cinnamate central linkages involving 1,3,5-trisubstituted pyrazolone ring system and their Cu(II) complexes. Liq. Cryst. 2013;40:1296–1309.

[31] Prajapati AK, Bonde N. Synthesis of two naphthyl-containing homologous series of mesogenic ligands and the related metallomesogens containing Cu(II). Liq. Cryst. 2006;33:1189–1197.

[32] Wang H, Wang Y, Hu H, et al. Novel metallomesogens derived from heterocyclic benzoxazoles. Tetrahedron. 2008;64:4939–4948.

[33] Parra M, Vergara J, Alderete J, et al. Synthesis and mesomorphic properties of esters derived from Schiff's bases containing 1,3,4-thiadiazole. Liq. Cryst. 2004;31:1531–1537.

[34] Kaszyński P, Kapuściński S, Ciastek-Iskrzycka S. Chapter Four - Liquid crystalline derivatives of heterocyclic radicals. In: Scriven EF V, Ramsden CABT-A in HC, editors. Adv. Heterocycl. Chem. Academic Press; 2019. p. 263–331.

[35] Gallardo H, Favarin I. New mesogenic thiophene and furan derivatives. Liq. Cryst. 1993;13:115–125.

[36] Ha S-T, Koh T-M, Lin H-C, et al. Heterocyclic benzothiazole-based liquid crystals: synthesis and mesomorphic properties. Liq. Cryst. 2009;36:917–925.

[37] Chong YT, Muhamad Sarih N, Ha ST, et al. New homologues series of heterocyclic schiff base ester: synthesis and characterization. Adv. Phys. Chem. 2016;2016.

[38] Reddy MK, Reddy KS, Prakash M, et al. Synthesis and characterization of two phenyl ring core-based thiophene mesogens. Mol. Cryst. Liq. Cryst. 2013;582:1–14.

[39] Cai R, Samulski ET. New thermotropic liquid crystals derived from thiophenes. Liq. Cryst. 1991;9:617–634.

[40] Hariprasad S, Srinivasa HT. Symmetric 3 , 5-pyrazole and isoxazole heterocycles comprising a bent core unit : synthesis and mesomorphic characterisation. Liquid Crystals .2015; 42(11): 1612-1620.

[41] Yeap G-Y, Mohammad A-T, Osman H. Synthesis, spectroscopic and mesomorphic studies on heterocyclic liquid crystals with 1,3-oxazepine-4,7-dione, 1,3-oxazepane-4,7-dione and 1,3-oxazepine-1,5-dione cores. J. Mol. Struct. 2010;982:33–44.

[42] Vicentini F, Barrouillet J, Laversanne R, et al. Side chain liquid crystalline polypyrrole Part I: synthesis and characterization. Liq. Cryst. 1995;19:235–240.

[43] Langley PJ, Davis FJ, Mitchell GR. Synthetic routes to polypyrroles with pendant mesogenic groups. Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A. Mol. Cryst. Liq. Cryst. 1993;236:225–230.

[44] Langley PJ, Davis FJ, Mitchell R. Synthesis , phase behaviour and polymerisation of mesogenic materials based on 3-substituted pyrroles. Journal of the Chemical Society, Perkin Transactions 2.1997;2229–2239.

[45] Benkhaya S, Souad M, Ahmed EI. Classifications , properties , recent synthesis and applications of azo dyes. Heliyon .2020;6: e03271.

[46] Hegde RS, Sunil BN, Hegde G, et al. In fl uence of alkyl and alkoxy groups on photoresponsive behaviour of bent-core azo mesogens : Synthesis , mesomorphic and photoswitching properties. J. Mol. Liq. 2020;309:113091.

[47] Madiahlagan E, B N S, Ngaini Z, et al. Synthesis, liquid crystalline properties and photo switching properties of coumarin-azo bearing aliphatic chains: Application in optical storage devices. J. Mol. Liq. 2019;292:111328.

[48] Hegde G, Kozenkov VM, Chigrinov VG, et al. Photoisomerization in photoaligned azo dyes exhibiting photostability. Mol. Cryst. Liq. Cryst. 2009;507:41–50.

[49] Niezgoda I, Jaworska J, Pociecha D, et al. The kinetics of the E-Z-E isomerisation and liquid-crystalline properties of selected azobenzene derivatives investigated by the prism of the ester group inversion. Liq. Cryst. 2015;42:1148–1158.

[50] Wang X, Li Z, Zhao H, et al. New azobenzene liquid crystal with dihydropyrazole heterocycle and photoisomerization studies: New azobenzene liquid crystal. R. Soc. Open Sci. 2020;7.

[51] Hegde G, Shanker G, Gan SM, et al. Synthesis and liquid crystalline behaviour of substituted (E)-phenyl-4-(phenyldiazenyl) benzoate derivatives and their photo switching ability. Liq. Cryst. 2016;43:1578–1588.

[52] Westphal E, Bechtold IH, Gallardo H. Synthesis and optical/thermal behavior of new Azo photoisomerizable discotic liquid crystals. Macromolecules.

2010;43:1319–1328.

[53] Rahman L, Kumar T, Sarkar SM, et al. New U-shaped liquid crystals azobenzene derived from catechol for photoswitching properties. J. Mol. Liq. 2015;202:125–133.

[54] Lin J, Ji X, Guo H, et al. Novel perylene columnar liquid crystal tuned by azo isomerization on bay-positions. J. Mol. Liq. 2019;290:111228.

[55] Pham VP, Manivannan G, Lessard RA, et al. New azo-dye-doped polymer systems as dynamic holographic recording media. 1995;242:239–242.

[56] Rahmouni A, Bougdid Y, Moujdi S, et al. Photoassisted holography in azo dye doped polymer films. J. Phys. Chem. B. 2016;120: 11317–11322.

[57] Zakerhamidi MS, Kiani S, Tajalli H, et al. Role of specific and nonspecific intermolecular interaction in electro-optical response of doped 6CHBT nematic liquid crystal with azo dyes. J. Mol. Liq. 2016;221:608–616.

[58] Natansohn A, Rochon P. Photoinduced motions in azo-containing polymers. Chem. Rev. 2002;102: 4139–4176.

[59] Mustroph H, Stollenwerk M, Bressau V. Current developments in optical data storage with organic dyes.Angew Chem. Int. Ed. Engl. 2006;45:2016-2035.

[60] Rochon P, Batalla E, Natansohn A, et al. Optically induced surface gratings on azoaromatic polymer films. Appl. Phys. Lett.1995;66:136.

[61] Gan SM, Yuvaraj AR, Lutfor MR, et al. Synthesis, liquid crystal characterization and photo-switching studies on fluorine substituted azobenzene based esters.RSC Adv. 2015;5:6279–6285.

[62] Manna AK, Mondal J, Chandra R, et al. A fluorescent colorimetric azo dye based chemosensor for detection of S2− in perfect aqueous solution and its application in real sample analysis and building a molecular logic gate. Anal. Methods. 2018;10:2317–2326.

[63] Iftime M, Cozan V, Airinei A et al. Asymmetric azomethine amines with azobenzene moieties – liquid crystalline and optical properties. Liq. Cryst. 2019;00:1–11.

[64] Ahmed NHS, Saad GR, Ahmed HA et.al. New wide-stability four-ring azo/ester/Schiff base liquid crystals: synthesis, mesomorphic, photophysical, and DFT approaches. RSC Adv.2020;10:9643–9656.

[65] Nakum KJ, Katariya KD, Jadeja RN, et al. Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone and their Cu (II) complexes : synthesis , characterization and mesomorphic behavior. Mol. Cryst. Liq. Cryst. 2019;690:1–13.

[66] Heng BT, Yeap GY, Mahmood WAK, et al. Alkyl chain self ordering, induction and suppression of mesophase by Cu(II) containing [1,2,3]-triazole-based bidentate salicylaldimine ligands: synthesis, characterisation and X-ray diffraction studies. Liq. Cryst. 2014;41:1897–1910.

[67] Yelamaggad C V, Tamilenthi VP. Synthesis and thermal properties of liquid crystal trimers comprising cyanobiphenyl and salicylaldimine anisometric segments. Tetrahedron 2009;65:6403–6409.

[68] Abbasi AR, Rezvani Z, Nejati K. Synthesis and properties of new liquid crystalline compounds containing an alkoxyphenylazo group. Dye. Pigment.

2006;70:71–75.

[69] Ahmed NHS, Saad GR. Effect of replacing the terminal phenyl ring with 3-pyridyl and inversion of imine linkage on the mesophase behaviour of four-ring azo/ester/Schiff base compounds. Liq. Cryst. 2020;00:1–14.

[70] Thaker BT, Kanojiya JB, Tandel RS. Effects of different terminal substituents on the mesomorphic behavior of some azo-Schiff base and azo-ester-based liquid crystals. Mol. Cryst. Liq. Cryst. 2010;528:120–137.

[71] Hamryszak L, Janeczek H, Schab-Balcerzak E. New thermotropic symmetrical and unsymmetrical azomethine with azobenzene unit and fluorinated alkyl chain: Synthesis and characterization. J. Mol. Liq. 2012;165:12–20.

[72] Iwan A, Janeczek H, Domanski M, et al. Synthesis, characterization and mesomorphic properties of new unsymmetrical azomethine-type liquid crystals derived from 4-biphenyl carboxaldehyde. J. Mol. Liq. 2010;151:30–38.

[73] Nejati K, Rezvani Z, Alizadeh E, et al. Synthesis and mesomorphic properties of symmetric tetradentate Schiff bases based on azo-containing salicylaldimines and their copper(II) complexes. J. Coord. Chem. 2011;64:1859–1870.

[74] Abid KK, Al-barody SM. Synthesis, characterisation and liquid crystalline behaviour of some lanthanides complexes containing two azobenzene Schiff base. Liq. Cryst. 2014;41:1303–1314.

[75] Zhang X bing, Tang B chen, Zhang P, et al. Synthesis and characterization of 1,3,4-oxadiazole derivatives containing alkoxy chains with different lengths. J. Mol. Struct. 2007;846:55–64.

Published Papers

From Present Work

1. **Kiran J. Nakum**, Kanubhai D. Katariya & Rajendrasinh N. Jadeja (2020) Synthesis, characterization, and mesomorphic properties of some new Schiff base homologues series and their Cu(II) complexes, Molecular Crystals and Liquid Crystals, 708:1, 1-13.

2. **Kiran J. Nakum**, Kanubhai D. Katariya, R. N. Jadeja & A. K. Prajapati (2019) Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone and their Cu(II) complexes: synthesis, characterization and mesomorphic behavior, Molecular Crystals and Liquid Crystals, 690:1, 1-13.

3. **Kiran J. Nakum,** Kanubhai D. Katariya, Vivek K.Gupta & Rajendrasinh N. Jadeja. Synthesis, characterization, crystal structure and mesomorphic behaviour of thiophene based homologous series, (Communicated in Phase Transitions A Multinational Journal , Manuscript Id : GPHT-2021-0135).

4. **Kiran J. Nakum**, Kanubhai D. Katariya, Chirag J Savani & Rajendrasinh N. Jadeja. The influence of molecular flexibility on the mesogenic behaviour of a new homologous series based on azo-azomethine: synthesis, characterization, photoisomerization and DFT study. (Communicated in Journal of Molecular Structure, Manuscript Id : MOLSTRUC-S-21-04776

From Other Work

1. **K. J. Nakum**, J. R. Patel, V. K. Gupta, and R. N. Jadeja(2019) Crystal Structure of 5- Butoxy-4-((3- butoxyphenyl)diazenyl)-3- methyl-1-phenyl-1Hpyrazole. *Crystallography Reports,Vol. 64, No. 7, pp. 1051–1054*

2. **Kiran Nakum** and Rajendrasinh N. Jadeja, Synthesis, characterization, and electrochemical study of a mononuclear Cu(II) complex with a 4-acyl pyrazolone ligand. Z. Naturforsch. 2018; 73(10)b: 713–718.

3. G. N. Bhola, **Kiran Nakum**, Kaushal Karia & U. C. Bhoya (2015) Mesomorphism Dependence on Molecular Flexibility in an Azoester Series, Molecular Crystals and Liquid Crystals, 608:1, 125-134.

4. Balbir Kumar, **Kiran J. Nakum**, R. N. Jadeja, Rajni Kant, and Vivek K. Gupta. Crystal structure of [1-(3-chlorophenyl)- 5-hydroxy-3-methyl-1H-pyrazol-4-yl](ptolyl) methanone (2015)Acta Cryst. (2015). E71, o280–o281

Paper Presented in Conferences

1	Indian Council of Chemists 38th Annual National conference at Veer Narmad South Gujarat University (VNSGU) Surat, 11th April-2021.
2	ICSM 2020 4th International Conference on Soft Materials, organised by SMRS Jaipur and MNIT Jaipur at MNIT Jaipur, 13-18th December 2020
3.	National Conference on New Dimensions in Chemistry and Chemistry Education and National Convention of Chemistry Teachers, NCCT-2019 organised by Department of Chemistry, Sant Gagde Baba Amravati University, Amravati and ACT,TIFR, Mumbai, 5-7th December-2019 at Sant Gagde Baba Amravati University, Amravati
4	International Conference on Recent Trends in Chemical Sciences organized by Indian Chemical Society, Hosted by SOS, Pt. Ravishankar Shukla University, Raipur on-14-16th November 2019.
5.	National Conference on Organic Molecules as synthons and Reagents for innovation(OMSRI-2019) organised by Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee during 8-10th February-2019.
6	Indian Council of Chemists 37th Annual National conference at National Institute of Technology Karnataka (NITK) Surathkal, Mangalore 12-14th December 2018.
7	National Conference on Recent advances in Material Sciences, NCRAMS-18 Faculty of Science, The M.S University of Baroda, Gujarat 23rd-24th Nov-2018
8	7th All Gujarat Research Scholar Meet, AGRSM-VII ICS, Vadodara Chapter The M.S University of Baroda, Gujarat 25th Feb-2018

Participated in workshop and seminar

1	Workshop on Computational Chemistry, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 3-7th March-2020
2	Science Conclave-2020, Faculty of Science The MS University of Baroda ,Gujarat, 28th Feb-2020
3	National Seminar on Advances in Chemistry of bioactive Molecules ACBAM-2020, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 17-18th Jan-2020
4	National Workshop on Advanced Analytical Techniques For Elemental Analysis, AAT-2019, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 28th Dec-2019
5	Industrial Catalysis, ICAT-2019, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 23rd Nov-2019
6	National Symposium on Advances in Chemical Research, ACR-2019, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 24th Feb-2019
7	National Conference On Chirality, NCC-2017, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 10-11th Nov-2017
8	Science Conclave-2017, Faculty of Science The MS University of Baroda ,Gujarat, 28th Feb-2017
9	MDCT-2016 Materials design using Computational tools, SVNIT-Surat Gujarat,12th Dec-2016
10	Frontiers in Heterogeneous Catalysis-2016, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 10th Dec-2016
11	National Seminar on Structure and Chemistry of Materials, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 15th Octo-2016
12	National Seminar on Frontier Areas in Chemical sciences, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 19 March-2016
13	National School on NMR Spectroscopy , Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat, 18-23 th Sept-2015
14	National workshop on X-ray Crystallography, Department of Chemistry Faculty of Science The MS University of Baroda ,Gujarat ,19 -25th Jan-2015