Aim and Objective

The field of liquid crystals has fascinated scientists as well as technologists, over several decades by now. Their applications in numerous fields of modern technology have developed further interest in search for new mesogens and exploration of fundamental causes of the captivating phenomenon. The gamut of liquid crystal in ever widening giving rise to wider vista of new thinking and in turn creating a necessity of continued efforts for their basic study. Inspired thus, the present investigation in planned to explore a number of possibilities.

Thus, the prime and foremost aim set forth for this investigation is to synthesize new homologous series of high mesomorphic value, with specific considerations. Certain molecular structures have been altered, while some have been maintained as common to all the homologous series. The objective in doing so is to be able to short out and assays the effect of the structural aspects on mesomorphism. It has been visualized that immense light will be shed to the advantage of the subject matter by such an investigation.

Synthesis and characterization of cholesterogenic, nematogenic and smectogenic compound containing an azomethine and azo pendent group has been another significant study. Potential applications in non-linear optics, optical storage and electro optical devices has developed considerable interest in the synthesis and structural investigations of liquid crystalline mesogens with azo, azomethine and chalcone groups in the mesogenic units.

The addition of metals to calamitic liquid crystals can enhance their usefulness in a number of ways. Metals are highly polarizable i.e. they have high electron densities that can be easily distorted in an electric field. Because the stability of liquid crystal phases is thought to depend on their ability to polarize, incorporating metals into liquid crystals could increase their stability. The higher polarizability of a metal would also increase birefringence in the liquid crystal. Also, many metal complexes are colored; so, if the metal forms a complex with a calamitic liquid crystal, colored liquid crystal displays can be made without costly filters. And, as many metals are paramagnetic i.e. they have unpaired electrons which respond to external magnetic fields. Metals that do maintain the linear rod-like geometry needed for a liquid crystal include nickel, palladium and platinum, copper, silver and gold, rhodium and iridium.
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2.1 Introduction

The detailed study of many mesogenic homologous series has helped to evolve some general rules for the effect of chemical constitution in the nematogenic and smectogenic compounds [1]. There have been a variety of compounds reported with liquid crystalline properties, but heterocyclic moieties less explored, compared to homocyclic moieties [2]. Furthermore heteroatoms offer the possibility of several modes of co-ordination. Thermotropic liquid crystals are of great technological importance [3-20]. Many series of liquid crystalline compounds containing heterocyclic groups have been synthesized because of their interesting properties [21]. Various mesomorphic heterocyclic compounds have been reported [22-27]. Heterocyclic compounds provide a great synthetic and structural versatility due to their having a number of potential substitution positions.

One of the earlier contributions to the revival of metal-containing liquid crystal systems was the synthesis of the ortho-metallated palladium complexes of mesogenic azobenzenes by Ghedini and co-workers, which represented the first systematic attempt to coordinate metals to known liquid crystal systems [28].

The fact that complexation of such systems enhances mesophase stability was further demonstrated in the azopalladium(II) complexes with 4-alkyl-4'-alkoxyazobenzenes for which induction and/or mesophase stabilization were observed ((1): M=Pd, R¹=H, CH₃, C₂H₅, C₃H₇, R²=OCnH₂n+1, n=1, 2, 7, 12, 18), X=Cl [29–31]. All the complexes were found to exist as equimolar mixtures of cis and trans isomers. Enantiotropic nematic phases, with in some cases additional smectic phases (Sm-A and Sm-C), were obtained; for short-chain-length complexes (n=1, m=1,2,7), mesomorphism occurred above 200°C, whereas for the derivatives with long alkoxy chains (n=1, m=12, 18; m=12, n=2, 3), mesophases appeared between melting points in the range 130–180°C and clearing points around 160–200°C. Molecular and macroscopic biaxiality have been claimed for these materials on the basis of order parameter measurements made by infrared techniques, calorimetry, and optical microscopy[32]. Later investigations by neutron scattering and small-angle diffraction studies[33,34] suggested that the phases were uniaxial, although it is difficult to see how techniques which monitor rather short-range order could validate such a conclusion.
In order to obtain low-melting metallomesogens, several unsymmetric, mononuclear, orthometallated complexes combining 4,4′-bis(alkoxy)azobenzene and various types of simple chelating ligands have been prepared. Such dinuclear, chloro-bridged complexes may be reacted with anionic chelating ligand, and be converted to a stable, mononuclear species. Thus, complexes (2) ((2): M=Pd, n=m=6) with chelating ligand Y–Z such as the o, o-monoanionic acac, hfac (hfac is the 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato anion.), and tropolonate, the N,O 2-aminophenate and 2-amino-2-methyl-1-propanoate, [35] as well as cyclopentadienyl[36] ligands were prepared, but none of them was mesomorphic, probably due to the bulkiness of the co-ligands relative to the small anisotropy of the complex. Note that luminescence was induced by cyclopalladation [37]. The related ortho-metallated gold [38] and mercury [39] complexes were not mesomorphic either. Low-temperature N* and SmA phases were nevertheless observed at longer chain lengths in some related, chiral, palladium(II) complexes with an acac co-ligand Y–Z ((2): M=Pd, n=7, 10, 12, 14, OC\text{m}H_{2m+1}=(R)-(\alpha)-2-octanol, (S)-(\alpha)-\beta-citronellol) [40].
Other heteroligand palladium complexes (2) with Y–Z being either an non-chiral N-[4′-(dodecyloxy) resorcylidene]-4-alkylaniline or a chiral N-[4′-(dodecyloxy)resorcylidene]-4-alkoxyanilines ((2): M=Pd, n=14, \( \text{OC}_{m}\text{H}_{2m+1}=(R)-(\alpha)-2\)-octanol, (S)-(\alpha)-\beta-citronellol) have been prepared. They showed chiral mesophases over narrow temperature ranges [41].

A number of homologous series with two phenyl rings bridged through a variety of central linking groups, which causes variation in the molecular rigidity and flexibility, were reported earlier [42,43]. Such differences in the molecular rigidity cause a difference in the types and degrees of mesomorphism exhibited by the substance. The ester homologous series formed by –COO- and –CH=CH-COO-linking groups considerably affect molecular rigidity. Liquid crystals are important materials in several different fields, particularly display devices and in the medical fields. Therefore, the present homologous series was designed and synthesized with a cinnamate linking group, and its effects on the type of mesophase and degree of mesomorphism were determined. Thus, the present study is aimed at developing structure–property relationships in liquid crystals.

Metallomesogens have attracted increasing attention due to the possibility of combining the physico-chemical properties contributed by the metal (color, magnetism, polarizability, redox behavior, geometry, etc.) with those of the organic framework [44-46]. The understanding and control of phase behavior, however, is a function of molecular chain length, the nature of the substituent's on the ligands, the spacer groups and the metal ions. Their synthesis is often fraught with challenges, but a number of metal complexes exhibiting novel mesomorphic properties have continued to be reported and their physical properties studied [47–50]. Among the first row transition metals, metallomesogens with copper (II) exhibiting various smectic, nematic as well as columnar liquid crystalline phases have been prepared and studied [51-52]. Due to the paramagnetism induced by the copper (II) center, these metallomesogens show interesting chemical and physical properties which can lead to potential applications [53-54].

This chapter contains synthesis and characterization of two liquid crystalline homologous series and two metallomesogen series with Cu(II) metal as described below.
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[A] 4-(((4-chlorophenyl)diazynyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate

[B] 3-hydroxy-4-((4-nitrophenyl)diazynyl)phenyl 6-alkoxy-2-naphthoate

[MC] Bis (2-((4-chlorophenyl)diazynyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy)copper(II)

[MD] Bis (2-((4-nitrophenyl)diazynyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy)copper(II)
2.2 Experimental

2.2.1 Reagent and Technique

For the synthesis of compounds of the homologous series, following materials were used. 4-Hydroxy benzoic acid, alkyl bromide (Lancaster, England), 4-chloro aniline, 4-nitro aniline, resorcinol, 6-hydroxy-2-naphthoic acid obtained from H.L.Chemical & Engineer Pvt. Ltd., Maroli (Surat), DMAP (N,N-dimethylaminopyridine) were purchased from Merck (Germany), CuCl₂·2H₂O and DCC (Dicyclohexylcarbodiimide) were purchased from Fluka Chemie (Switzerland). The solvent was used after purification using the standard methods described in the literature [55]. Anhydrous potassium carbonate, acetone, ethanol, methanol, acetic acid, ethyl acetate, dichloromethane, pyridine, petroleum ether, diethyl ether, DMF, POCl₃, HCl, H₂SO₄, ammonia, etc., were used as received. Column chromatography was performed by Acme's Silica Gel (100–200 mesh). Solvents were dried and distilled prior to use.

2.2.2 Synthesis

The synthetic route for the preparation of series-A, B, MC and MD compounds is illustrated as under.

2.2.2.1a Synthesis of 6-alkoxy-2-naphthoic acid

6-Hydroxy-2-naphthoic acid (2.5 g, 13 m mol) and KOH (1.46 g, 26 m mol) were dissolved in ethanol/water (100 mL, 9/1) and the solution was stirred for 20 min; n-alkyl bromide (32.5 m mol) was then added and the mixture heated under reflux for 24 h. When the reaction was completed, KOH (0.73 g, 13 m mol) was added and the mixture heated under reflux for a further 4 h. The ethanol was evaporated, and the mixture poured into water and acidified to approximately pH = 2-3 with acetic acid. The precipitate was filtered and washed with water and ether, and then recrystallized twice from glacial acetic acid than from ethanol to give 71~80% yield. The synthetic route has also been described in the literature [56, 57].

2.2.2.1b Synthesis of 4-chloro -2'·4'-dihydroxy azobenzene

A well stirred mixture of 4-chloro aniline (1.28 gm, 0.01 mol) and (40 mL) of 1:1 Conc. HCl was cooled below 5°C and a solution of NaNO₂ (0.76 gm, 0.011 mol) in water (20 mL) was added drop wise in such a way that the temperature of the mixture was in the range 0-5 °C. The cold, dark yellow solution was added drop wise to a cold mixture of resorcinol (1.1 gm, 0.01 mol), NaOH (5 g, 10%) and water (50
mL), during which the temperature of the mixture was maintained below 8°C. After the diazotized solution, the material was stirred for about thirty minutes and then acidification with aqueous HCl furnished the crude product which was collected by filtration, dried in air, and crystallized several times form alcohol; yield 65%.

2.2.2.1c Synthesis of 4-nitro-2′-4′-dihydroxy azobenzene

A well stirred mixture of 4-nitro aniline (1.40 gm, 0.01 mol) and (40 ml) of 1:1 Conc. HCl was cooled below 5°C and a solution of NaNO₂ (0.76 gm, 0.011 mol) in water (20 ml) was added drop wise in such a way that the temperature of the mixture was in the range 0-5 °C. The cold, dark yellow solution was added drop wise to a cold mixture of resorcinol (1.1 gm, 0.01 mol), NaOH (5 g, 10%) and water (50 ml), during which the temperature of the mixture was maintained below 8°C. After the diazotized solution, the material was stirred for about thirty minutes and then acidification with aqueous HCl furnished the crude product which was collected by filtration, dried in air, and crystallized several times form alcohol; yield 68%.

2.2.2.1d Synthesis of 4-(4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate [Series-A]

4-n-Alkoxybenzoic acids were heated under reflux with thionyl chloride to produce the corresponding acid chloride. The monoester of series I and II were prepared by condensing equimolar quantities of respective 4-n-alkoxybenzoyl chlorides with 4-chloro -2′-4′-dihydroxy azobenzene in dry pyridine by Schotten–Baumann reaction following the method reported earlier [58].

2.2.2.1e Synthesis of 4-(4-nitrophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate [Series-B]

4-n-Alkoxybenzoic acids were heated under reflux with thionyl chloride to produce the corresponding acid chloride. The monoester of series I and II were prepared by condensing equimolar quantities of respective 4-n-alkoxybenzoyl chlorides with 4-nitro -2′-4′-dihydroxy azobenzene in dry pyridine by Schotten–Baumann reaction following the method reported earlier.

2.2.2.1d Synthesis of bis(2-(4-chlorophenyl)diazenyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy) Cu(II) [Series-MC] & bis(2-(4-nitrophenyl)diazenyl)-5-(6-alkoxy-2-naphthoyloxy)phenoxy) Cu(II) [Series-MD]
Dissolved CuCl$_2$.2H$_2$O (0.170 g, 1 mmol) in methanol (10 mL) and add ammonia to it till the colour of the solution become blue. Then dissolved 2 mmol of appropriate ligand (Series-A or Series-B) in methanol (20 mL). To a metal solution added ligand solution and refluxed the reaction mixture for 3 to 4 hrs. Brown-black precipitate was formed. The precipitate was filtered off and washed with methanol twice or thrice.

**Data: Compound A$_8$**

4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-octyloxy-2-naphthoate  
[Series-A]

**Molecular Formula:** C$_{31}$H$_{31}$ClO$_4$N$_2$; **Yield:** 80%; **Clearing Point:** 209°C; **UV (CHCl$_3$) $\lambda_{\text{max}}$:** 258 nm; **Elemental analysis data:** Found; C:70.38%, H:5.68%, N:5.00%; Calculated: C:70.11%, H:5.88%, N:5.28%; **FT-IR (KBr):** $\nu_{\text{max}}$/cm$^{-1}$ 3351 cm$^{-1}$ (O-H str. of –OH group attached to aromatic ring), 3042 cm$^{-1}$ (C-H str. aromatic), 2931, 2855 cm$^{-1}$ (C-H str. aliphatic), 1732 cm$^{-1}$ (C=O str. of ester linkage), 1606 cm$^{-1}$ (N=N Schiff base), 1542 cm$^{-1}$ (C=C str. of aromatic), 1219 cm$^{-1}$ (C-O-C asym. str.), 1057 cm$^{-1}$ (C-O-C sym. str.); **$^1$H NMR:** (400 MHz, CDCl$_3$): 0.86-0.89 ppm (t, CH$_3$ of aliphatic chain), 1.26-1.84 ppm (m, CH$_2$ of aliphatic chain), 4.05-4.08 ppm (t, OCH$_2$ attached with naphthalene ring), 7.10-7.72 ppm (m, Phenyl multiple), 11.25 ppm (s, OH proton of Phenyl); **$^{13}$C NMR (CDCl$_3$):** 14.13 ppm (C$_3$H$_3$ of aliphatic chain), 22.63-33.85 ppm (C$_2$H of aliphatic chain), 68.23 ppm (OCH$_2$ carbon of alkoxy attached with Naphthalene ring), 165.34 ppm (C=O- of ester linkage); **Mass (GC-MS):** MS ES+ m/z (rel.int%): 531.04 (M+2) $^+$ m/z.

**Data: Compound B$_{16}$**

3-hydroxy-4-((4-nitrophenyl)diazenyl)phenyl 6-hexadecyloxy-2-naphthoate  
[Series-B]

**Molecular Formula:** C$_{39}$H$_{47}$O$_3$N$_3$; **Yield:** 78%; **Clearing Point:** 212°C; **UV (CHCl$_3$) $\lambda_{\text{max}}$:** 254 nm; **Elemental analysis data:** Found; C:71.91%, H:7.08%, N:6.15%; Calculated: C:71.64%, H:7.25%, N:6.43%; **FT-IR (KBr):** $\nu_{\text{max}}$/cm$^{-1}$ 3327 cm$^{-1}$ (O-H str. of –OH group attached to aromatic ring), 3034 cm$^{-1}$ (C-H str. aromatic), 2921, 2850 cm$^{-1}$ (C-H str. aliphatic), 1678 cm$^{-1}$ (C=O str. of ester linkage), 1608 cm$^{-1}$ (N=N Schiff base), 1626 cm$^{-1}$ (C=C str. of aromatic), 1255 cm$^{-1}$ (C-O-C asym. str.), 1045 cm$^{-1}$ (C-O-C sym. str.); **$^1$H NMR:** (400 MHz, CDCl$_3$): 0.85-0.89 ppm (t, CH$_3$ of aliphatic chain), 1.29-1.81 ppm (m, CH$_2$ of aliphatic chain), 4.01-4.03 ppm (t, OCH$_2$
attached with naphthalene ring), 7.20-8.79 ppm (m, Phenyl multiplate), 11.39 ppm (s, OH proton of Phenyl) $^{13}$C NMR (CDCl$_3$): 14.13 ppm (CH$_3$ of aliphatic chain), 22.70-33.85 ppm (CH$_2$ of aliphatic chain), 68.24 ppm (OCH$_2$ carbon of alkoxy attached with naphthalene ring), 163.29 ppm (C=O- of ester linkage) Mass (GC-MS): MS ES+ m/z (rel.int%): 653.8 (M+3)$^+$ m/z.

**Data: Compound MC$_{18}$**

Bis(2-((4-chlorophenyl)diazenyl)-5-(6-octadecyloxy-2-napthoyloxy)phenoxy)

Cu(II) [Series-MC]

Molecular Formula: C$_{82}$H$_{100}$Cl$_2$O$_8$N$_4$Cu; Yield: 70%; Heating upto: 205°C;

UV (CHCl$_3$) $\lambda_{max}$: 254nm, 300nm; **Elemental analysis data:** Found; C:70.38%, H:7.42%, N:3.76%, Cu:4.30%, Calculated; C:70.14%, H:7.18%, N:3.99%, Cu:4.53%;

FT-IR (KBr): $\nu_{max}/cm^{-1}$: 3078 cm$^{-1}$ (C-H str. aromatic), 2925, 2865 cm$^{-1}$ (C-H str. aliphatic), 1738 cm$^{-1}$ (C=O str. of ester linkage), 1624 cm$^{-1}$ (N=N Schiff base), 1582 cm$^{-1}$ (C=C str. of aromatic), 1211 cm$^{-1}$ (C-O-C asym. str.), 1042 cm$^{-1}$ (C-O-C sym. str.);

$^1$H NMR: (400 MHz, CDCl$_3$): 0.85-0.89 ppm (t, CH$_3$ of aliphatic chain), 1.25-1.89 ppm (m, CH$_2$ of aliphatic chain), 4.09-4.11 ppm (t, OCH$_2$ attached with naphthalene ring), 7.10-8.70 ppm (m, Phenyl multiplate), $^{13}$C NMR (CDCl$_3$): 14.13 ppm (CCH$_3$ of aliphatic chain), 22.70-33.85 ppm (CH$_2$ of aliphatic chain), 68.45 ppm (OCH$_2$ carbon of alkoxy attached with Naphthalene ring), 166.43 ppm (C=O- of ester linkage) Mass (GC-MS): MS ES+ m/z (rel.int%): 1404.14 (M+3)$^+$ m/z.

**Data: Compound MD$_{18}$**

Bis-{4-[(5-hydroxy-3-methyl-1-p-tolyl-4,5-dihydro-1H-pyrazol-4-yl)methyleneamino]phenyl3-(4-n-heptyloxyphenyl)acrylate}Cu(II) [Series-MB]

Molecular Formula: C$_{82}$H$_{100}$O$_{12}$N$_6$Cu; Yield: 66%; Heating upto: 203°C;

UV (CHCl$_3$) $\lambda_{max}$: 252nm, 304nm; **Elemental analysis data:** Found; C:69.35%, H:7.21%, N:5.54%, Cu:4.30%, Calculated; C:69.10%, H:7.07%, N:5.90%, Cu:4.46%;

FT-IR (KBr): $\nu_{max}/cm^{-1}$: 3080 cm$^{-1}$ (C-H str. aromatic), 2918, 2825 cm$^{-1}$ (C-H str. aliphatic), 1753 cm$^{-1}$ (C=O str. of ester linkage), 1626 cm$^{-1}$ (N=N Schiff base), 1584 cm$^{-1}$ (C=C str. of aromatic), 1202 cm$^{-1}$ (C-O-C asym. str.), 1038 cm$^{-1}$ (C-O-C sym. str.);

$^1$H NMR: (400 MHz, CDCl$_3$): 0.85-0.88 ppm (t, CH$_3$ of aliphatic chain), 1.25-1.87 ppm (m, CH$_2$ of aliphatic chain), 4.10-4.12 ppm (t, OCH$_2$ attached with naphthalene ring), 7.12-8.72 ppm (m, Phenyl multiplate), $^{13}$C NMR (CDCl$_3$): 14.19 ppm (CH$_3$ of aliphatic chain), 22.94-33.97 ppm (CH$_2$ of aliphatic chain), 68.45 ppm
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(OCH₂ carbon of alkoxy attached with naphthalene ring), 168.02 ppm (C=O- of ester linkage) Mass (GC-MS): MS ES+ m/z (rel.int%): 1425.25 (M+3)+ m/z.

Scheme 1(Series-A&B):

(I) Synthesis of 6-alkoxy-2-naphthoic acid

6- hydroxyl-2-naphthoic acid

Where R= CₙH₂ₙ₊₁, n= 1 to 8, 10, 12, 14, 16, 18

(II) Synthesis of 4-chloro/nitro-2'-'4'-dihydroxy azobenzene (B)

4-chloro/nitro-2'-'4'-dihydroxy azobenzene [B]

[A] + [B] (Equimolar) → Dry pyridine Cold 1:1 aq. HCl

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X = Cl  4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate  
Series-A
X = NO₂  3-hydroxy-4-((4-nitrophenyl)diazenyl)phenyl 6-alkoxy-2-naphthoate  
Series-B

Scheme 2 (Series-MC&MD):

Where, X = Cl; Bis(2-((4-chlorophenyl)diazenyl)-5-(6-alkoxy-2-naphthoyoxy)phenoxy) Cu(II)  [Series-MC]
X = NO₂; Bis(2-((4-nitrophenyl)diazenyl)-5-(6-alkoxy-2-naphthoyoxy)phenoxy) Cu(II)  [Series-MD]
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2.2.3. Method of Characterization:

Elemental Analysis

Elemental analysis (C, H, and N) data was performed on Thermo Finnegan EA 1112 Flash Elemental Analyzer at G.N.F.C. (Gujarat Narmada Valley Fertilizer Company Ltd., Bharuch). The results are compared and well agree with the C, H, and N contents of their predicted structure.

UV/Visible Spectral study

For the study of UV/Visible absorption spectra, Thermo Scientific evolution 300 UV/Visible spectrophotometer was used at our department, V.N.S.G.U.Surat. Quartz cells having 1 cm path length were used for reference and sample cells. The compounds which have been used for the spectral measurement are soluble in CHCl3. For this spectral study following equation was used,

\[ \text{No of g sample} = \frac{\text{Required Volume in (g)}}{1000} \times \text{Re quiredconce .(mole / lit)} \times M.W. \]

FT-IR Spectral Study

Infrared spectra were recorded with a Thermo Scientific Nicolet ISO-10 spectrophotometer in the frequency range 4000–400 cm\(^{-1}\) with samples embedded in KBr discs at our department. The KBr pellets were prepared taking necessary precautions to avoid moisture from the spectra; the characteristic frequencies were assigned to different functional groups.

\(^1\)H-NMR & \(^{13}\)C-NMR Spectra

High resolution (400 MHz) NMR spectra of the mesogenic compounds were recorded at room temperature as 15-20% solution in CDCl3 using TMS as internal standard on a Bruker Avance II 400 NMR spectrometer at SAIF (Sofisticated Analytical Instrument Facilities), Panjab University, Chandigarh.

Mass Spectra

Mass spectra (MS ES+) of the compounds were recorded using Finnigan MAT-8230 Mass Spectrometer at SAIF (Sofisticated Analytical Instrument Facilities), Panjab University, Chandigarh.

Thermal Studies

Differential Scanning Calorimetric (DSC) analyses of the liquid crystalline compounds were carried out from Mettler Todelo, India Pvt. Ltd, Powai, Mumbai. DSC analyses were performed on METTELER M-3 thermo balance (Switzerland)
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with microprocessor TA-300 instrument at a heating rate of 10 °C/min in N₂ atmosphere. Some of the samples were analyzed for DSC at DDIT, Nadiad on Thermo DSC analyzer.

Determination of Transition Temperatures

The transition temperatures were determined by using polarizing microscope Nikon Eclipse 50i POL (Japan) furnished with a CCD camera and equipped with Linkam Analysa-LTS420 hot stage (London) at our department as standard procedure.

Slides are prepared by three different methods

(a) In the first method, the substance is taken on a slide and heated to a little more than the mesomorphic temperature at which stage a cover slip is placed over it and then made to cool off.

(b) In the second method, the compound is heated up to the isotropic liquid point then a cover slip is put over it and allowed to cool off.

(c) In the third method the substance is first dissolved in a suitable solvent and then a few drops of the solution are placed on a slide and the solvent is allowed to evaporate. There after a cover slip is placed over it.

The microscope was standardize by taking melting points and/or transition temperatures of very pure but known substances like benzoic acid, succinic acid, p-azoxyanisole, vanillin, p-anisal-p'-phenetidine, p-azoxyphenetole. To determine the various transition a glass slide carrying a thin section of the material with a cover slip on it was observed under the microscope. The slide was inserted in to the specimen chamber of the heating stage and the temperature was raised fast (10°C/min) to find the approximate transition temperatures. The measurements were then reported and near the transition to be observed, the rate of heating was regulated to about 5°C /min. the changing textures over the temperature ranges are carefully observed and recorded as the appearance of focal-conic, plane homeotropic and threaded structures of smectic and nematic phases emerge under polarized light. Formation of isotropic liquid is clearly marked by the field of vision becoming extinct in polarize light. All observation was reported several times, is subjected to the study under microscope.

Differential Scanning Calorimetry

The term “differential scanning calorimetry” has become a source of confusion in thermal analysis the past several years. This confusion is understandable because at the present time there are two entirely different types of instruments which use the
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same name. These two instruments are different in designs of which one is actually a differential thermal analysis apparatus. The instrument are (a) differential scanning calorimeters which are heat-flow recording instruments, \((\mathrm{d}g/\mathrm{d}t)_{\Delta T} = 0\) (Perkin-Elmer, Deltatherm and others). (b) Differential Scanning Calorimeters which are differential temperature recording or DTA instruments \((\Delta T \neq 0)\) (Dupont, Stone Fisher, Linseis and others). The term differential scanning calorimetry (DSC) was apparently first used by Waston et al. This technique maintained the sample and reference materials isothermal to each other by proper application of electric energy, as they were heated or cooled at a linear rate. The curve obtained is a recording of heat flow \(\mathrm{d}H/\mathrm{d}t\), in mcal/sec, as a function of temperature. In the true thermodynamic sense, an endothermic curve is indicated by a peak in the upward direction (increase in enthalpy) while an exothermic peak is recorded in the opposite direction. In all appearances, the DSC curve looks very similar to that of a DTA curve except for the ordinate axis units. As in DTA the area enclosed by the DSC curve peak is directly proportional to enthalpy change.

Area = \(K\Delta H_m\) (\(K\) is boltzman constant) except that \(K\) is independent of temperature.

Calculation of Enthalpy Changes

The calculations for the enthalpy changes \((\Delta H)\) at different transitions were carried out by measuring the area of the peaks and applying the equations given in the manual of Dupont Company.

\[
\Delta H = \frac{A}{m} (60 \times B \times E \times \Delta 95 \times \text{Mol.wt} \times 10^{-3})
\]

Where,

\(\Delta H = \text{kcal/mol}\)

\(A = \text{area of peak (in}^2\)\)

\(m = \text{weight of the sample (mg)}\)

\(B = \text{Time base setting (minute/inch)}\)

\(E = \text{Cell calibration Coefficient}\)

\(\Delta 95 = \text{y-axis range (mcal/sec/in)}\)

\(\text{mol.wt} = \text{Molecular weight of the sample.}\)

Entropy changes are also calculated by using equation,

\[
\Delta S = \Delta H/T
\]

Where \(\Delta S = \text{kcal/mol}/\text{K}\) and \(T = \text{Temperature in K}\).
2.3 Results and Discussion

In present study 12 homologues from each of the two ligand series 4-((4-chlorophenyl)diazenyl)-3-hydroxyphenyl 6-alkoxy-2-naphthoate[Series-A] and 3-hydroxy-4-((4-nitrophenyl)diazenyl)phenyl 6-alkoxy-2-naphthoate[Series-B] are synthesized as per synthetic route given in Scheme-1 and their mesomorphic properties are studied. The general molecular structure of the Series-A and Series-B is shown below:

![Molecular structure of Series-A and Series-B](image)

Where, X = Cl[Series-A] or NO₂[Series-B]
R = CₙH₂ₙ₊₁, n=2 to 8, 10, 12, 14, 16 and 18.

We also synthesized 7 homologues from each of the two complex series Bis(2-((4-chlorophenyl)diazenyl)-5-(6-alkoxy-2-naphthoxy)phenoxy) Cu(II) [Series-MC] and Bis(2-((4-nitrophenyl)diazenyl)-5-(6-alkoxy-2-naphthoxy)phenoxy) Cu(II) [Series-MD] as per the synthetic route given in Scheme 2 and studied their mesomorphic properties. The general molecular structure of Series-MC and Series-MD is shown in below:

![Molecular structure of Series-MC and Series-MD](image)

Where, X = Cl; Bis(2-((4-chlorophenyl)diazenyl)-5-(6-alkoxy-2-
naphthoxy)phenoxy) Cu(II) [Series-MC]
X = NO₂; Bis(2-((4-nitrophenyl)diazenyl)-5-(6-alkoxy-2-
naphthoxy)phenoxy) Cu(II) [Series-MD].
These compounds have been subjected for elemental analysis. The elemental analysis data and other physical parameters are given in Table-1, 2, 3 and 4. The elemental analysis data are agreed with theoretical values as per expected structure. The metal copper was estimated by gravimetrically as CuO. The compound has been subjected for thin layer chromatography (Merck kiesel gel 60 F254 per-coated plates). It shows one spot, indicating single compound. All the compound have been purified by column chromatography on silica gel (80-120 mesh) using mixture of ethyl acetate/petroleum ether [7/3] followed by repeated recrystallization from ethanol.

**FT-IR Spectral Study**

The FT-IR spectra of liquid crystalline compounds of Series-A and Series-B based on ester-azo linkages that exhibit different vibrational modes corresponding to stretching and bending of different functional groups present in the molecule. The FT-IR spectra of representative compounds (A_8, A_{16}, B_8 and B_{16}) are shown in Figure-1(a, b), 2 (a, b) and position of bands and their assignments are given in Table-5 & 6. The sharp band observed at around 3352-3327 cm\(^{-1}\) region is due to free \(-\text{OH}\) of phenyl moiety. In the present case all the spectra of mesomorphic compounds show two sharp bands at around 2933-2919 cm\(^{-1}\) and 2856-2850 cm\(^{-1}\) are due to aliphatic \(\nu(\text{C-H})\) asymmetrical and symmetrical stretching vibration of \(-\text{CH}_3\) and \(-\text{CH}_2\) groups of n-alkyl chain, respectively. There is also a medium band appeared at 1732 cm\(^{-1}\) (A_8), 1735 cm\(^{-1}\) (A_{16}), 1724 cm\(^{-1}\)(B_8) and 1678 cm\(^{-1}\)(B_{16}) attributed to \(\nu(\text{C=O})\) of the ester. The spectra also observed the strong band at 1606 cm\(^{-1}\) (A_8), 1607 cm\(^{-1}\)(A_{16}), 1629 cm\(^{-1}\) (B_8) and 1626 cm\(^{-1}\) (B_{16}) in Series-A and Series-B are attributed to \(\nu(\text{N=N})\) stretching vibration of azo central linking group. The sharp and medium band observed at around 1629-1542 cm\(^{-1}\) region due to aromatic \(\nu(\text{C=C})\) stretching. Another two bands are also observed 1060-1045 cm\(^{-1}\) and 1255-1224 cm\(^{-1}\) is due to \(\nu(\text{C-O-C})\) symmetric and asymmetric stretching [59] respectively. The weak band observed at around 725-718 cm\(^{-1}\) is due to rocking vibration of \(-\text{CH}_2\) groups of alkyl chain. Out of plane deformation of ring hydrogen bond is establishing the position of substituted aromatic nuclei is well known. Although correlation can often be useful in analysis of spectra of the mesomorphic compounds but their performance is variable.

The FT-IR spectra of liquid crystalline compounds of Series-MC and Series-MD gives similar bands as the compounds of Series-A and Series-B except \(-\text{N=N}\) linkage of schiff base. The FT-IR spectra of representative compounds (MC_{18} and
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MD_{18}) are shown in Figure-3 (a, b) and position of bands and their assignments are given in Table-7. The ν (-OH) band is absent in the infrared spectra of all the metal complexes.

Infrared spectra of the present class of the compounds often show long wavelength regions crowded with a large number of bands of similar intensities, and it is difficult to know which bands belongs to this class.

\textbf{\(^1\)H-NMR study}

Compounds of Series-A and Series-B were subjected for \(^1\)H-NMR spectral studies. \(^1\)H-NMR spectra of representative compounds are shown in Figure-4 (a, b) and Figure-5 (a, b) and the chemical shifts (δ, ppm) are noted in Table-8.

The \(^1\)H-NMR spectra of Series-A & Series B exhibit sharp triplet observed at 0.85–0.90 ppm is assigned to terminal methyl proton of alkoxy chain. The signals at 1.26-1.86 ppm is attributed to –(CH2)- group attached to aliphatic chain. The signal at around 4.00-4.11 ppm in triplet is attributed to -OCH\_2- proton of n-alkoxy group attached to naphthalene ring. The free –OH of phenyl gives signal at 11.25 ppm (A_8), 11.24 ppm (A_{16}), 11.38 ppm (B_8) and 11.39 ppm (B_{16}). The multiplet observed in all compounds between 7.09-8.79 ppm is due to substituted phenyl ring. Compounds of Series-MC and Series-MD were subjected for \(^1\)H-NMR spectral studies. \(^1\)H-NMR spectra of representative compounds are shown in Figure-6 (a, b) and the chemical shifts (δ, ppm) are noted in Table-9. The disappearance of the –OH signal from the spectrum of the metal complex indicates that the -OH group has been deprotonated and the resulting phenyl oxygen is bonded to the metal. The \(^1\)H-NMR signals are appeared broad compared to ligand itself, this may be due to metal complexes are paramagnetic, having one unpaired electron, which affect the NMR signals.

\textbf{\(^{13}\)C-NMR study}

The representative compounds of Series-A & Series-B were subjected for \(^{13}\)C-NMR spectral studies. \(^{13}\)C -NMR spectra of representative compounds are shown in Figure-7 (a, b) and Figure-8 (a, b) and the chemical shifts (δ, ppm) are noted in Table-10.

The \(^{13}\)C -NMR spectra of Series-A & Series-B exhibit signal at 14.13 ppm (A_8), 14.22 ppm (A_{16}), 14.14 ppm (B_8) and 14.13 ppm (B_{16}) are assigned to terminal methyl carbon of alkoxy chain. The signals at ~ 22.63-33.92 ppm are observed due to methylene -(CH\_2)_n- carbon of straight alkyl chain of alkoxy group. The signal at
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around 68.23 ppm (A₈), 67.76 ppm (A₁₆), 68.15 ppm (B₈) and 68.24 ppm (B₁₆) are attributed to -OCH₂- carbon of n-alkoxy group attached to benzene ring. The signals at around 165.34 ppm (A₈), 164.52 ppm (A₁₆), 167.45 ppm (B₈) and 163.29 ppm (B₁₆) are due to the carbon of (-C=O) group of ester linkage. The signals observed in all compounds between 114.07-163.06 ppm are due to substituted phenyl ring.

The representative compounds of Series-MC & Series-MD were subjected for ¹³C-NMR spectral studies. ¹³C -NMR spectra of representative compounds are shown in Figure-9 (a, b) and the chemical shifts (δ, ppm) are noted in Table-11.

Mass Spectral Study

The mass spectrum of the compounds of Series-A are shown in Figure-10 (a, b), which gives molecular ion peak at m/z = 533.5 (M+2)⁺ (A₈) & 642.4 (M-1)⁺ (A₁₆). The mass spectrum of the compounds of Series-B are shown in Figure-11 (a, b), which gives molecular ion peak at m/z = 538.30 (M-3)⁺ (B₈) & 653.78 (M⁺) (B₁₆). The mass spectrum of the compounds of Series-MC & MD are shown in Figure-12 (a, b) respectively, which gives molecular ion peak at m/z = 1404.23 (M⁺) (MC₁₈) & 1425.32 (M+1)⁺ (MD₁₈). The m/z ratios obtained from the spectra of representative samples are matched with their molecular ion peak.

UV/Visible Spectral Study

The liquid crystalline compounds of Series-A, B, MC and MD synthesized in present work are colored and therefore, they are subjected for electronic spectral study to know which types of transitions occur in these compounds. Electronic spectra of all the compounds were taken in solution state having 10⁻⁵ M concentration using CHCl₃ as solvent. The electronic spectra of all the compounds are given in Figure-13 (a, b) & 14(a, b) and their relevant data are reported in Table-12, 13, 14 & 15.

The bands observed at around 260, 258 and 256 nm in the electronic spectrum of Series-A & Series-B are assigned to n→π* and π→π* transitions. In the spectrum of the complex series (Series-MC & MD), the bands are observed at 304, 300, 254 and 252 nm because of interligand and charge transfer transition. The d-d band is not observed due to very low concentration [60]. The remaining bands are attributed to the n→π* and π→π* transitions of the ligand or it may be charge transfer transitions.

Molar conductance

The molar conductivity data of Series-MC & Series-MD are given in Table-3 & 4. The molar conductance of the Cu(II) complexes in 10⁻³ M in CHCl₃ as solvent
observed in the range 0.59-0.68 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) for Series-MA and 0.58-0.67 for the Series-MB, respectively. The low conductivity values in CHCl\(_3\) reveal that all complexes are nonelectrolytic in nature and there is no counter ion present outside the coordination sphere of complexes [61, 62].

**Thermal and phase behavior**

The melting points and transition temperature of the compound of Series-A and B are given in Table-16 and 17 respectively.

Optical microscopy reveals that series-A compound exhibit the enantiotropic nematic phase (A\(_2\), A\(_3\), A\(_5\)-A\(_8\), A\(_{16}\), and A\(_{18}\)) homologues except A\(_4\) compound. A\(_4\) homolog in which carbon chain is (C\(_4\)H\(_9\)) exhibits monotropic in nature. The Smectic-A phase appeared in compound A\(_8\), A\(_{10}\)-A\(_{18}\). Compound A\(_{10}\) again exhibit monotropic Sm-A phase. The plot of transition temperatures verses the number of carbon atoms in the alkoxy chain (Figure-15-a) exhibits no odd-even effect for any type of transition temperature. The transition temperature of Sm-A phase decreased as the series was ascended. This was due to the fact an increase in number of –CH\(_2\)- groups in the alkoxy straight chain i.e. called dilution effect.

Similarly Cr-N and Sm-N transition temperature also show falling tendency as series was ascended.

In case of Series B, the transition temperature of the compounds are given in Table-17. In this series, ethoxy to n-octadecyloxy derivatives exhibit an enantiotropic nematic mesophase as in Series-A except n-pentyloxy and n-dodecyloxy derivatives display monotropic nematic mesophase. The Smectic-A (Sm-A) mesophase commences from the n-heptyloxy derivative and persist up to the last member of the homologous series except dodecyl derivative shows monotropic Sm-A mesophase. In this series, B\(_{12}\) compound is fully monotropic in nature.

The plot of transition temperature versus the number of carbon atoms in the alkoxy chain (Figure-15-b) exhibits falling tendency in Cr-N, N-I, Sm-N and Cr-Sm transition temperatures, and no odd-even effect could be seen in these types of transition temperatures.

The transition temperatures of Series -MC & -MD are recorded in Table-18 and 19. And a plot of corresponding transition temperatures against the number of carbon atoms in the alkoxy chain given in Figure-16 (a & b). In case of Series MC, seven homologues are synthesized, but only two MC\(_{16}\) and MC\(_{18}\) exhibit schlieren
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texture of nematic phase. It shows a steady fall in temperature towards isotropic transitions. Similarly, seven homologues of MD are also synthesized. Compound MD\textsubscript{10}, MD\textsubscript{16} and MD\textsubscript{18} exhibit threaded texture of nematic phase.

DSC is a valuable method for the detection of phase transitions. It gives quantitative results; therefore, we may draw conclusions concerning the nature of the phases that occur during the enthalpy of two derivatives of Series-A and –B are reported in Table-20 which helps to further confirm the mesophase. Table-20 shows the phase transition temperatures, the associated enthalpy (ΔH) and the molar entropy (ΔS) for compounds of Series-A (A\textsubscript{8} and A\textsubscript{16}) and Series-B (B\textsubscript{8} and B\textsubscript{16}). Enthalpy values of the various transitions agree well with the existing related literature values [63].

The representative compounds of Series-A and Series-B are shown in Figure-17 (a & b) and 18 (a & b). Monotropic transition temperatures values are almost similar to DSC data.

At one end the polar group is changed i.e. for Series-A having –Cl , Series-B having –NO\textsubscript{2} and the alkoxy chain length of 6-alkoxy-2-naphtoic acid is varied. It has been observed that in Series-B compounds the transition temperature is higher than that of the Series-A compounds. This may be attributed to the –NO\textsubscript{2} group is more polar giving (higher stability) and higher temperatures than that of–Cl group.

In metal complexes Series MC & MD also show a steady fall in the temperature towards isotropic transition. Infect, in present case, metal mesogens never give exact isotropic temperature. The DSC thermogram of MC\textsubscript{18} and MD\textsubscript{18} are shown in Figure-19 (a & b). The transition temperature data obtained from POM and DSC are almost same and these data are shown in Table-20 and their textures obtained from POM are shown in Figure-20.

We have heated beyond melting of the substance till we observed different phases. To obtain isotropic temperature, the compound would be heated above 300°C, at this temperature compound may decomposed. So, we never go beyond 300°C.
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