A SYNOPSIS

of the thesis

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

To be Submitted
As a partial fulfilment for the award of the degree of

DOCTOR OF PHILOSOPHY

in
Chemistry

By
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Synopsis of the Thesis

To be submitted to The Maharaja Sayajirao University of Baroda for the award of the degree of DOCTOR OF PHILOSOPHY in Chemistry.

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Title of the Thesis: "Synthesis & characterization of some novel Schiff base derivatives, their metal complexes and study of their mesomorphic behavior"

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Date of Registration: 29th Sept 2015

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The Thesis will be presented in form of the following chapters:

Chapter I
Introduction

Chapter II (A)
Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone: synthesis, characterisation and mesomorphic behavior.

Chapter II(B)
Synthesis and mesomorphic behavior of Cu(II) complexes of Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone.
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Chapter III(A)
Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetanilide: synthesis, characterisation and mesomorphic behavior.

Chapter III(B)
Synthesis and mesomorphic behavior of Cu(II) complexes of Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetanilide.

Chapter IV (A)
Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with thiophene derivative: synthesis, characterisation and mesomorphic behavior.

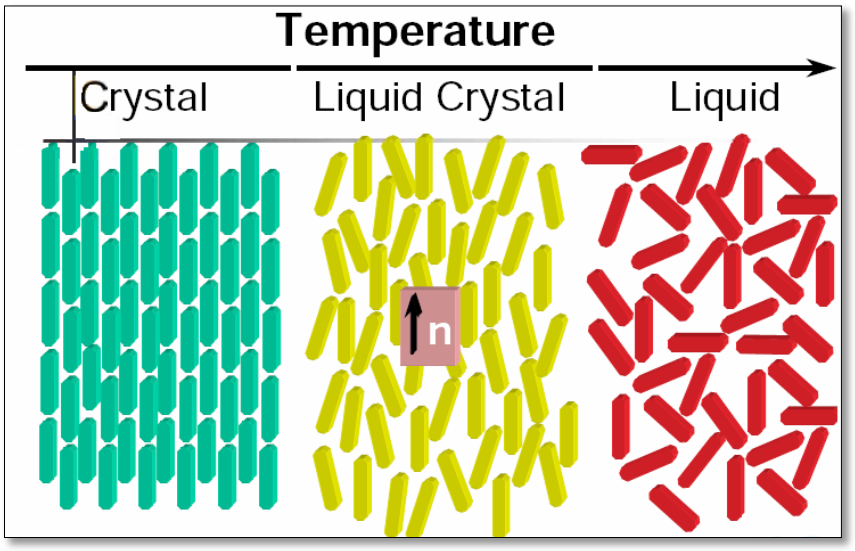
Chapter IV (B)
Schiff base of 4-n-alkoxybenzaldehyde with thiophene derivative: synthesis, characterisation and mesomorphic behavior.

Chapter V
Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 1,3 phenylenediamine derivative : synthesis, characterisation and mesomorphic behavior.

Chapter: I
Introduction

What are Liquid Crystal?

The term 'Liquid Crystals' means substance is in two quite different state of matter at the same time, As most substances are heated, they go from a solid to an isotropic liquid. Some substances, however, exhibit intermediate states lacking some of the order found in solids, but possessing more order than found in liquids. These ordered fluids are called liquid crystals.Liquid crystal can flow like a liquid, due to loss of 3-D positional order, Liquid crystal is optically birefringent, due to its orientational order.



Classification of Liquid crystal

(A) Thermotropic liquid crystals (mesophase formation is temperature dependent)

Thermotropic liquid crystals are those that occur in a certain range of temperature If the temperature rise is too high, thermal motion will destroy the delicate and balance ordering of molecules, forcing the material to go into a usual isotropic liquid phase [1].

(B) Lyotropic liquid crystals (mesophase formation is solvent and concentration dependent).

Mesophase morphologies of thermotropic liquid crystals

In thermotropic mesogens, there are three types of mesophases namely the nematic, cholesteric and smectic originally classified by Friedel based on the degree of positional and orientational order [2].

(a)Smectic mesophase

In some phases the molecular center of gravity is on an average arranged in equidistant planes, so that in addition to orientational order, positional order is also present which leads to a layered structure such phases have been called Smectics. Smectic A (SmA) phase has molecules organized into layers; in the smectic C (SmC) phase, the molecules are tilted inside the layers.

(b)Nematic mesophase

In this phase the constituent molecules have no positional order but are on an average, oriented about a particular direction called the director, n [3]

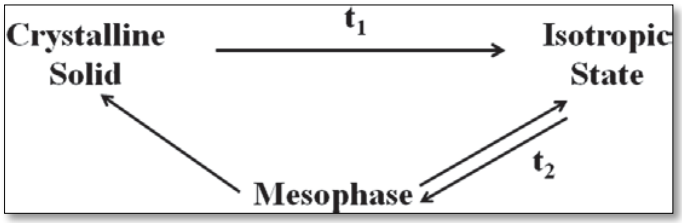
(c)Cholesteric mesophase

Cholesteric mesophase is the chiral variant of the nematic mesophase and therefore it is also called chiral nematic phase. It occurs in systems where constituent molecules are chiral [4]. It can also be obtained by doping the nematic LC with optically active molecules.

Further thermotropic liquid crystals categories in three types.

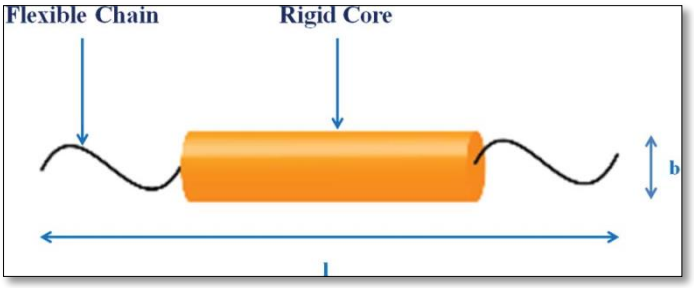
Enantiotropic Liquid Crystals : When thermodynamically stable mesophases are detect both on heating and on cooling then the phases are termed as *enantiotropic.*

Monotropic Liquid Crystals : In this type of mesomorphic state where, t_2 is at lower temperature than t_1 and is observed only on cooling is known as *monotropic mesophase.*



Criteria to achieve the Liquid Crystalline phase

Liquid crystalline materials are normally constituted by aromatic ring attached with aliphatic tail. The aromatic ring provides the rigidity like solids whereas the aliphatic tail provides the fluidity to the liquid crystal molecules.



Aim and Objectives

- ✓ Synthesis of novel Schiff base derivatives and study their mesomorphic behavior.
- ✓ Synthesis of metal complexes of Schiff base derivatives and study the effect of metal on the mesomorphic behavior.
- ✓ To characterize synthesized compounds by various technique such as IR, NMR, Mass, DSC etc.
- ✓ Investigation of the effect of terminal alkoxy chain length variation on mesomorphic behavior of synthesised compounds.
- ✓ To study the effect of terminal end group on the mesomorphic behavior of synthesised compounds.
- ✓ To study the effect of variation in linking group on the mesomorphic behavior of synthesised compounds.

Chapter: II

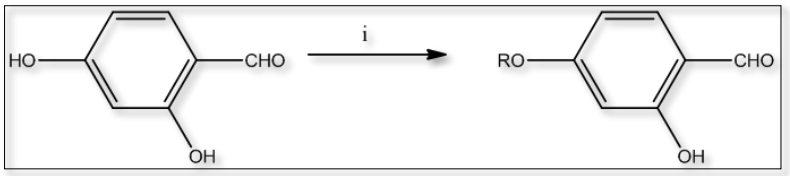
Introduction:

Metallomesogens, the metal containing liquid crystal have been extensively studied due to their unique geometrical structure possibilities and potential of combining optical, electronic and magnetic properties of transition metal complexes with liquid crystalline ligand. Salicylaldimine derivatives have been widely used as ligand due to several substitution possibility, easy preparation and ability to coordinate with wide variety of metals [5, 6]. Salicylaldimine based liquid crystals are thermally stable due to presence of intra-molecular hydrogen bonding between the hydroxyl group and imine group [7]. Transition metal complexes derived from salicylaldimines are among one of the most known complexes that exhibited mesogenic properties in metallo-mesogens. Almost all 3d transition metal complexes derived from Salicylaldimines exhibited mesomorphic properties [8].

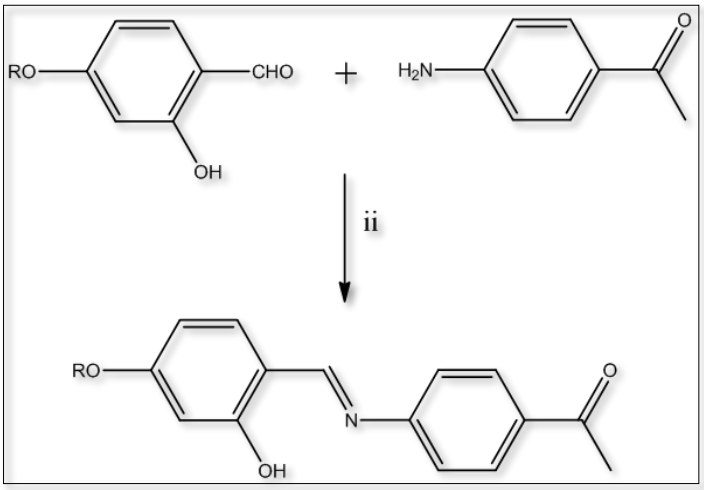
Chapter: II(A)

Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone: synthesis, characterisation and mesomorphic behavior.

Synthesis of 2-Hydroxy-4- n-alkoxybenzaldehyde.



Synthesis of (4-((2-Hydroxy-4-n-alkoxy) benzylidene) amino) phenyl) ethanone.



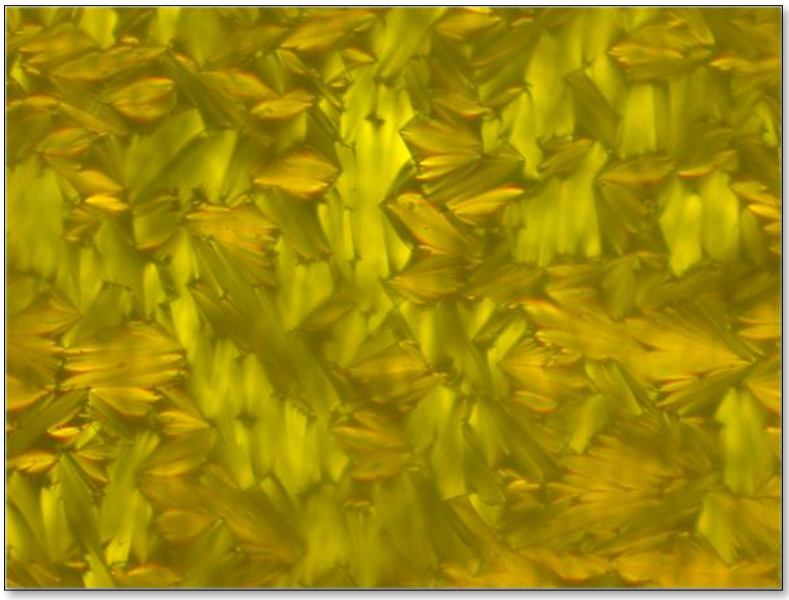
Where R = C_nH_{2n+1}; n = 2 to 8,10,12,14,16,18.

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

ii) glacial AcOH, absolute EtOH, reflux 4 hr

Mesomorphic behavior

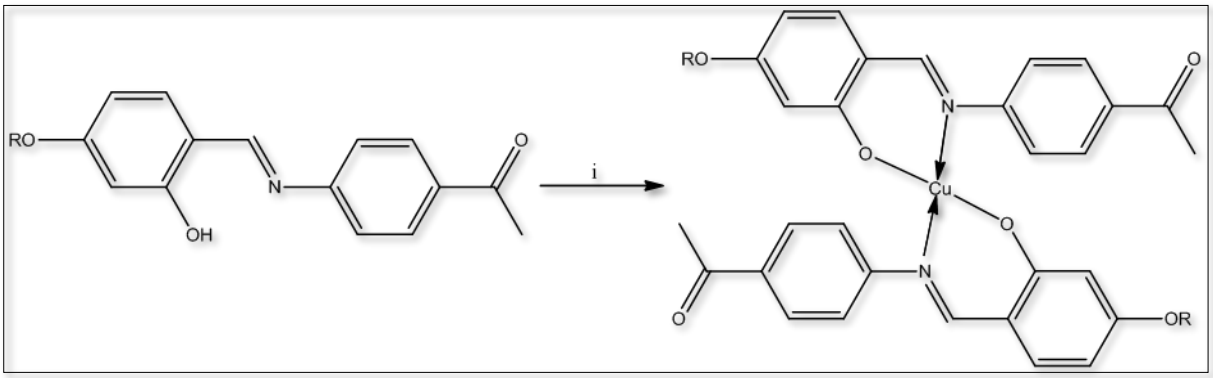
The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The synthesised series is purely smectogenic, in the homologous series SmA mesophase commence from n-propyloxy derivative as monotropy. Then, all the members of homologous series of ligands are shown enantiotropic SmA behavior.



Chapter: II(B)

Synthesis and mesomorphic behavior of Cu(II) complexes of Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetophenone

Synthesis of Cu(II) complexes

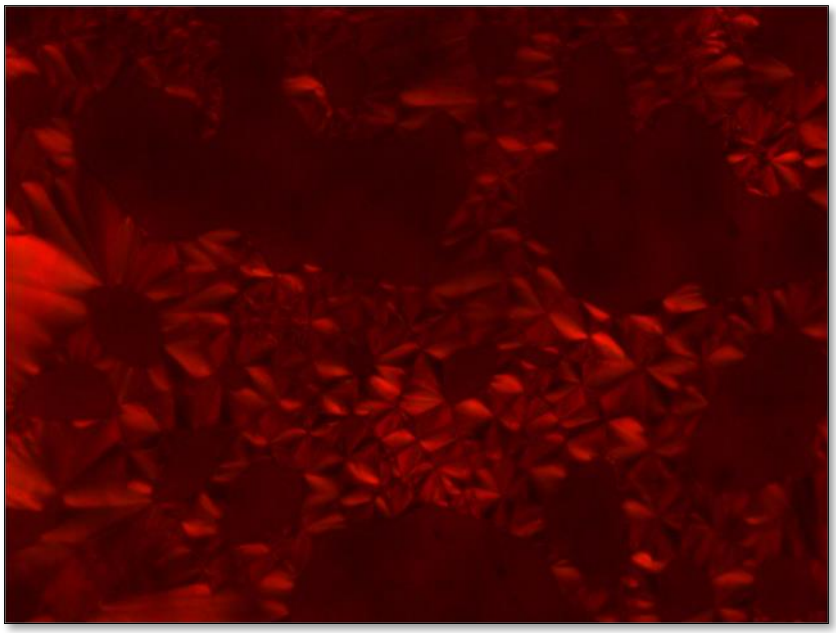


Where R = C_nH_{2n+1}; n = 2 to 8,10,12,14,16,18.

i) absolute EtOH, reflux 4 hr.

Mesomorphic behavior

The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The synthesised series is purely smectogenic, SmA mesophase commence from n-pentyloxy derivative as monotropy and n-hexyloxy derivative also shows monotropy. Whereas n-hyptyloxy to n-octadecyloxy derivatives exhibit enantiotropic SmA mesophase.



Chapter: III

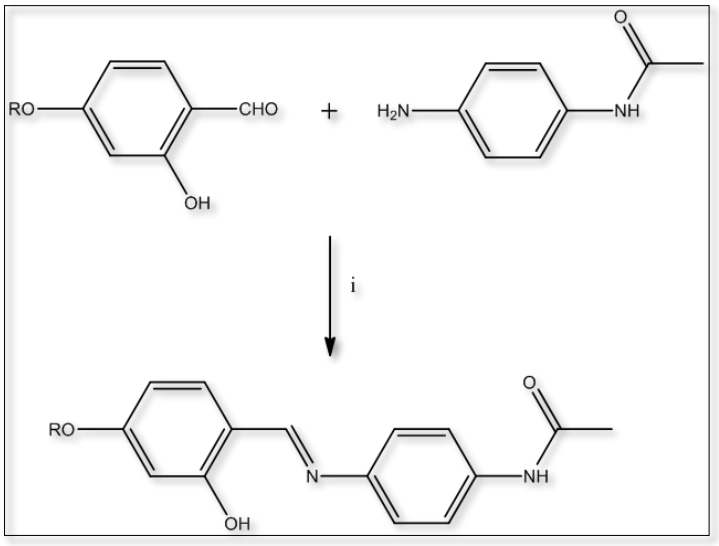
Introduction:

Several distinctive compounds with a diversity of molecular shapes along with Schiff base functionality have been prepared and found to show remarkable mesomorphic properties [9–12].Schiff bases are the frequently studied compounds ever since the discovery of 4-methoxybenzylidene-4′-butylaniline (MBBA) which displays a nematic mesophase at room temperature .Literature review revealed that liquid crystals possessing Schiff base unit has been widely studied and employed as a connecting group for the preparation of different kinds of liquid crystals[9-12]. On the other hand, compounds that combine the liquid crystalline property along with those of metal ions are an important objective of research now a days and have resulted in variety of structural types, including a range of metals. Metallomesogens are well known to possess both discotic as well as calamitic liquid crystalline properties. Along with the different geometry of complexes, variable oxidation states, magnetism and redox behaviors are the added advantageous properties of Metallomesogens [13].It is also worth to say that complexation can also results in difference in mesomorphic properties of the uncoordinated ligands.

Chapter: III(A)

Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetanilide: synthesis, characterisation and mesomorphic behavior

Synthesis of Synthesis of N-(4-((4-n-Alkoxy-2-hydroxybenzylidene)amino) phenyl) acetamide.



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

i) glacial AcOH, absolute EtOH, reflux 4 hr

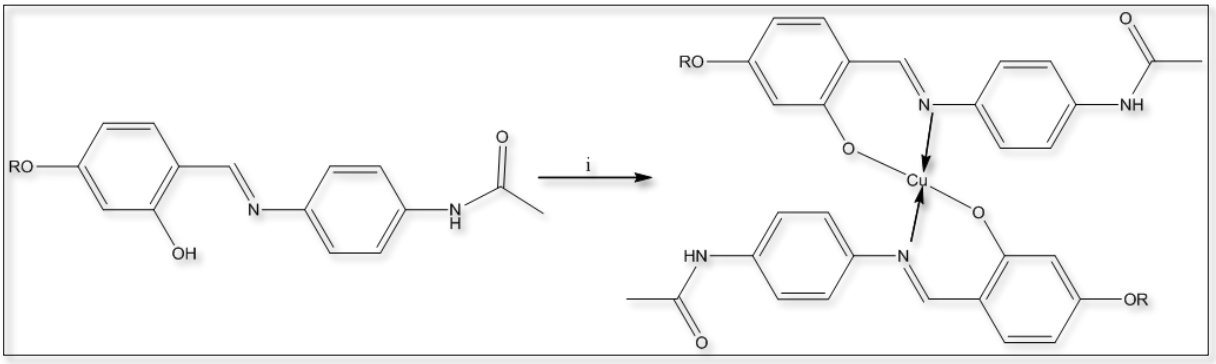
Mesomorphic behavior

The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The smectic A phase, in the homologues series of ligands mesomorphic property commence from hexyloxy(-OC_6H_{13}) terminal end group.

Chapter: III(B)

Synthesis and mesomorphic behavior of Cu(II) complexes of Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 4-amino acetanilide

Synthesis of Cu(II) complexes

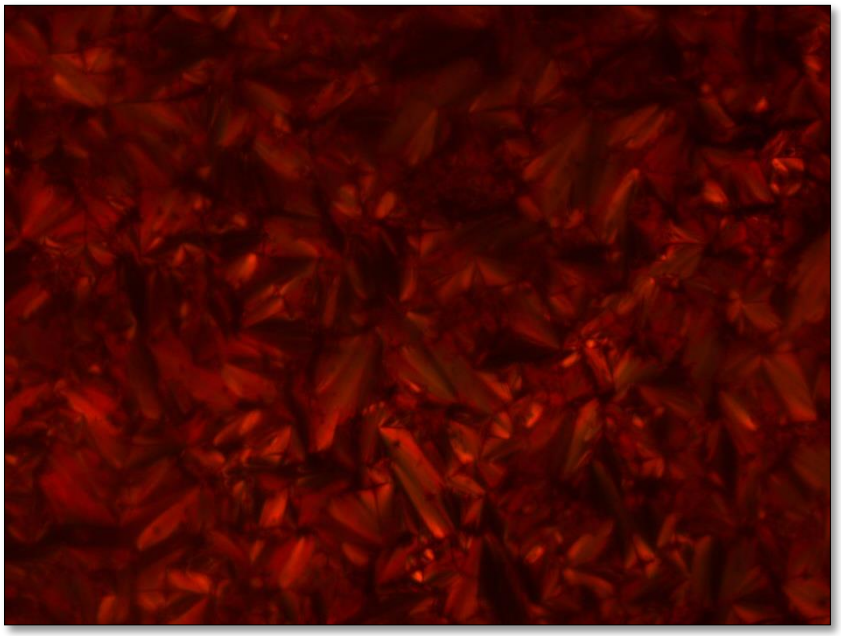


Where R = C_nH_{2n+1}; n = 2 to 8,10,12,14,16,18.

i) absolute EtOH, reflux 4 hr.

Mesomorphic behavior

The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The smectic A phase, in the homologues series of ligands mesomorphic property commence from octyloxy(-OC_8H_{17}) terminal end group.



Chapter: IV

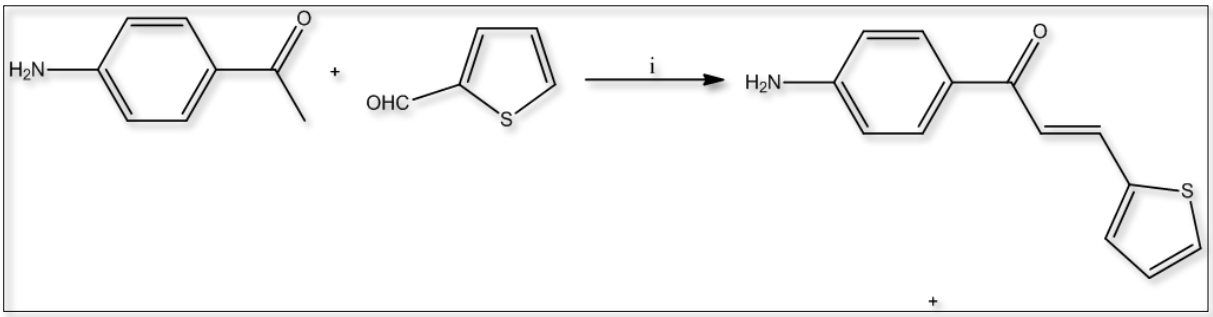
Introduction:

The research of based on heterocyclic liquid crystals has attracted much more attention in recent years due to larger choices in the design and synthesis of novel heterocycle containing mesogenic compounds [14,15].Numerous compounds containing heterocyclic moiety such as furan, thiophene, pyrrole, benzothiazole, pyridine, pyrimidine, oxadiazolehave been reported to possess variety of mesogenic properties[16,17] Chalcones and their derivatives have been used as a biogenetic precursors to cure human degenerative diseases such as anti-inflammatory, anti-invasive , antimalarial , anticancer and antioxidant , as well as for protective efficacy against radiation induced oxidative stress.

Chapter: IV(A)

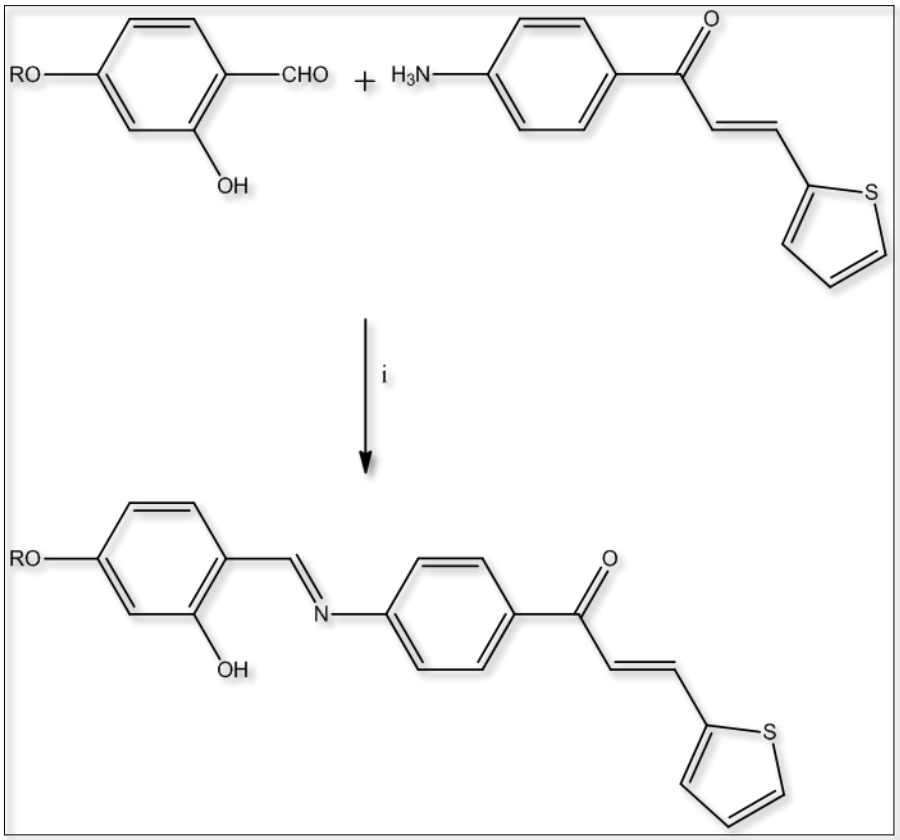
Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with thiophene derivative: synthesis, characterisation and mesomorphic behavior.

Synthesis (E)-1-(4-aminophenyl)-3-(thiophen-2-yl)prop-2-en-1-one.



i) aq.NaOH, alcohol.

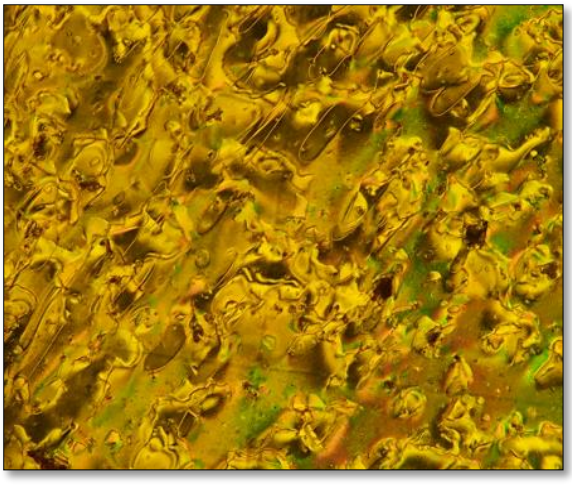
Synthesis of (E)-1-(4-((E)-(2-hydroxy-4-methoxybenzylidene)amino)phenyl) -3-(thiophen-2-yl)prop-2-en-1-one.



Where
R = C_nH_{2n+1};
n = 2 to 8, 10, 12, 14, 16, 18
i) Few drops of glacial AcOH, absolute EtOH, reflux 4 hr

Mesomorphic behavior

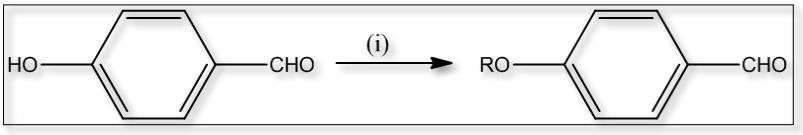
The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The mesomorphic property commence from hexyloxy(-OC_6H_{13}) terminal end group show monotropic nematic phase. Then, from heptyloxy(-OC_7H_{15}) to dodecyloxy (-$OC_{12}H_{25}$) terminal end group show enantiotropic nematic pahse. From tetradecyloxy(-$OC_{14}H_{29}$) to octadecyloxy(-$OC_{18}H_{37}$) derivatives exhibits enantiotropic Smactic phase.



Chapter: IV(B)

Schiff base of 4-n-alkoxybenzaldehyde with thiophene derivative: synthesis, characterisation and mesomorphic behavior

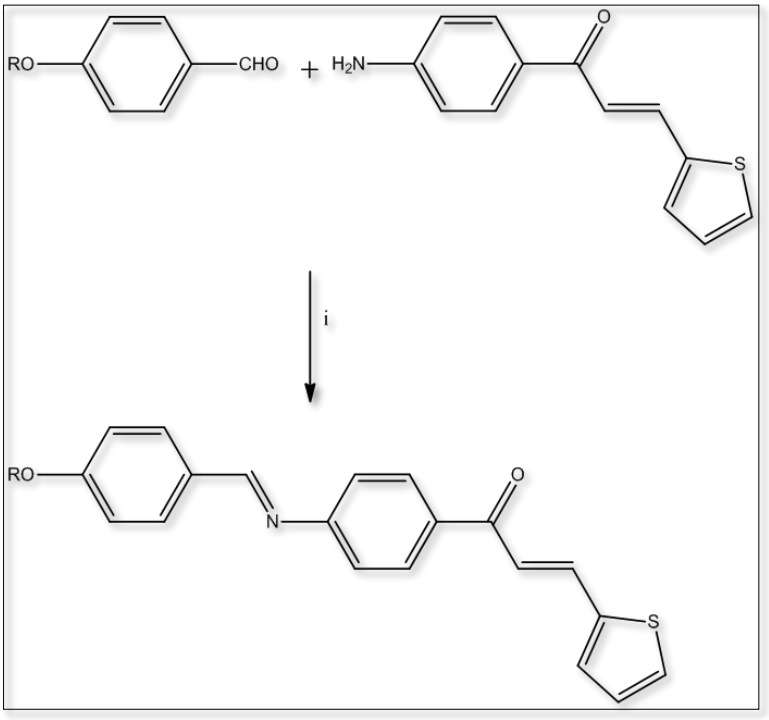
Synthesis of 4-n-alkoxy benzaldehyde.



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

i) RBr, K_2CO_3, dry acetone, reflux 8-12 hr

Synthesis of (E)-1-(4-((E)-(4-n-alkoxybenzylidene) amino) phenyl)-3-(thiophen-2-yl) prop-2-en-1-one



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

i)Few drops of glacial AcOH, absolute EtOH, reflux 4 hr .

Mesomorphic behavior

The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The mesomorphic property commence from hexyloxy(-OC_6H_{13}) terminal end group and continue to tetradecyloxy(-$OC_{14}H_{29}$) as monotropic nematic phase. Remaining all compounds of the series were non-mesogenic.

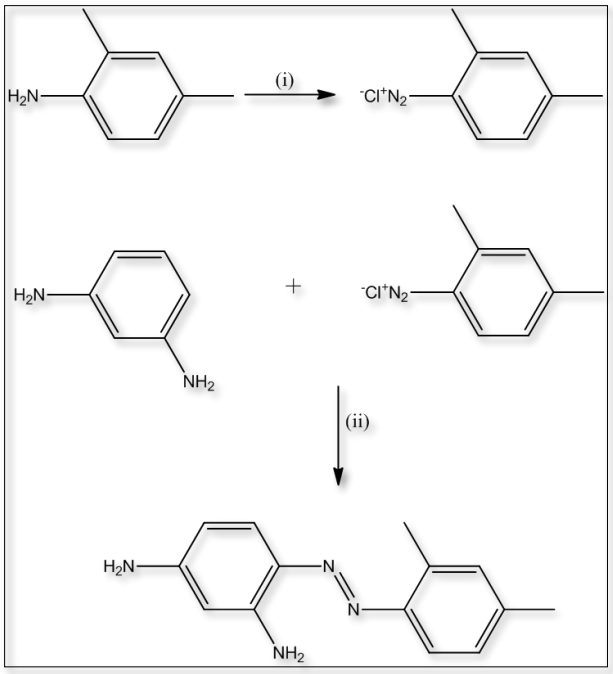
Chapter: V

Schiff base of 4-n-alkoxy-2-hydroxy benzaldehyde with 1,3 phenylenediamine derivative : synthesis, characterisation and mesomorphic behavior

***Introduction*:**

Azobenzene derivatives were among the first recognised groups of liquid crystalline molecules.[18]. Initially, they were considered to be of no use in LCDs industry because of their photosensitive nature. But today, the same phenomenon is the basis of their new applications. Azo based materials are well known for potential applications in photonics, such as optical data storage, photochemical molecular switches, polarisation holography and nonlinear optics [19,20]. Combining photoswitchable azo benzenes with liquid crystalline ferroelectrics also provides access to potential new multifunctional materials where polar response can be modulated by light. W. Weiss• flog et al. prepared homologues series of N,N'-bis[4-(4-n-alkyloxybenzoyloxy)benzylidene]-phenylene-1,3-diamines and reported mesophase behavior of the compounds [21].Veena Prasad synthesised Bent - Shaped Achiral Azo Compounds from 1,3 phenylenediamine derivatives which exhibiting Banana Mesophases.[22]Nandiraju V. S. Rao et al . reported smectic mesophase by W-shaped molecular system of N,N'-bis[2-hydroxy-5-(4'-ntetradecylphenylazo) benzylidene]-4-nitro-1,3-phenylenediamine.[23]

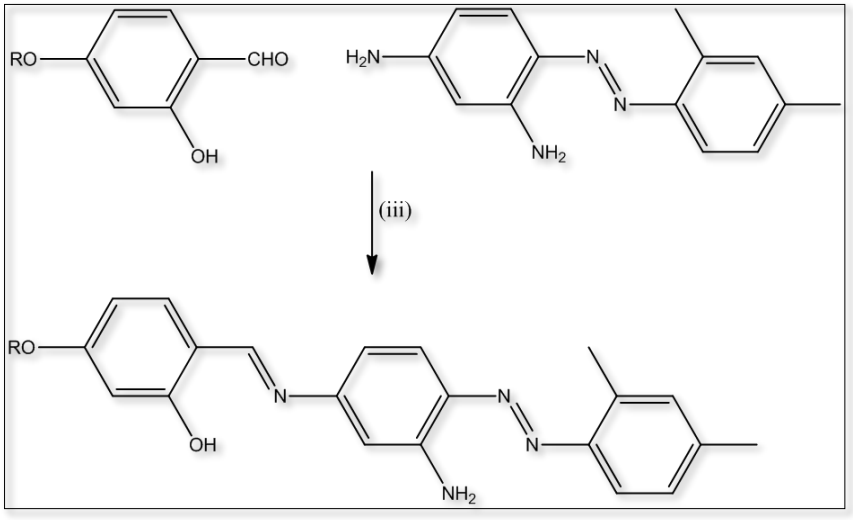
Synthesis of (E)-4-((2,4-dimethylphenyl)diazenyl)benzene-1,3-diamine.



i) HCl + $NaNO_2$,H_20,0-5 ºC

ii) 0-5 ºC,CH_3COONa

Synthesis of 2-((E)-((3-amino-4-((E)-(2,4-dimethylphenyl)diazenyl)phenyl) imino)methyl)-5-n-alkoxyphenol.



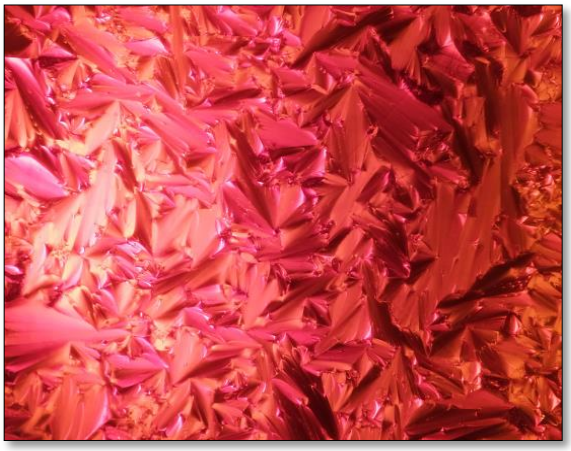
Where R = C_nH_{2n+1}; n = 2 to 8,10,12,14,16,18

iii) glacial AcOH, absolute EtOH, reflux 4 hr

Mesomorphic behavior

The mesophase exhibits by the synthesised series has been confirmed with the optical textural observation under POM and DSC thermogram studies. The mesomorphic property commence from hexyloxy(-OC_6H_{13}) terminal end group and continue to tetradecyloxy(-

$OC_{14}H_{29}$) as monotropic nematic phase. Remaining all compounds of the series were non-mesogenic.



Conclusion:

A number of novel Schiff base derivatives homologues series have been synthesised. All the synthesised homologues series have variation in alkoxy chain length of terminal end group. All the synthesised homologues series are structurally vary in either different terminal end group or different in linking group structure. All synthesized compounds characterize by various technique such as IR, NMR, Mass etc.The newly synthesized compounds are studied for their mesomorphic behavior using POM and confirmed by DSC analysis. All the reported series exhibits different types of mesophase with different stability temperature of respective phase.

References:

[1]P. J. Collings and M. Hird, *Introduction to Liquid Crystals Chemistry and Physics, Taylor and Francis, London,* 1997.

[2]S. Chandrasekhar; B. K. Sadashiva; K. A. Suresh, *Pramana.*, (1977), 9, 471.

[3]G. Friedel,*Ann. Physique.*, (1922), 18, 273.

[4]H. S. Kitzerow; C. Bahr, *Chirality in Liquid Crystals, Springer-Verlag,* New York, 2001.

[5]Chen,C. J., Wang,I.W., Sheu,H.S, Lee, G.H.& Lai,C.K. *Tetrahedron.*, (2011). 67 , 8120-8130.

[6]Binnemans, K. & C.G.Walrand., *Chem. Rev.,* (2002). 102, 2303-2345.

[7]Heng,B. T., Yeap,G.Y., Mahmood, W.A. K., Han,C.C., Lin H.C.,Takano, S.&Takeuchi.D., .Liq. Cryst., (2014)Vol. 41, No. 12, 1897–1910.

[8]Rezvani,Z., Nejati, K.,Seyedahmadian,M. & Divband B.. Mol. Cryst. Liq. Cryst., (2008) 493:1, 71-81.

[9]Ha, S-T., Koh, T-M., &Yeap, G-Y., *Phase Transitions.,* (2010),83, 195–204.

[10]Ha, S-T., Ong, L-K., &Wong, JP-W., *Phase Transitions*., (2009),82, 387–397.

[11]Kala, A., Harohally, N., &Naveen, S., *Mol. Cryst. Liq. Cryst*. (2016),629, 146–157.

[12]Sharma, V., &Patel, R.*Mol. Cryst. Liq. Cryst*.,(2017),643, 141–158.

[13]Marcos, M., Omenat, A., &Barberá, J,*J. Mater. Chem*., (2004), 14, 3321–3327.

[14]H.-C. Wang, Y.-J. Wang, H.-M. Hu, G.-H. Lee and C. K. Lai, *Tetrahedron*, (2008), 64, 4939.

[15]M. Parra, J. Vergara, J. Alderete and C. Zúñiga, *Liq. Cryst.*, (2004), 31, 1531.

[16]S. Hariprasad and H. T. Srinivasa, *Liq. Cryst.*, (2015), 42, 1612.

[17]G.-Y. Yeap, A.-T. Mohammad and H. Osman, *J. Mol. Struct.*, (2010), 982, 33.

[18]Bogojawlenski A, Winogradov N. *Z Phys Chemie.* (1908);64:229–242.

[19] Natansohn A, Rochon P. *Chem Rev.* (2002);102:4139– 4175.

[20] Manickasundaram S, Kannan P, Hassan QMA, et al. *J Mater Sci Mater Electron*. .(2008);19:1045–1053.

[21] W. Weissflog , I. Wirth , S. Diele , G. Pelzl , H. Schmalfuss , T. Schoss & A. Würflinger *Liquid Crystals*, (2001) 28:11, 1603-1609.

[22] Veena Prasad ,*Molecular Crystals and Liquid Crystals Science and Technology. Section A.Molecular Crystals and Liquid Crystals*, (2001),363:1, 167-179.

[23] Nandiraju V. S. Rao et al *J. Mater. Chem*., (2003), 13, 2880–2884.

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