The present chapter comprises two sections:

**Section-I** comprises the details about techniques used for characterization.

**Section-II** deals with the synthesis of 5-chloromethyl-8-hydroxyquinoline and various derivatives of 2,2’-(arylanizediyl)diethanol based on reported method.

### SECTION-I

#### 2.1 Techniques used for characterization of bis-ligands and their coordination polymers

2.1.1 *Elemental analyses*

The majority of ligands and polymers are composed of a relatively small number of elements. The most important ones are: carbon, hydrogen, oxygen, nitrogen, iodine, chlorine, etc.

Elementary quantitative organic analysis is used to determine the content of carbon, hydrogen, nitrogen and other elements in the molecule of an organic compound.

**Experimental:**

C, H, N analyses of all the samples were carried out on Perkin Elmer 2400 C-H-S-O analyzer series II.

2.1.2 *Spectrometry*

Fundamental to modern techniques of structure determination is the field of spectroscopy, the study of the interaction of matter and light (or other electromagnetic radiations). Spectroscopy has been immensely important to many areas of chemistry and physics. For example, much of what is known about orbitals and bonding comes from spectroscopy. But spectroscopy is also important to the organic chemist because it can be used to determine unknown molecular structures. Although this presentation of spectroscopy will focus
largely on its applications, some fundamentals of spectroscopic theory must be considered first.

### 2.1.3 Infrared Spectroscopy

Infrared spectroscopic technique is of an immense importance to organic chemists for the identification of the presence of functional groups in the organic compounds although it does not provide the complete information regarding the molecular structure of the organic compounds. However it is used for the identification of the compounds.

Infrared spectroscopic technique gives the information about the molecular vibrations or more precisely on the transitions between rotational and vibration energy levels in the molecule and due to this characteristic; it is of immense help to organic chemists.

When infrared light is passed through a sample, some of the frequencies are absorbed while other frequencies are transmitted through the sample. The absorption of infrared radiation results in increasing the energy of vibration or rotation associated with covalent bond in a molecule.

Absorption of radiation in the infrared region results in the excitation of bond deformations, either stretching or bending. Various stretching and bending vibrations occur at certain quantized frequencies. When infrared light of that frequency is incident or impart on to the molecule, energy is absorbed and the amplitude of that vibration is increased.

"An infrared spectrum is obtained when the frequency of molecular vibrations corresponds to the frequency of the infrared radiations absorbed."

The material under study is usually in the form of a solid, a neat liquid or a solution. However, a compound in the gas or vapor phase is studied. Under these conditions, in addition to changes in vibrational energy, simultaneous changes in rotational energy can occur and consequently some fine structures may be observed on the
vibrational band. Infrared spectrum of a compound represents its energy absorption pattern in the infrared region and is obtained by plotting percentage absorbance or transmittance of infrared radiation as a function of wavelength or wave number over a particular range.

Infrared spectroscopy is usually divided into three regions.

a) Near infrared (overtone region) – between 14290cm\(^{-1}\) - 4000cm\(^{-1}\)

b) Middle infrared (fundamental vibrational region) – between 4000cm\(^{-1}\) - 400 cm\(^{-1}\)

c) Far infrared (pure rotational region) – between 700cm\(^{-1}\) - 200cm\(^{-1}\)

The normal or middle infrared region is particularly meant for organic chemists since the vibrations induced in organic molecules are absorbed in this region. This fundamental vibrational region is divided into the functional group region (4000cm\(^{-1}\)-1500cm\(^{-1}\)) and fingerprint region (1500cm\(^{-1}\)-600cm\(^{-1}\)). The normal and far infrared regions contain absorptions due to fundamental harmonic and combination bands.

The use of linear-in-frequency instruments results in a considerable expansion of the high frequency end of the infrared region, resulting in an increased ability to resolve bands and define their positions. The position of absorption in the spectrum is usually expressed in terms of wave number (cm\(^{-1}\)) of the absorbed light.

The infrared spectrum is the simplest, most rapid and often most reliable means for assigning a compound to its class. It can also provide a variety of information on structure, symmetry, purity, geometrical isomers and hydrogen bonding.

**Experimental:**

The IR spectra of all samples were recorded in KBr pellets using a Perkin Elmer spectrum 100 FT-IR.
2.1.4 Proton Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is supplementary technique to IR spectroscopy to get details information about structure of organic compounds. Most widely studied nucleus is proton (^1H) and hence the technique is called proton magnetic resonance (PMR) spectroscopy.

IR spectra give information about the functional group while PMR spectra provide information about the exact nature of proton and its environment. Thus this technique is more useful in the elucidation of an organic compound. IR spectra of isomers may appear same but their PMR spectra will markedly differ.

The phenomenon of nuclear magnetic resonance was first reported independently in 1946 by two groups of physicists: Block, Hansen and Packard at Stanford University detected a signal from the protons of water and Purcell, Torrey and Pound at Harvard University observed a signal from the protons in paraffin wax. Block and Purcell were jointly awarded the Nobel Prize for physics in 1952 for this discovery. Since that time, the advances in NMR techniques leading to wide spread applications in various branches of science resulted in the Nobel Prize in chemistry in 1991. The applications of NMR in clinical, solid state and biophysical sciences are really marvelous.

The proton magnetic resonance (PMR) spectroscopy is the most important technique used for the characterization of organic compounds. It gives information about the different kinds of protons in the molecule. In other words it tells one about different kinds of environments of the hydrogen atoms in the molecule. PMR also gives information about the number of protons of each type and the ratio of different types of protons in the molecule.

It is well known that all nuclei carry a positive charge. In some nuclei this charge 'spins' on the nuclear axis and circulation of nuclear charge generates a magnetic dipole along the axis. Thus, the nucleus behaves like a tiny bar magnet. The angular momentum of the spinning charge is described in terms of spin number (I). The
magnitude of generated dipole is expressed in terms of nuclear magnetic moment (\(\mu\)).

The spinning nucleus of a hydrogen atom (\(^1\text{H}\) or proton) is the simplest and is commonly encountered in organic compounds. The hydrogen nucleus has a magnetic moment, \(\mu = 2.79268\) and its spin number (\(I\)) is \(\pm \frac{1}{2}\). Hence, in an applied external magnetic field, its magnetic moment may have two possible orientations.

The orientations in which the magnetic moment is aligned with the applied magnetic field is more stable (lower energy) than in which the magnetic moment is aligned against the field (high energy). The energy required for flipping the proton from its lower energy alignment to the higher energy alignment depends upon the difference in energy (\(\Delta E\)) between the two states and is equal to \(h\nu\) (\(\Delta E = h\nu\))

In principle, the substance could be placed in a magnetic field of constant strength and then the spectrum can be obtained in the same way as an infrared or an ultraviolet spectrum by passing radiation of steadily changing frequency through the substance and observing the frequency at which radiation is absorbed. In practice, it has been found to be more convenient to keep the radiation frequency constant and vary the strength of the magnetic field. At some value of the field strength the energy required to flip the proton matches the energy of the radiation, absorption occurs and a signal is obtained. Such a spectrum is called a nuclear magnetic resonance (NMR) spectrum.

Two types of NMR spectrometers are commonly encountered. They are:

a) Continuous wave (CW) NMR spectrometer

b) Fourier transforms (FT) NMR spectrometer.

The CW-NMR spectrometer detects the resonance frequencies of nuclei in a sample placed in a magnetic field by sweeping the frequency of RF radiation through a given range and directly recording the intensity of absorption as a function of frequency. The spectrum is usually recorded and plotted simultaneously with a recorder synchronized to the frequency of the RF source.
In FT-NMR spectroscopy, the sample is subjected to a high power short duration pulse of RF radiation. This pulse of radiation contains a broad band of frequencies and causes all the spin-active nuclei to resonate all at once at their Larmor frequencies. Immediately following the pulse, the sample radiates a signal called free induction decay (FID), which is modulated by all the frequencies of the nuclei excited by the pulse. The signal detected as the nuclei return to equilibrium (intensity as a function of time) is recorded, digitized and stored as an array of numbers in a computer. Fourier transformation of the data affords a conventional (intensity as a function of frequency) representation of the spectrum.

The first step in running NMR spectrum is the complete dissociation of a requisite amount of the sample in the appropriate volume of a suitable NMR solvent. Commonly used solvents are: CCl₄, deuterated chloroform, deuterated DMSO, deuterated methanol, deuterium water, deuterated benzene, deuterated trifluoracetic acid, etc.

TMS is generally employed as internal standard for measuring the position of ¹H, ¹³C, ¹⁵N, ¹⁹F and ²⁹Si in the NMR spectrum because it gives a single sharp peak, is chemically inert and miscible with a large range of solvents, being a highly volatile can be easily removed if the sample has to be recovered, does not involve in an intramolecular association with the sample.

**Interpretation of the PMR Spectra**

It is not possible to prescribe a set of rules which is applicable on all occasions. The amount of additional information available will most probably determine the amount of information it is necessary to obtain from the PMR spectrum. However, the following general procedure will form a useful initial approach to the interpretation of most spectra.

a) By making table of the chemical shifts of all the groups of absorptions in the spectrum. In some cases it will not be
possible to decide whether a particular group of absorptions arises from separate sets of nuclei, or from a part of one complex multiplet. In such cases it is probably best to initially include them under one group and to note the spread of chemical shift values.

b) By measuring and recording the heights of the integration steps corresponding to each group of absorptions. With overlapping groups of protons it may not be possible to measure these exactly, in which case a range should be noted. Work out possible proton ratios for the range of heights measured then dividing by the lowest height and multiplying as appropriate to give integral values.

c) By noting any obvious splitting of the absorptions in the table (e.g., doublet, triplet, etc.). For spectra which appear to show first-order splitting, the coupling constants of each multiples should be determined by measuring the separation between adjacent peaks in the multiplet. Any other recognizable patterns which are not first order should be noted.

d) By noting any additional information such as the effect of shaking with D₂O, use of shift reagent, etc.

e) By considering both the relative intensities and the multiplicities of the absorptions in determining which groups of protons are coupled together. The magnitude of the coupling constant may give indication of the nature of the proton involved.

f) By relating the information obtained to the other information available on the compound under consideration.

**Experimental:**

¹H-NMR spectra of all samples were recorded on Bruker Avance 400 spectrometer, operating at 400 MHz.
2.1.5 $^{13}$C NMR and DEPT Spectroscopy

Besides the PMR spectroscopy, the CMR spectroscopy is now more précised method to determine the structure or organic molecules. Considerably greater sensitivity is required for $^{13}$C than for $^1$H due to low natural abundance of $^{13}$C and the lower magnetic moment compared to that of the proton. However, greater resolution is possible with $^{13}$C.

In contrast to $^1$H spectra, it is not possible to determine the relative ratio of carbon atoms in a compound by integration of the peak areas in the $^{13}$C FT-NMR spectrum. There are two reasons for this. The first reason is the different relaxation times of carbon atoms in different environments. This means that some atoms with long relaxation times may still be partly saturated when the next pulse of radiation is received and the resulting absorption peak areas will not be proportional to the number of different carbon atoms. Carbon atoms without hydrogen attached have longer relaxation times and are therefore likely to give rise to peaks of lower intensity in the spectrum. The second reason is due to the Nuclear Overhauser Effect (NOE). This is the enhancement of some signals in the $^{13}$C spectrum as a result of the spin-decoupling process which is used to produce the normal, noise-decoupled spectrum by removing the interaction between carbon and hydrogen nuclei. The NOE is not the same for all nuclei. The maximum effect is for carbon atoms with hydrogen attached. The consequence is that carbon atoms without hydrogen attached appear without any NOE enhancement. As a result of these two effects, it is often possible to identify by inspection, as a result of their lower intensity, those peaks in the $^{13}$C spectrum which result from carbon atoms not attached to hydrogen, including those in aromatic rings which carry a substituent.

A considerable amount of the data is available which correlates the position of absorptions in the $^{13}$C NMR spectrum with the structure of an organic molecule, and it is these imperial correlations which provide the main basis for the use of the technique in structure
determination. The values for the chemical shifts are normally related to the tetramethylsilane carbon absorption, with positive values increasing to lower field (corresponding to the δ scale in PMR spectroscopy). The vast majority of absorptions fall in a range of 0-200 ppm between the carbonyl absorptions at low field and the methyl absorptions at high field.

Hybridization of the carbon atom has a significant effect on the chemical shifts, $sp^3$-hybridized carbon absorbs at high field (0-60 ppm downfield from TMS), $sp^2$ – carbon at low field (80-200 ppm) and $sp$-carbon at intermediate values. The precise position of absorption of a particular atom is largely determined by the electronic effects of any substituent, and the fact that these are approximately additive enables fairly accurate predictions of chemical shifts to be made, provided that similar compounds of known structure are available for reference purposes.

Only one of the three items of information normally available from PMR spectra (i.e. chemical shift, coupling constant and relative numbers of absorbing nuclei) is routinely available from the $^{13}$C spectrum and that is the chemical shift. Quantitative coupling constants are not normally obtained and relative numbers of nuclei cannot usually be derived from measurement of peak areas. The large $^{13}$C - $^1$H coupling constant (125-200 Hz for directly bonded protons) results in multiples which overlap to a considerable extent, and in the absence of decoupling makes the spectrum difficult to analyze. Spectra are therefore normally spin-decoupled and each absorption appears as a sharp singlet; this technique is known as wide-band or noise decoupling. Although the sensitivity is thus increased, all the information normally available from spin-spin splitting pattern is lost. An alternative method of decoupling (off resonance decoupling) does however allow coupling of directly bonded carbon and hydrogen to be observed, although the separation of the peaks of the multiplets produced by this method is not equal to the true $^{13}$C - $^1$H coupling constant. It is thus possible to identify carbon atoms associated with
methyl, methylene and methine groups since the absorptions appear as quartets, triplets and doublets respectively provided that the bonded hydrogen are equivalent.

DEPT (distortionless enhancement by polarization transfer) is a very useful method for determining the presence of primary, secondary and tertiary carbon atoms. The DEPT experiment differentiates between \(-\text{CH}, -\text{CH}_2, -\text{CH}_3\) groups by variation of the selection angle parameter.

a) 45° angle gives all carbons with attached protons (regardless of number) in phase.
b) 90° angle gives only CH groups, other being suppressed.
c) 135° angle gives all CH and CH\(_3\) in a phase opposite to CH\(_2\) signals from quaternary carbons and other carbons with no attached protons are always absent (due to the lack of attached protons).

The polarization transfer from \(^1\text{H}\) and \(^{13}\text{C}\) has the secondary advantage of increasing the sensitivity over the normal \(^{13}\text{C}\) (which has a modest enhancement from the NOE (Nuclear Overhouse effect) due to the \(^1\text{H}\) decoupling).

**Experimental:**

\(^1\text{H}\)-NMR spectra of all the samples were recorded on Bruker Avance 400 spectrometer, operating at 100 MHz.

The chemical shift is recorded in δ value using TMS as an internal standard in D\(_6\)-DMSO.

**2.1.6 Thermogravimetric analysis of coordination polymers**

Thermogravimetric analysis of polymer is a very useful technique in assessing the thermal stability of polymers. The methods usually employed are differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivatographic analysis\(^5\)\(^-\)\(^6\) for comparative study of thermal behavior of related polymer samples, each sample is analyzed by any
one or more of these methods of analysis under identical experimental conditions. For example TGA is carried out in air and in oxygen free nitrogen. It is carried out at different heating rates. It may be noted that the results of a thermal analysis of a given polymer sample by a given method depends on various aspects. It is also possible to know the temperature at which the material starts decomposing. It is possible to know whether the decomposition occurs in one or more stages.

Besides the quantitative information derived on more inspection of the thermogram, other information about the order of the degradation reaction and energy of activation of the degradation reaction can be obtained by the analysis of the thermal data furnished by either DTA or TGA. Using the TGA following can be done.

**Decomposition of metal salts and coordination polymers:** In this study we can know the amount of byproducts and intermediates, final product and the composition of the material.

**Analysis of mixture:** The studies show the difference between the behaviors of substances on heating and if those behaviors are significantly different on temperature scale, the individual reactions of substances may be identified and measured. The moisture content, total volatile content, metal content, organic matter content and ash content may be measured in coal, soil and natural material analysis.

**Oxidation studies:** The study concern with oxidation of organic compounds, oxidation of metal, alloy and their compounds.

**Reduction studies:** TGA measures continuously the composition of hydrogen during reaction, has given many useful data on catalyst preparation and allowed the detection of overlapping reactions and the study of kinetics. With the help of TGA of polymer blends, fuel additives and drugs; we can know their thermal properties and we can improve the properties.

The thermogravimetric analysis (TGA) of samples has been carried out on “Universal V2.6D TA Instruments” in slow stream of air. The boat prepared from platinum foil holds the polymer sample for
analysis. This was properly washed and dried. It was then suspended on a quartz rod in the TGA balance. The powdered sample (about 5mg) was placed in the boat. The sample in the boat was covered by a quartz tube in which the flow of air was maintained. The weight of sample was noted on the TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on the quartz rod. The experiment was started by heating the system at a constant rate of 10°C/min. simultaneously; change in the weight was recorded automatically with time/temperature. This will reveal percentage weight loss of the material as a function of time and also temperature. The experiment was stopped at about 750°C when there was no further decrease in weight. The thermograms were analyzed to obtain information about the percentage weight loss at different temperatures.

**Experimental and method of calculation of activation energy**

Broido method\(^{19}\) was used to calculated activation energy (Ea) as follows where on heating a polymeric substance, it undergoes pyrolysis. It is assumed that the pyrolysed products are volatile. Continuous weighing of the sample with time follows the progress of the reaction. It is reasonable to assume that the weight of the material at a time “t” is related to the fraction (y) of the number of initial molecules not yet decomposed by the equation (2.1).

\[ Y = \frac{N}{N_0} = \frac{W_1 - W_r}{W_0 - W_r} \]  

Where, \( W_1 \) is the weight when the reaction is completed.

For pyrolysis at a given temperature, the reaction rate is given by

\[ \frac{dy}{dt} = -ky^n \]  

Where, \( n \) is the order of the pyrolysis reaction.

The rate constant \( k \) changes with the absolute temperature according to the Arrhenius equation.

\[ k = Ae^{-\frac{E_a}{RT}} \]

From (2.2) and (2.3) it follows,

\[ \frac{dy}{y^n} = -kdt = -Ae^{-\frac{E_a}{RT}}dt \]

Where, A= Proportionality constntsnt, Ea= Energy of activation.
If, instead of operating the reaction isothermally, the reaction is operated at increasing temperature, and if temperature $T$ is a linear function of time $t$, then,

$$T = t_0 + ut \quad \text{.................................................... (2.5)}$$

$$dT = U \cdot dt \quad \text{..................................................... (2.6)}$$

From (2.4) and (2.6) it follows,

$$\frac{dy}{y^n} = -\frac{(A/U)e^{\frac{E_a}{RT}}dt}{\text{........................................ (2.7)}}$$

Integrating the equation (2.7) from $t_0$ to $t$ and $y$ to $1$.

$$\int_{y}^{1} \frac{dy}{y^n} = \int_{y}^{1} \frac{dy}{y} = -\ln y = \ln \frac{1}{y} \quad \text{........................................ (2.9)}$$

Conversely, the integration of right hand side (R.H.S.) of equation (2.6) is not that simple. However, Vallet$^{20}$, in a monograph published in 1961 reported values of integration of terms like those involved in equation (2.8). From this data, the values of integration of the L.H.S. were obtained by Broido$^{19}$.

Van Krevelen and his co-workers$^{21}$ revealed that almost the entire measurable reaction usually occurs within ± 10% of $T_m$, the temperature of maximum reaction rate, and they applied certain approximations and obtained the following relation.

$$\ln (\ln \frac{1}{y}) = 2.303\left(\frac{E_a}{RT_m} + 1\right) \ln T + \text{const} \quad \text{................. (2.10)}$$

According to this relation (2.10), a plot of $\log (\ln1/y)$ vs $\ln T$ would be linear and their slope is related to the activation energy.

Horowitz and Metzger$^{22}$ introduced two alternate approximations and developed relation (2.11) and (2.12).

$$\log (\ln1/y) = 2.303 \left(\frac{E_a}{RT_m^2}\right) T + \text{const} \quad \text{............... (2.11)}$$

$$= -2.303\left(\frac{E_a}{R}\right) \frac{1}{T} + \text{const} \quad \text{............... (2.12)}$$
The expression (2.12) has been found to be most accurate of all the three equations, (2.10), (2.11), (2.12). The last numbered relation is employed here to correlate the experimental data of the all coordination polymer samples. The estimated values of activation energy (Ea) for all the polymer samples are discussed in chapter 4.

**Experimental:**

TG/DTG was obtained by a model 5000/2960 SDT, TA Instruments, USA. The experiments were performed in an N$_2$ atmosphere at a heating rate of 10$^{\circ}$C min$^{-1}$ in the temperature range 50-800$^{\circ}$C, using an Al$_2$O$_3$ crucible.

**2.1.7 U. V. visible Spectroscopy**

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in which fluorescence deals with transition from the excited state to the ground state, while absorption measures transition from the ground state to the excited state$^{23}$.

Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water soluble compounds or ethanol for organic soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound.
Experimental:

U. V. Visible Spectra of the ligands were recorded on Shimadzu 160A UV-visible spectrophotometer using DMF as the solvent blank.

2.1.8 **Electronic spectral analysis and magnetic measurement**

Reflectance spectroscopy deals with the measurements of absorption of energy when electrons are promoted to higher energy level from ground energy level, this electron transitions is occurred when electromagnetic radiation of the proper energy is provided. The structural information related to molecule such as different transitions, geometries, forces and nature are obtained from the electronic spectrum studied. The physical and chemical behavior such as conformational analysis, configurationally correlation, electromagnetic and electrochemical of system has been suitably interpreted by bonding theories\(^{24}\).

The d-orbitals of an isolated transition metal ion are degenerate. However, the electrostatic crystal field theory predicts that complex formation will partially remove the d-orbital degeneracy, so transition within the d-levels become possible. For structures in which there is an inversion center, d-d transition are forbidden by the laporte rule\(^{25}\) and can occur only because of transitory loss of the inversion center via molecular vibrations. Consequently d-d transitions are invariably weak (\(\varepsilon < 200\)), they generally occur in the visible or near infrared regions and are responsible for the colors of many complexes. The d-d absorptions are commonly referred to as ligands field bands. Charge transfer absorption bands nearly always occur at higher energies than d-d transitions and are frequently found in the blue or ultraviolet regions.

A colored compound owe their color to the presence of no more unsaturated groups responsible for electronic absorption, the group is called as chromophores; an oxochrome represents a saturated group containing unshared electron which when attached to a chromophore changes both the intensity as well as the wavelength of the absorption maximum. Shift of an absorption maximum to a longer wavelength is
called bathochromic or red shift, while a shift of absorption maximum to a shorter wavelength is called as hypsochromic or blue shift. The effect of leading to increased absorption intensity is known as hyperchromic effect and vice versa is known as hypochromic effect.

The magneto chemistry reveals the magnetic properties of material; it shows whether the material will be attracted or repelled by magnet. In this study there are several methodologies such as nuclear spin, electron spin, electron orbital motion; which are useful to generate magnetic fields in material. The raised magnetic fields interact with external magnetic field and each other. The interaction may vary from material to material. NMR and ESR are the spectroscopy used for measurements of interaction with nuclear spins.

Gouy’s method for the measurements of magnetic susceptibility has been used in present study. In this methodology sample is hanged between external applied magnetic field, the force exerted by sample have been measured by weighing technique on digital electronic balance.

The measurement of magnetic susceptibility has been done at 298 K using gouy balance (Citizen balance, Japan). The Gouy tube was calibrated using mercury tetrathiocynate cobaltate(II)-Hg[Co(CNS)₄] (xₙ = 16.44 × 10⁻⁶ c.g.s. units at 298 K). The samples were weighed in presence and absence of applied magnetic field (4 amp and 6 amp), the µₑffective and xₙ were calculated using difference in weight according to reported calculations²⁶. The molar susceptibility is obtained by multiplying the gram susceptibility xₙ by the molecular weight of complexes. Pascal’s constant was used to apply diamagnetic corrections and corrected molar susceptibility x’m have been obtained²⁷-²⁸. The effective magnetic moment µₑffective was calculated according to following equation:

$$\mu_{\text{effective}} = 2.84 \left( x'_{m} \times T \right)^{\frac{1}{2}}$$

where T is absolute temperature in K.

**Experimental:**

Electronic spectra of the samples were recorded on Shimadzu 160A UV-visible spectrophotometer using DMF as the solvent blank.
SECTION – II

2.2 Synthesis and characterization of 5-chloromethyl-8-quinolinol (CMQ)

5-Chloromethyl-8-quinolinol (CMQ) was prepared by chloromethylation of 8-hydroxyquinoline (oxine) according to the method reported in literature\textsuperscript{29-30}. The detail of the procedure is given below.

In a 250 mL three necked round bottom flask, a stream of hydrogen chloride gas was blown through a solution of 8-hydroxyquinoline (0.1mol) and formaldehyde (20 mL, 37%) in 37% hydrochloric acid (50 mL) for 8 hours at 50°C under stirring. After filtration, the product was washed with 37% hydrochloric acid and dried to afford CMQ in 85% yield. The preparation of 5-chloromethyl-8-hydroxyquinoline (CMQ) is shown in scheme 2.1.

Scheme 2.1 Preparation of 5-chloromethyl-8-hydroxyquinoline (CMQ)

The complete analysis of CMQ is presented in Table 2.1. The respective spectral figures are shown in Figs. 2.1 to 2.3.
Table 2.1 Characterization of CMQ

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Formula</td>
<td>C_{10}H_{8}NOCl</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>193.62 gram/mole</td>
</tr>
<tr>
<td>Melting Point</td>
<td>280°C (Uncorrected)</td>
</tr>
<tr>
<td>Yield</td>
<td>62%</td>
</tr>
<tr>
<td>Elemental analysis:</td>
<td>%C</td>
</tr>
<tr>
<td>Calculated</td>
<td>62.03</td>
</tr>
<tr>
<td>Found</td>
<td>62.00</td>
</tr>
<tr>
<td>$^1$H NMR (400 MHz, DMSO-$d_6$) $\delta_H$ (ppm):</td>
<td>4.67 (2H, singlet, CH$_2$), 7.11(dd, 1H), 7.44-7.68(m, 3H), 8.84(dd, 1H), 9.82(1H, broad singlet, OH, D$_2$O exchangeable).</td>
</tr>
<tr>
<td>$^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta_c$ (ppm):</td>
<td>43.35(-CH$_2$-), 115.82(CH), 124.44(CH), 128.80(C), 129.05(CH), 132.76(C), 135.15(CH), 139.25(C), 148.72(CH), 153.26(C).</td>
</tr>
<tr>
<td>DEPT-135</td>
<td>43.37(-CH$_2$-), 115.80, 124.45, 129.05, 135.14, 148.72</td>
</tr>
</tbody>
</table>

Fig. 2.1 The $^1$H NMR spectrum of 5-chloromethyl-8-hydroxyquinoline
Fig. 2.2 The $^{13}$C NMR spectrum of 5-chloromethyl-8-hydroxyquinoline

Fig. 2.3 The DEPT-135 spectrum of 5-chloromethyl-8-hydroxyquinoline
2.3 Synthesis and characterization of various 2, 2’-(arylazanediyl) diethanol

The various derivatives of 2,2’-(arylazanediyl) diethanol were derived by the condensation reaction of aniline and 2-chloroethanol in presence of calcium carbonate.31.

2.3.1 Experimental

The synthesis and characterization of various 2,2’-(arylazanediyl) diethanols are summarized in this section.

2.3.2 Materials

All the chemicals used were of analytical grade. The organic solvents were purified by standard methods32. The compounds aniline was purchased from E. Merck Ltd (India). Various aniline derivatives (1a-h) are listed in Table 2.2.

Table 2.2 Aniline derivatives (1a-h) used for the formation of 2,2’-(arylazanediyl) diethanol

<table>
<thead>
<tr>
<th>No.</th>
<th>Aniline derivatives</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Aniline</td>
<td>(\text{NH}_2)</td>
</tr>
<tr>
<td>1b</td>
<td>3-Chloro aniline</td>
<td>(\text{NH}_2) Cl</td>
</tr>
<tr>
<td>1c</td>
<td>4-Methyl aniline</td>
<td>(\text{H}_3\text{C}) (\text{NH}_2)</td>
</tr>
<tr>
<td>1d</td>
<td>N-(3-aminophenyl) acetamide</td>
<td>(\text{H}_3\text{COCHN}) (\text{NH}_2)</td>
</tr>
</tbody>
</table>
2.3.3 General process for preparation of 2,2’ -(arylazanediyl) diethanol

A mixture of aniline derivative (Table 2.1) (4.5 ml, 48.6 mmol) and 2-chloroethanol (14.3 ml, 196 mmol) was added to a suspension of calcium carbonate (10.0 g in 250.0 ml of water). The turbid mixture was refluxed for 24h with stirring and additional 2-chloroethanol and calcium carbonate were added in two equivalent portions over the following 48 h. The reaction mixture was cooled, pH adjusted to pH 7 with sodium hydroxide solution (10%) and extracted with ethyl acetate (4 x 200.0 ml). The combined organic layer was dried and solvent removed under reduced pressure to get product by reported method\textsuperscript{31}. All the derivatives were designated as (2a-h).
Where \( R = H, \)

- 3-Cl,
- 4-CH\(_3\),
- 3-NHCOCH\(_3\),
- 2-OCH\(_3\), 5-NHCOCH\(_3\),
- 3-NO\(_2\),
- 4-COCH\(_3\),
- 2-COCH\(_3\), 5-CH\(_3\).

**Scheme 2.2** Preparations of 2,2'-(arylanediyli) diethanols from various aniline derivatives

The elemental analysis of all the \((2a-h)\) derivatives are summarized in the Table 2.3. Typical spectra of compound 2a are shown in Figs. 2.4 to 2.6.
Table 2.3 Characterization of various derivatives of 2,2’-(arylazanediyl) diethanol

<table>
<thead>
<tr>
<th>No.</th>
<th>2,2’-(arylazanediyl) diethanol derivatives</th>
<th>b.p(°C)</th>
<th>Elemental analysis</th>
</tr>
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<tr>
<td>2a</td>
<td>2,2’-(phenyl azanediyl) diethanol</td>
<td>178</td>
<td>%C       %H       %N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated : 66.27</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Found :     66.25</td>
</tr>
<tr>
<td>2b</td>
<td>2,2’-((3-chlorophenyl) azanediyl) diethanol</td>
<td>179</td>
<td>%C       %H       %N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated : 55.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found :     55.70</td>
</tr>
<tr>
<td>2c</td>
<td>2,2’-(p-tolylazanediyl) diethanol</td>
<td>176</td>
<td>%C       %H       %N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated : 67.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found :     67.65</td>
</tr>
<tr>
<td>2d</td>
<td>N-(3-(bis(2-hydroxyethyl) amino) phenyl) acetamide</td>
<td>178</td>
<td>%C       %H       %N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated : 60.49</td>
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<tr>
<td></td>
<td></td>
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<tr>
<td>2e</td>
<td>N-(3-(bis(2-hydroxyethyl) amino)-4-methoxyphenyl) acetamide</td>
<td>175</td>
<td>%C       %H       %N</td>
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<td></td>
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<tr>
<td>2f</td>
<td>2,2’-((3-nitrophenyl) azanediyl) diethanol</td>
<td>179</td>
<td>%C       %H       %N</td>
</tr>
<tr>
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<td>Calculated : 53.09</td>
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<tr>
<td>2g</td>
<td>1-(4-(bis(2-hydroxyethyl) amino)phenyl) ethanone</td>
<td>176</td>
<td>%C       %H       %N</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Calculated : 64.55</td>
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<td></td>
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<td>Found :     64.56</td>
</tr>
<tr>
<td>2h</td>
<td>1-(2-(bis(2-hydroxyethyl) amino)-4-methylphenyl) ethanone</td>
<td>177</td>
<td>%C       %H       %N</td>
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<tr>
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</table>
Fig. 2.4 The $^1$H NMR spectrum of 2,2'- (phenylazanediyl) diethanol (2a)

Fig. 2.5 The $^{13}$C NMR spectrum of 2,2'-(phenylazanediyl) diethanol (2a)
**Fig. 2.6** The DEPT-135 spectrum of 2,2'- (phenylazanediyl) diethanol (2a)
References


