A SPECTROSCOPIC STUDY OF THE ELECTRONIC EFFECTS ON COPPER(II) AND COPPER(I) COMPLEXES OF LIGANDS DERIVED FROM VARIOUS SUBSTITUTED BENZYALDEHYDE- AND CINNAMALDEHYDE-BASED SCHIFF BASES

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By

Nomampondo Penelope Magwa

ABSTRACT

Several Schiff base ligands, N, N'-(aryl)benzyaldiimine ligands (R-BEN); N, N'-(aryl)benzyaldiamine dihydrochloride ligands (R-BENH•2HCl); N, N'-(aryl)benzyaldiamine ligands (R-BENH); N, N'-*bis*(cinnamaldiimine) ligands (R-CA_2EN) were synthesized for the investigation of the electronic effect of the substituents at para-position of the Schiff base ligands and their copper complexes.

The synthesis of Schiff bases was carried out by reacting a series of para-substituted benzyaldehyde, and para-substituted cinnamaldehyde with ethylenediamine. The imine group of Schiff bases, N, N'-(aryl)benzyaldiimine ligands and N, N'-*bis*(cinnamaldiimine) ligands were reduced to corresponding amines with sodium borohydride in methanol.

These ligands, N, N'-(aryl)benzyaldiamine ligands (H-BENH), N, N'-*bis*(cinnamaldiimine) ligands (CA_2EN) were reacted with copper(II) dihalide and copper(I) monohalide ions respectively to form complexes. The ligands and their complexes were analysed using elemental analyses, FT-IR spectroscopy (mid-IR), UV/vis in aprotic and protic solvents, while mass spectrometry, ^{1}H-NMR and ^{13}C-NMR were used to further analyse the ligands.

By using substituent parameters, both the single and dual substituent parameters with the spectroscopic data obtained from the spectroscopic techiques mentioned above, it was hoped to monitor and determine whether the electronic effects (resonance or inductive effcets) was predominantly within the Schiff base ligands and copper complexes.

The NMR studies with dual substituent parameters suggest that the effects of the substituents are transimitted through the ligands, *via* resonance effects and that the phenyl group is non-planar with the azomethine in N, N'-(aryl)benzyaldiimine ligands. The presence of an extra

double bond in Schiff base {(N, N'-*bis*(cinnamaldiimine) ligand)} altered the electron density.

The UV/vis studies showed that the symmetry of the N, N'-*bis*(4-R-benzyl)-1, 2-diaminoethanedihalidecopper(II) complexes were predominantly tetrahedral for both chloro and bromo complexes. The correlation studies from mid-infrared were beneficial in monitoring the effect experienced by N, N'-(aryl)benzaldiimine ligands, the studies suggest that the inductive effect is more pronounced at the νC=N.

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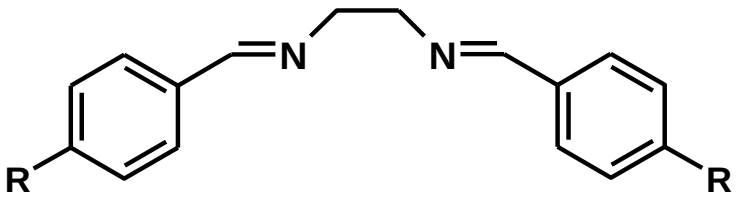
CONTENTS

LIST OF ABBRIVIATIONS

Abs	absorbance
APCI	atmospheric pressure chemical ionization mass spectrometry
BEN	N, N'-*bis*(benzyl)-1, 2-diiminoethane
CA_2EN	N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane
CH_3CN	acetonitrile
$CHCl_3$	chloroform
cm^{-1}	wavenumber
^{13}C-NMR	carbon nuclear magnetic resonance
DCM	dichloromethane
DSP	dual substituent parameters
ESI	electrospray mass spectrometry
EtOH	ethanol
ε	molar extinction coefficient
g.c.i	grating change in the instrument
^{1}H-NMR	proton nuclear magnetic resonance
IR	infrared
I	intensity
kK	kiloKayser
MS	mass spectrometry
mmol	millimole
mid-IR	mid-infrared
nm	nanometres
ppm	part per million
ρ	reaction constant
R	generalized substituent
r	correlation coefficient
SSP	single substituent parametrs
UV/vis	ultrviolet visible spectroscopy

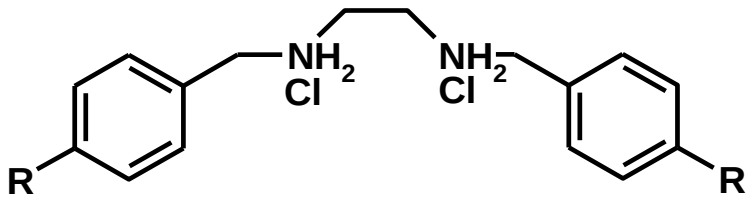
LIST OF FORMULAE AND ABBREVIATIONS OF LIGANDS AND COMPLEXES APPEARING IN THE TEXT.



N, N'-(aryl)benzaldiimine ligands

R = NO_2;	N, N'- *bis*(4-nitrobenzyl)-1, 2-diiminoethane	(NO_2-BEN)
R = Cl;	N, N'- *bis*(4-chlorobenzyl)-1, 2-diiminoethane	(Cl-BEN)
R = Br;	N, N'- *bis*(4-bromobenzyl)-1, 2-diiminoethane	(Br-BEN)
R = H;	N, N'- *bis*(benzyl)-1, 2-diiminoethane	(H-BEN)
R = CH_3	N, N'- *bis*(4-methylbenzyl)-1, 2-diiminoethane	(CH_3-BEN)
R = OCH_3;	N, N'- *bis*(4-methoxybenzyl)-1, 2-diiminoethane	(OCH_3-BEN)
R = $N(CH_3)_2$;	N, N'- *bis*(4-dimethylaminobenzyl)-1, 2-diiminoethane	{($N(CH_3)_2$-BEN)}

General abbreviation: (R-BEN)



N, N'-(aryl)benzaldiamine dihydrochloride salts

R = NO_2; N, N'-*bis*(4-nitrobenzyl)-1, 2-diaminoethane dihydrochloride (NO_2-BENH•2HCl)

R = Cl; N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethane dihydrochloride (Cl-BENH•2HCl)

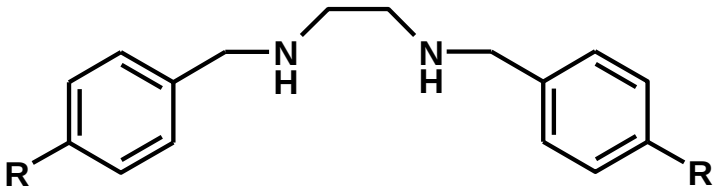
R = Br; N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane dihydrochloride (Br-BENH•2HCl)

R = H; N, N'-*bis*(benzyl)-1, 2-diaminoethane dihydrochloride (H-BENH•2HCl)

R = CH_3; N, N'- *bis* (4-methylbenzyl)-1, 2-diaminoethane dihydrochloride (CH_3-BENH•2HCl)

R = OCH_3; N, N'- *bis*(4-methoxybenzyl)-1, 2-diaminoethane dihydrochloride (OCH_3-BENH•2HCl)

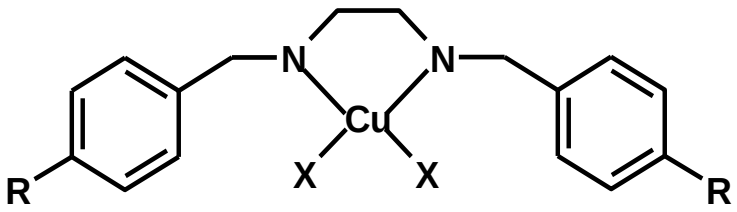
General abbreviation: (R-BENH•2HCl)



N, N'-(aryl)benzaldiamine ligands

R	=	NO_2;	N, N'-*bis*(4-nitrobenzyl)-1, 2-diaminoethane	(NO_2-BENH)
R	=	Cl;	N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethane	(Cl-BENH)
R	=	Br;	N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane	(Br-BENH)
R	=	H;	N, N'-*bis*(benzyl)-1, 2-diaminoethane	(H-BENH)
R	=	CH_3;	N, N'-*bis*(4-methylbenzyl)-1, 2-diaminoethane	(CH_3-BENH)
R	=	OCH_3;	N, N'-*bis*(4-methoxybenzyl)-1, 2-diaminoethane	(OCH_3-BENH)

General abbreviation: (R-BENH)



X = Br

R = NO_2; N, N'-*bis*(4-nitrobenzyl)-1, 2-diaminoethanedibromocopper(II)

Cu(II)(NO_2-BENH)Br_2

R = Cl; N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethanedibromocopper(II)

Cu(II)(Cl-BENH)Br_2

R = Br; N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethanedibromocopper(II)

Cu(II)(Br-BENH)Br_2

R = H; N, N'-*bis*(benzyl)-1, 2-diaminoethanedibromocopper(II)

Cu(II)(H-BENH)Br_2

R = CH_3; N, N'-*bis*(4-methylbenzyl)-1, 2-diaminoethanedibromocopper(II)

Cu(II)(CH_3-BENH)Br_2

R = OCH_3; N, N'-*bis*(4-methoxybenzyl)-1, 2-diaminoethanedibromocopper(II)

Cu(II)(OCH_3-BENH)Br_2

General abbreviation: Cu(R-BENH)Br_2

X = Cl

R = NO_2; N, N'-*bis*(4-nitrobenzyl)-1, 2-diaminoethanedichlorocopper(II)

$Cu(NO_2\text{-}BENH)Cl_2$

R = Cl; N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethanedichlorocopper(II)

$Cu(Cl\text{-}BENH)Cl_2$

R = Br; N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethanedichlorocopper(II)

$Cu(Br\text{-}BENH)Cl_2$

R = H; N, N'-*bis*(benzyl)-1, 2-diaminoethanedichlorocopper(II)

$Cu(H\text{-}BENH)Cl_2$

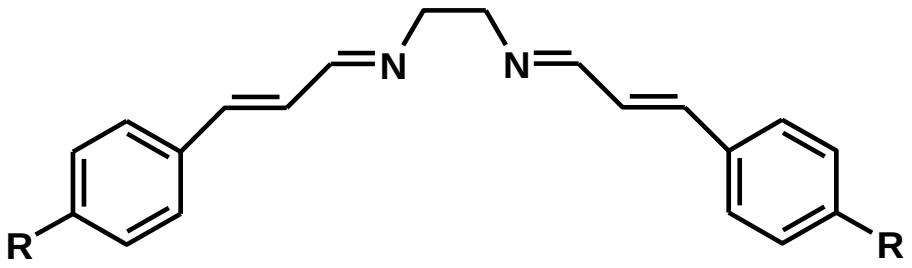
R = CH_3; N, N'-*bis*(4-methylbenzyl)-1, 2-diaminoethanedichlorocopper(II)

$Cu(CH_3\text{-}BENH)Cl_2$

R = OCH_3; N, N'-*bis*(4-methoxybenzyl)-1, 2-diaminoethanedichlorocopper(II)

$Cu(OCH_3\text{-}BENH)Cl_2$

General abbreviation: $Cu(R\text{-}BENH)Cl_2$



N, N'-*bis*(cinnamaldiimine) ligands

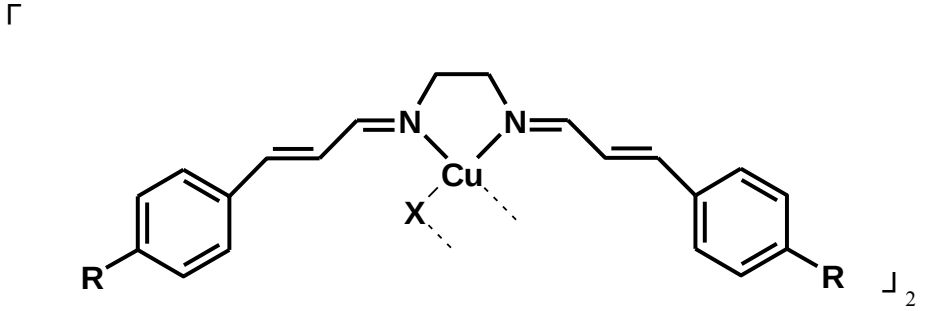
R=H; N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane

CA_2EN

$R=N(CH_3)_2$; N, N'-*bis*(4-dimethylaminocinnamaldehyde)-1, 2-diiminoethane

$N(CH_3)_2$-CA_2EN

General abbreviation: R-CA_2EN



R = H, X = Br; N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane copper(I)bromo

$[Cu(CA_2EN)Br]_2$

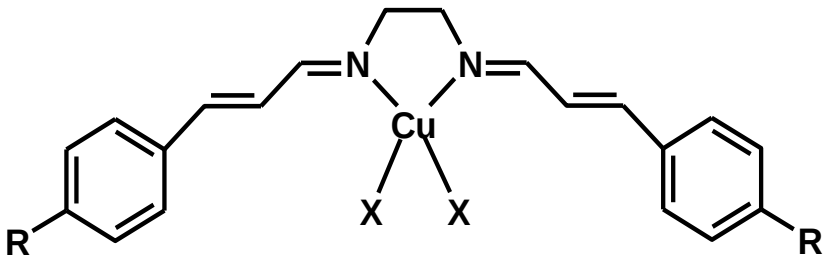
R = H, X = Cl; N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane copper(I)chloro

$[Cu(CA_2EN)Cl]_2$

R = H, X = I; N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane copper(I)iodo

$[Cu(CA_2EN)I]_2$

General abbreviation: $[Cu(CA_2EN)X]_2$



R = H, X = Br; N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethanedibromocopper(II)

R = H, X = Cl; N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethanedichlorocopper(II)

General abbreviation: $[Cu(CA_2EN)X_2]$

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1. INTRODUCTION

This study is concerned with the synthesis, characterization and the investigation of the transmission of electronic effects of substituents in Schiff bases and their copper(II) halide complexes, for structural elucidation of the compounds. Accordingly, this chapter covers a brief overview of Schiff bases and their amine ligands with respect to this work, a literature review of Schiff bases, amine ligands and their copper(II) or copper(I) complexes that are relevant to this study. More information will be given later when discussing the substituent parameters with respect to spectroscopic properties.

1.1 Schiff bases

1.1.1 Background

A Schiff base is a neutral molecule with an electron pair and contains a carbon-nitrogen double bond. This class of compound was discovered in 1864 by Hugo Schiff, when he reacted an aldehyde and amine, leading to a Schiff base [1]. The compound, an azomethine was named after him in reference to the condensation reaction products he obtained.

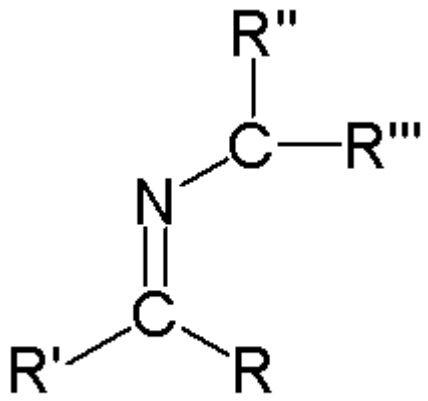


Figure 1.1 The representative structure of Schiff base

Schiff bases are classified according to the number of electrons that the molecule has or to the type of atoms or donor atom groups that the molecule contains. The donor atom can be nitrogen, oxygen, phosphorous or a sulphur. It is these donor atoms that stabilize the structure of Schiff base ligands and that determine the ligand's bioactivity. In the nitrogen compound the presence of a –C=N- group in Schiff bases enhances bioactivity [2-3], and most of the nitrogen donor ligand complexes have been used as precursors in different homogeneous catalytic reactions [4-7].

Schiff base ligands are capable of stabilizing many different metals in various oxidation states to form complexes using their lone paired electrons. The complex formation occurs through coordination of the metal via the azomethine nitrogen. Schiff base ligands have played an integral role in the development of coordination chemistry since the late nineteenth century. In fact, most of Schiff base ligands require a metal ion for activity [8].

1.1.2 Applications and properties of Schiff bases

Schiff bases are part of very popular class of compounds in coordination chemistry, particulary in bioinorganic chemistry. They are easily formed and easily broken; their synthesis is a reversible acid catalyzed reaction. These materials are considered special due to their facile synthesis and the flexible skeleton structure that makes it possible to access diverse structural modification by introducing different substituents.

Schiff bases have played an important role in the development of the chemical industry and biochemistry owing to their applications and their biological activities and they played a major role in organic synthesis.

Generally Schiff bases are well known due to their applications as intermediates in the synthesis of medicinal products such as aminoalkylpyridine [9-11] and hydrozone [12]. Schiff bases derivered from primary amine and substituted benzaldehyde are known to have antibacterial [2, 13-14], antitumor [15-16], anticonvulsant [17] and anti-HIV [18] activities. In addition to

their biological properties Schiff bases play other biological roles [19], for example in vision, in determining the flexibility of the wall of the veins.

These compounds are not only important intermediates in the synthesis of medicinal products. Schiff bases of pyrazolone have played a crucial role in the petrochemical industry [20] and they are useful reagents for the extraction and separation of various metal ions [21].

In industry the imines, Retinyl Schiff base salts (ATRSBS) are known to have similar properties to rhodopsin, and they have been used in the military industry as anti-radar shield for aircraft [22]. Rhodopsin (visual purple or light sensitive protein) is a chemical substance that is found in the retina at the back of the eye and it belong to the G-protein receptor family and it appears as redish-purple. The diagram of rhodopsin is given in figure 1.2. This chemical molecule, rhodopsin is very sensitive to photons of light and it transforms the absorbed light (green-blue light) into an image signal, in which these signals are transferred to the brain. This process allows the rhodopsin to go through conformational change, from *cis* to *trans*-conformation as shown in figure 1.3.

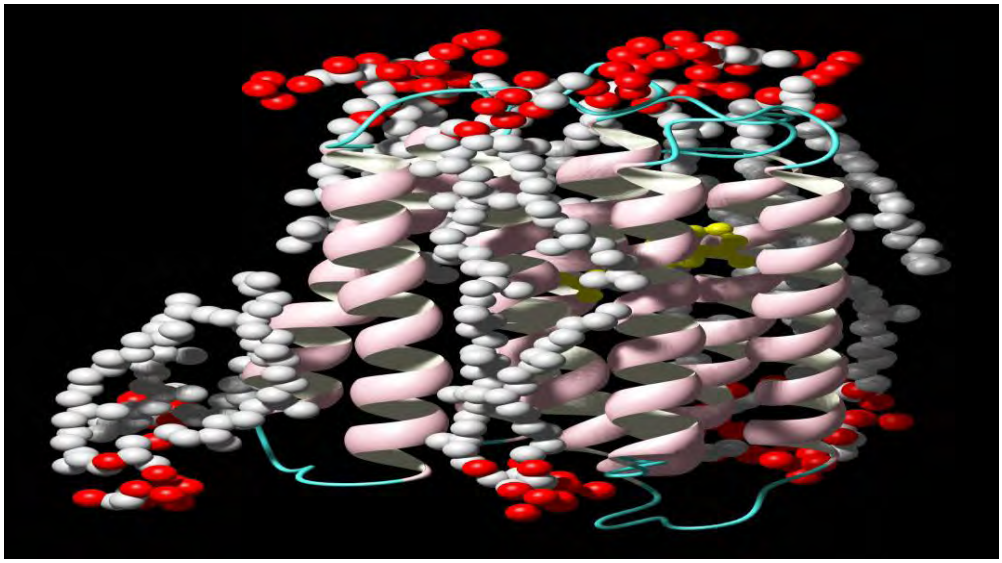


Figure 1.2 The sensory rhodopsin embedded in a lipid bilayer. Red and purple ribbons represent rhodopsin, white ribbon represents fluid lipid bilayer

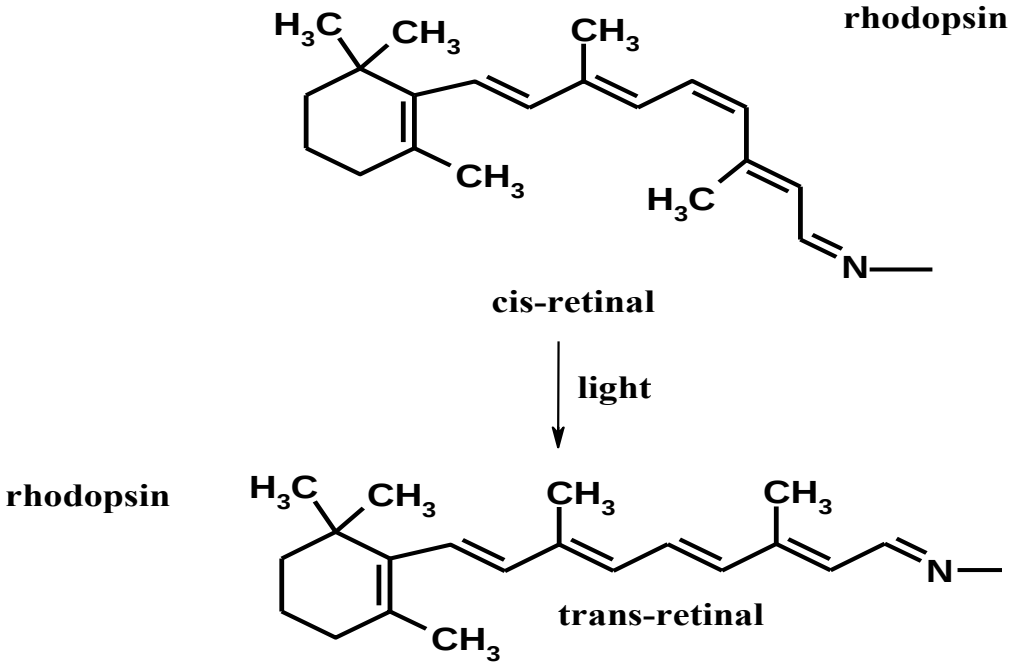


Figure 1.3 Cis and trans conformation of rhodospin

Biological studies of the Schiff bases of the structural formula of ligand, N, N'-*bis*(benzyl)ethylenediimine and their analogous unconjugated diimine has not been covered comprehensively previously [23]. This may largely be attributed due to the instability of their coordination compounds with most transitional metals, as the result of the hydrolysis of the ligand upon complexation. It has been observed that these Schiff base complexes hydrolised in the presence of copper(II) giving mixed products [24].

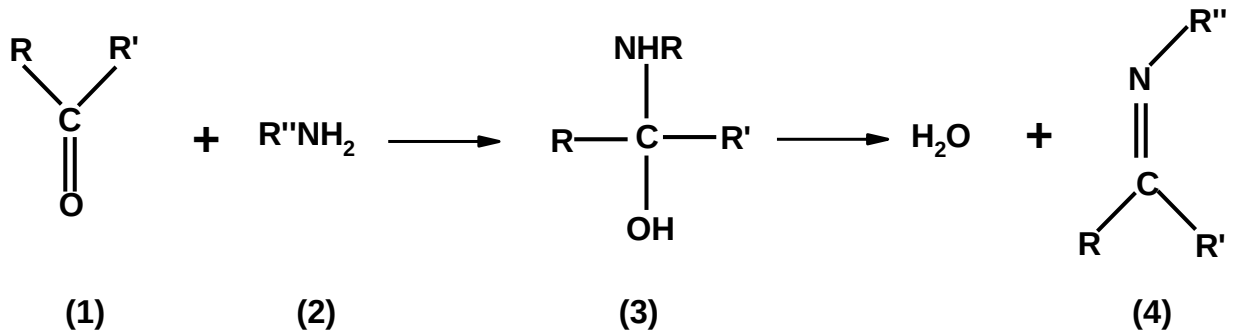
However, Schiff base N, N'-*bis*(benzyl)ethylenediimine have been used as anticorrosion inhibitors of zinc in sulphuric acid [25-26] and in hydrochloric acid [27]. In addition to their applications these materials have also been used as modulators of structural and electronic properties of transition metal centre for nickel metal [27]. In electrochemistry their nickel complexes have been exploited as a catalyst in the detection of organochlorinated pollutants [28]. In addition to the properties mentioned above, Schiff bases have been investigated for their interesting electronic and structural features.

Salicylidene type Schiff bases (or 2-hydroxybenzaldimine compounds) exhibit thermochromic or photochromic properties. They have been used as modulators of both structural and electronic properties of the transition metal centre, because of their ability to bind with metal ions. The stability of the complexes is enhanced by chelation due to the presence of the o-hydroxyl groups.

1.1.3 Synthesis of Schiff bases

Schiff bases are often referred to as imines, azomethines or anils. They are indicated structurally as RR′C=NR″. The nature of the R groups bonded to the nitrogen or to the carbon atom are limited to alkyl or aryl substitutents, because these imines rapidly decompose or polymerize if a hydrogen atom is attached to the imino (C=N) carbon or nitrogen atom.

The most common method for the preparation of Schiff base is the reaction of an aldehyde and ketone with primary amines. It involves a condensation reaction between the carbonyl compound (1) and the primary amine (2). The condensation product, the Schiff base (4) is known to be formed by way of nucleophilic attack by the primary amine on the carbonyl carbon, to yield first a tetrahedral carbinolamine intermediate known [28] as a hemiaminol (3). This intermediate is very unstable, which is followed by elimination of water to generate the imine functional group characteristic of the Schiff base.



Scheme 1.1 Synthesis of a Schiff base from carbonyl compound with primary amine

It has been reported that the nature of the carbonyl compounds as well as that of the amines determines the position of the equilibrium and the reaction mechanism. For example, tertiary aliphatic and aromatic aldehydes react readily with amines to give the corresponding imines even at room temperature [29]. Aromatic aldehydes are so reactive that the product is formed even without the removal of the water formed during the reaction [1]. Para-substituted benzaldehyde with electron-donating groups decrease the reaction rate, while the reverse is true for similar para-substituted anilines [29]. In contrast, aliphatic ketones react with amines more slowly than aldehydes to form imines; the reaction requires a higher reaction temperature and longer reaction time. If the ketone is sterically hindered the reaction becomes slower than an unhindered ketone [30].

Normally the condensation reaction is acid catalyzed but this role may be often be taken by a metal ion. In this case the imine product is isolated as the metal complex. The product, a Schiff base metal complex, is obtained directly by the reaction between the metal ion, the aldehyde and the amine. The choice of metal ion is crucial in this method, because if there is a strong interaction between the primary amine and the metal ion, it may hinder or prevent the amine from engaging in nucleophilic attack at the carbonyl carbon atom. For example Ni(II) is a good choice for the synthesis of a ligand having a planar tetradentate mode of binding, rather than synthesis of a ligand having pentagonal or hexagonal planar donor atoms [31].

Schiff bases can also be synthesised through a reaction of nitriles with organometallic compounds. Moureau and Mignonac [32] were the first to obtain imine (ketimine), using an alkyl Grignard, aryl cyanide at 15 ^{o}C, treated with hydrogen chloride and with ammonia.

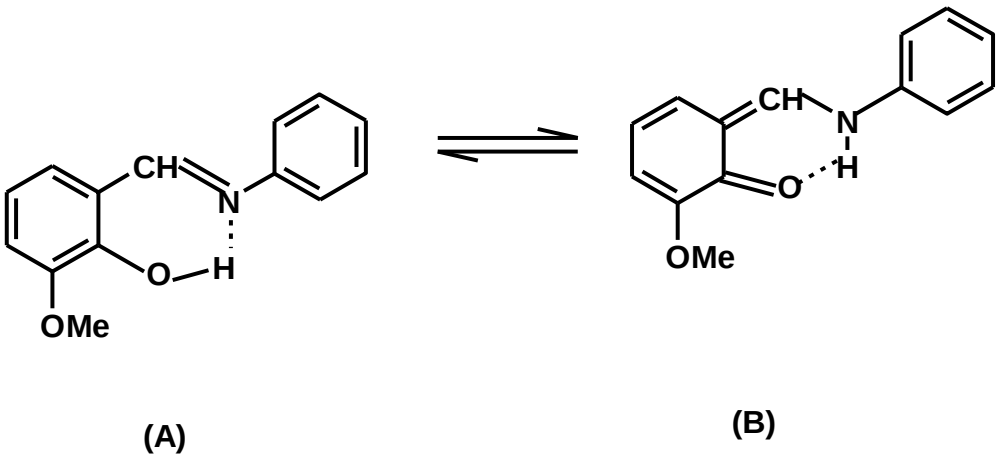
1.1.4 Spectroscopic properties

The most characteristic group frequency of Schiff bases employed in literature is νC=N. The infrared spectra of imines shows that the C=N stretching frequency absorbs in the region between 1680 and 1603 cm^{-1} when H, alkyl or phenyl groups are bonded to carbon and nitrogen atoms [33]. The region where the C=N stretch absorbs is guided by a number of

factors, the nature of the substituent groups and the physical state of the compound. In a conjugated system on the carbon and nitrogen atoms for the compound of the type $R_2C=NR$ the C=N bond absorbs at the lower wavenumber (1631-1613 cm^{-1}), while the unconjugated system absorbs at higher wavenumbers (1657-1631 cm^{-1}) [32]. The presence of a substituent in the phenyl ring such as halogen is known to decrease the conjugation which raises the absorption to a frequency range of 1656-1631 cm^{-1} [34].

Extensive studies on the Schiff bases have been done using electronic spectroscopy [35-38]. Ultraviolet and visible spectrophotometry has been used for the analysis of the chromophore of Schiff bases. The characterization of Schiff base compounds depends on the chromophores of the molecules. For compounds containing an unconjugated chromophore these groups are characterized by bands due to $n \rightarrow \pi^*$ transitions in the range 234-272 nm, while the conjugated chromophores, such as those with an alkene group, cause a strong band in the range 180-250 nm due to $\pi \rightarrow \pi^*$ transitions. The $n \rightarrow \pi^*$ transitions are very weak absorptions which can be covered (or masked) by $\pi \rightarrow \pi^*$ transitions.

It has been reported that the electronic spectra of Schiff base compounds derived from 2-hydroxybenzaldimine compounds are solvent dependent. The electronic spectra of these materials have been studied in both polar and non-polar solvents [39-44]. It has been observed that a band above 400 nm, which is associated with a tautomerization effect, is more intense in polar solvents and in acidic media, while it disappears in non-polar solvents [39-44]. This tautomerisation involves a formal migration of a hydrogen atom or proton, accompanied by a switch of a single bond and adjacent double bond, as shown in scheme 1.1. The tautomer equilibrium is widely observed in Schiff bases derived from 2-hydroxynaphthaldehyde and aniline, while in Schiff bases derived from salicylaldehyde and aniline the band at > 400nm is only observed in acidic media. For the Schiff base, N, N'-*bis*(benzyl)ethylenediimine and its analogues the tautomerisation is not expected.



(A) (B)

Scheme 1.2 Enol and keto tautomers

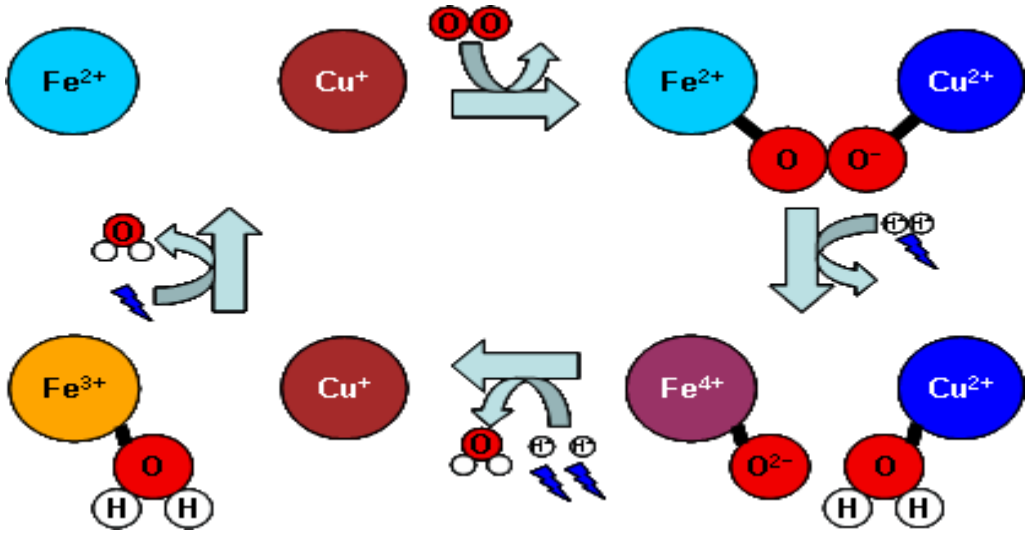
Nuclear magnetic resonance spectroscopy has been used to investigate the chemistry of Schiff bases in solution, this includes the study of intramolecular hydrogen bonding in Schiff bases [45] and the electronic effects produce by the substituents in substituted Schiff bases [46-48]. Schiff base ligands in solution may have two types of intramolecular hydrogen bonds, namely phenol-imine or keto-amine (N-H---O or N---H-O) and the predominance of both types depending on the conditions and have been confirmed by NMR [45].

Furthermore NMR chemical shifts are sensitive probes of electron-density distributions and have been found useful for the study of the transmission of electronic effects in organic molecules. The ^{1}H- and ^{13}C-NMR spectra of these materials have been reported and their data fit the Hammett relationship. The Hammett relationship is based on the principles of linear free energy relationships (LFER) [46-48].

1.2 Copper

Copper is a trace metal which is found in many foods such as liver and shellfish. And it is one of the six metals that are essential in living organisms [49]. In blood plasma copper is part of a number of key proteins, including many vital enzymes. The function [50] of copper in biological systems is primarily in redox reactions associated with the reduction of oxygen to water, meaning the transfer of oxygen to a substrate. This involves the abstraction of the dangerous by-product, such as the superoxide ion, through oxygenation reactions in the system (or blood plasma) and which results in the removal of highly reactive superoxide anion as shown in scheme 1.3.

The superoxide ion is the anion O_2^- and it is the product of the one-electron reduction of dioxygen, which occurs widely in nature. In living organisms the superoxide ion is a toxic oxygen species that has a high energy. It is formed through uncontrolled autoxidation of low-potential cytochromes, iron-sulphur proteins and flavoproteins, as well as by the decomposition of complexes such as oxyhaemoglobin and it is capable of forming hydrogen peroxide or oxygen either through reduction or oxidation. It is widely deployed by the immune system to kill invading microorganisms [51].



Scheme 1.3 Biological conversion of dioxygen species into water

The production of superoxide is quiet dangerous and it can induce the bacteriostatic action of milk xanthine oxidase and it is implicated in bacteriocidal activity of granular leucocytes.[49]

For the functions mentioned above, copper is tightly bound to enzymes (copper-containg proteins) such as phenolase, or hemocyanin {(Cu(I))} and ceruloplasmin in blood plasma. These enzymes regulate the level of oxygen and normalises the metabolic process [49].

In addition to the biological functions of the copper binding components, the enzymes control the transportation of copper in the human body, the intake and excretion of copper around the human body. This manages the level of copper and is essential in controlling disease caused by copper deficiency such as Menkes [52] and Wilson's [53] diseases.

Copper salts (e.g. $CuCl_2$) have been found to be very useful in prevention of fungal growth and killing algae [54]. On the other hand an excess concentration of copper can be dangerous, causing a number of toxic cellular effects.

The element copper has the electronic configuration (argon) $4s^2 3d^9$ and it has one *s* electron outside a completed *d* shell. Copper occurs in different oxidation states and this yields a variety of coordination compounds. The oxidation states include copper(0) in the metal, copper(I) in cuprous compounds, copper(II) in cupric compounds and the copper(III) and (IV) oxidation states. Copper(I) and copper(II) are the most common oxidation states but Cu(II) is the most stable state and is the more prolific in the formation of complexes and in the formation of good crystals [55-57]. The copper(I) oxidation state is obtained from the loss of the single s electron in the outermost shell and its chemistry is very much less extensive than that of copper(II) [55,56,58-60]. In addition to the properties of the copper(I) ion, the metal ion is very unstable in aqueous solution. This is the result of the disproportion process. The disproportion process of the copper(I) ion involves the exchange of electrons with one another to form copper(0) and copper(II) within the solution medium. While the (III) oxidation state occurs by extensive oxidation of Cu(II).

It is worthy to mention that the copper(III) ion is known to be much less electropositive; this means that the possibility to react by loss of electron is relatively smaller than copper(II), that is why Cu(II) is more stable than the rest of other oxidation states.

1.2.1 The copper(II) ion

Copper(II) ion is a borderline hard acid, it is stabilized by complex formation, and nitrogen is the best donor to copper(II) ion, while fluoride is known to be the best halide ligand towards the formation of copper(II) complex. The copper(II) ion is best known in four-coordinate square planar, tetrahedral, five-coordinate square pyramidal or five-coordinate trigonal bipyramidal and six-coordination octahedral stereochemistries and it is one of the transitional metal(II) cations that undergo a variety of distortions such as Jahn Teller distortion [61].

The distortion of geometries in copper(II) ion complexes is most common in a tetrahedral and in an octahedral environment. The distortion is due to the splitting of the d orbitals of the metal ion into energy levels of certain magnitude in order to remove degeneracy and it can be explained through the Jahn-Teller theorem [56].

The distorted geometry is influenced by a variety of contributions such as the coordination number of the ligands, the size and nature of the ligand coordinated to the metal centre and they determine the value of 10Dq. For example oxygen and nitrogen are larger donor atoms and they are capable of forming a short distance bond, that is between 1.9-2.1 Å. Halide ligands such as Cl^- and Br^- result in intermediate and long distance bonds which lie between 2.29-2.45 Å.

1.2.2 Electronic properties of the copper(II) ion

Complexes of copper(II) ion are generally blue or green [57, 59, 62]. The origin of the colour is due to the maximum of up to four electronic transitions: d-d transitions; charge transfer transitions (both metal to ligand and ligand to metal); internal ligand transitions. These electronic transitions occur between the ground state and the excited states of the crystal field levels, and are observed within the range 4.0-30.0 kK (kK = 1000 cm^{-1}). In this range the electronic transitions described above, plus combination and overtone vibrations of ligands occur [63].

The pure d-d transitions in copper(II) complexes tend to occur below 20 kK and their spectra most commonly show only a single broad band (half-width *ca.* 5000 cm^{-1}), while the charge transfer and internal ligand transitions are observed above 20-30 kK and the combination and overtone vibrations of ligands occur below 10 kK.

The d^9 ion is characterized by large distortions making it difficult to use electronic spectroscopy alone as a tool for identification of structure. However there is an enormous body of copper(II) electronic spectra in the literature, where the structure is known but the assignment is less certain.

For example, in regular octahedral copper(II) complexes for the $^2T_{2g} \rightarrow {}^2E_g$ transition, the $t_{2g} - e_g$ separation varies from about 13, 000 cm^{-1} for CuO_6 to about 18, 000 cm^{-1} for CuN_6. But in a tetragonanally distorted octahedral copper(II) complexes several absorption bands may be expected in this region, corresponding to the transitions from components of t_{2g} to dx^2-y^2 and dz^2; this is due to the splitting of the ^2E_g ground terms of an octahedron as the result of Jahn Teller distortion and it results in the overlapping of bands and a slightly more complex spectrum, with the appearance of a low energy shoulder.

For the tetrahedrally coordinated copper(II) complex, distorted square planar geometry is strongly favoured for the d^9 configuration. The distortion of this system lowers the symmetry from T_d to D_{2d} which retains the degeneracy of the d_{xz} and d_{yz}. This leads to three possible transitions, namely from the ground state $^2B_2$ to ^2E, to $^2B_1$ and to $^2A_1$ [64]. But commonly, four transitions may be observed, this reflects further distortion to D_2 symmetry due to the splitting of the E-level in D_{2d} by spin orbit coupling. The distored tetrahedrally square planar coordinated copper(II) ion complexes with the halogen ligands $[CuBr_4]^{2-}$ and $[CuCl_4]^{2-}$ have been studied extensively [65-70], and they exhibit absorptions below 20kK, while tetra-coordination of the copper(II) ion with stronger field ligands such as imines will naturally appear blue shifted. For example the absorption of the distorted tetrahedral CuN_4 chromophore occurs near 7000–8000, 10,000-11,000, 13,000 to 15,000 or even to 16,000 cm^{-1} [71-73] and these spectra are due to transitions within the spin orbital coupling components of ^2D in a D_{2d} field [73].

The spectra of copper(II) ion complexes may be measured in solution [74], as reflectance spectra [75] and as polarized single-crystal spectra [76,77]. In solution spectra accurate extinction coefficient data may be obtained. But with copper(II) complexes there is a high chance of ligand-solvent exchange or the possibility of more than one species in equilibrium, depending on the coordination number. While the reflectance and single-crystal spectra clearly relate to the crystal structure in solid state, neither yields accurate extinction coefficients [76, 77].

To identify the transitions within copper(II) ion complexes is difficult due to the large half-widths of the copper(II) spectra. In many cases the interpretation and resolution for a copper(II) spectrum has been obtained using software such as Gaussian analysis for the solution spectra, while for the solid spectra Kortuum-type analysis has been used [75].

1.3 Metal complexes of Schiff bases

There has been a great interest in the chemistry of metal complexes of Schiff bases with a large body of information confirming biological activities and stereochemistry of metal complexes of Schiff bases. The data resulting from the spectral analysis of these coordination complexes have been used in understanding the structure of the complexes and their various properties [76-79].

The interest in these materials is due to their applications in catalysis for various processes [80-83], in electrochemistry [84-85] and in their biological activities, (eg. some of the metal complexes have anticancer activities) [76].

Recently there has been a huge interest in the chemistry of metal complexes with tetradentate Schiff base ligands containing oxygen and nitrogen donors due to the structural features. The nickel(II) complex of a symmetric tetradentate Schiff base has been investigated because it has shown structural similarities to phthalocyanines, and it has been used as a modifying agent to produce chemically modified electrodes [28].

Coordination compounds of copper(II) ions have presented a great variety of biological activities ranging from suppression of inflammation to antimicrobial activity and other pathological process, including destroying cancel cells [86-87].

It has been observed that some drugs show increased activity when administered as metal complexes rather than as the free organic compounds [8,88]. For example, the antimitotic drug, Taxol is one drug that has a remarkable activity against drug-resistant human ovarian and breast tumours, but the detriments in the application of this drug in cancer chemotherapy are its limited bio-availability and poor water solubility. Test results from the active analogs of taxol, 10-deacetylbaccatinthiosemicarbazone (DABTSC), against human breast cancer cells line MCF-7, show that the compound is highly effective as an anti-proliferative compound when it is administered as copper(II) complex (Cu-DABTSC) [8].

In addition to the outstanding properties of the metal(II) complexes, coordination compounds of copper(I) ion and azomethine compounds have been extensively studied because of their instability and unusual structure features for use in solar energy and catalytic activity in photoredox reactions [89-93].

1.4 Amine ligands and their metal chelates

For years transitional metal complexes of inorganic amines have been extensively studied because of their interesting chemical properties [94], their contribution to chemotherapy and their structural resemblance with natural proteins and enzymes.

The first publication on a clinical application of metal inorganic complexes with an amine ligand, Ciplatin, as chemotherapeutic agent for ovarian cancer is date back in early 1974, by Wiltshaw and Cart [95]. Cisplatin was originally discovered by Michele Peyrone in 1844 [96], and is used as an antitumor agent. It currently is still considered as one of the most successful cancer chemotherapeutics. In addition to its application, Cisplatin is known to be more efficient for the inhibiting of a secondary tumour when is combined with ruthenium drugs [97].

Inorganic amines are compounds that may be synthesized through reduction of the corresponding compound that has the azomethine functional group. The literature is replete with the publications that document the applications of amine. Their applications are very different from those of the Schiff base ligand and they have been utilised in the pharmaceutical industry as an important intermediate for synthesis of leading drugs.

Amine ligands such as polyamine are found in all cells; they regulate and control cancer cellular growth [98-99]. They play an important role in transportation of drugs such as polyamine-drug conjugates to cancer cells [100-103]. Polyamine-drug conjugates, such as bleomycin A5 and peplomycin are clinically employed antitumor agents [104-105] and they have been investigated as an efficient drug-carrier [106].

Because of their basicity and the fact that they posses both lipophilic and hydrophilic moieties, and they have high binding constants for iron metal, amine ligands, and polydentate amines have been used for mobilization and excretion of excess iron in living organisms [94] and for the treatment of iron overload diseases such as Cooley's anaemia [107]. They have also been used to improve the antiarthritic properties of copper [108].

Again the structural feature of the amine group ($N-H_x$) has been found to be very useful as an active site in many leading compounds, such as chloroquine for treatment or prevention of malaria [109-110], nevirapine for the treatment of HIV-1 infection and AIDS [111-112], in pyrazinamide to treat tuberculosis [113]. For the antimalaria compounds such as primaquine and quinacrine it is known that the amine group on the side chain is essential for the effectiveness of the compound, with an amine containing a four carbon atom chain linked to an aromatic ring being a good pharmacophore for anti-malaria agents [114,115].

Furthermore amine ligands that contain the benzylamine group have been widely used as an important intermediate for the synthesis of antitumor drugs [116, 117].

1.4.1 Spectroscopic properties of amine ligands

The characterization of amine ligands using infrared spectroscopy has been found to be a very useful approach for analysis and interpretation of coordination compounds for many years [118-122]. The infrared spectra of amines are characterized by the NH absorption band and the position of the absorption band depends on nature of group attached on the nitrogen atom. The secondary amine exhibits an absorption band due to the N-H stretching vibrational mode near 3420 cm^{-1} and a weak bending absorption at 1500 to 1600 cm^{-1}. An infrared spectrum of a primary amine is characterized by four absorption bands, two NH stretching (both the asymmetric and symmetric stretches), a NH bending and a rock of the NH_2 group. Two of these absorption bands are found in the region 3500 – 3300 cm^{-1} and are due to the asymmetric and symmetric stretches. The third absorption band is due to the NH_2 bending and is observed at 1600 cm^{-1} [123]. The NH rock is found near 800 cm^{-1}.

The presence of a substituent on the amine ligands may shift the absorption frequency. It has been found that electron-withdrawing groups shift absorption bands to higher frequency while electron donating groups shift the absorption band to the lower frequency region [124-126].

The electronic spectra of free aromatic amine ligands is characterized by one electronic transition, $n \rightarrow \sigma^*$ transition. This transition appears in the far ultraviolet region. In most cases this transition may be submerged (or masked) by stronger absorption associated with $\pi \rightarrow \pi^*$ transitions [129].

Studies on free amine ligands using ^{1}H-NMR are of interest, because of the influence of the substituents on the stability and the configuration of these ligands and their complexes. Although the amine ligands are very useful, less attention has been given on the ^{1}H-NMR chemical shifts of the amino group [130-132]. The ^{1}H-NMR spectra of amine ligands exhibit a signal due to the chemical shift of NH hydrogen. The signal appears upfield in chloroform solution and the signal of the NH hydrogen varies depending to the solvent used.

1.5 Substituent constants

For many years, studies in physical organic chemistry have shown that there are quantitative relationships that exist between the structure of the compounds and their reactivity. It is known that before the 1930s, organic chemists were highly dependent on empirical and qualitative rules, rather than on models to understand these relationships. The earliest, successful and intensively investigated model for the study of these relationships are Linear Free Energy Relationships, which are reported first by Brönsted and Pedersen in 1924 [134]. Linear Free Energy Relationships are a concept that uses mathematic equations to relate observations of one system to observations on other similar systems.

Even though this concept was the first empirical model applicable to study the quantitative relationships, it was not widely recognised until January 1937 when the American Chemical Society published a short paper entitled, “The Effect of Structure upon the Reactions of Organic Compounds”, the author was the physical chemist Louis P. Hammett [135].

In the paper, Hammett presented equation 1, which describes the influence of the *meta*- or *para*-substituents on the rate constants or equilibrium constants of the side-chain reactions of benzene derivatives, as determined by the ionization of benzoic acid derivatives.

$$XArCOOH \rightleftharpoons XArCOO^- + H^+$$

$$\log(k / k_0) = \rho\zeta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where symbol k is a rate or equilibrium constant of ionization for a *meta* or *para* substituted benzoic acid, and k_0 is a rate or equilibrium constant of ionization for unsubstituted benzoic acid in water at 25 ^oC; ζ is the Hammett substituent constant that measures the electronic effect of replacing H by a given substituent in the *meta* or *para* position of the benzoic acid, and it also depends solely on the nature and position of substituent. The reaction constant, ρ depends on the nature of the reaction, including conditions such as temperature, and it measures the sensitivity of the reaction to the electronic effects of the substituents [136-139]. The ionization of substituted benzoic acid in water at 25 ^oC was chosen as a standard reaction type for which ρ is fixed at unity while ζ has its value set to zero.

With all these conditions Hammett was able to tabulate positive and negative ζ values. A positive ζ value for a substituent indicates that the substituent withdraws electrons relative to hydrogen; while substituents with negative ζ value repel electrons relative to hydrogen. The Hammett equation is limited only to the *meta* or *para* substituted benzene derivatives, since the *ortho* substituents can give rise to steric interactions which may make the quantitative relationships unreliable. The Hammett ζ values indicate the combination of inductive (field) and mesomeric (resonance) effects produced by the withdrawing or donating substituent.

The Hammett methodology was a success in studying and describing the influence of structure on chemical behaviour, but failed in tabulating ζ values for some substituents that show a strong interaction between the substituent and the reaction site, such as NO_2 or OH. This has led to the reviewing of the Hammett's equation by severally theoreticians. Jaffe [140]

successfully re-examined Hammett's substituent constants, he recalculated ζ values from more recent values of ionization and rate or equilibrium constants obtained for a wide series of reactions. McDaniel and Brown [141] redefined ζ_m and ζ_p values for the ionization of substituted benzoic acids and suggested that these values be used for substituent constants rather than the mean values derived from all available reactions.

Taft and Lewis [142,143] suggested that the resultant polar effects of substitutents on chemical reactivities and physical properties should be quantitatively separated into inductive and resonance effects. Taft's equation is an extension of the Hammett equation, as shown in equation 2.

$$\text{Log}(k / k_0) = \rho_I \zeta_I + \rho_R \zeta_R \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Here the inductive effect, denoted by ζ_I, is assumed to contribute a similar effect for the *meta*- and the *para*-position. The resonance effect is given by ζ_R and the contribution for *meta* is different to that of *para*-position. The ρ_I and ρ_R are the contribution to the reaction constant due to the substituents.

Swain-Lupton [144] and Yukawa-Tsuno [145] proposed assumptions that were closely related to Taft's. Robert and Moreland [146] extended the approach of Hammett in order to evaluate inductive effects in aliphatic, as oppose in aromatic systems.

The Hammett's structure-reactivity parameters and analogous parameters developed by others have been applied extensively to spectroscopy. Correlation analysis in NMR spectroscopy involves the exploration of the interrelationships between NMR data and molecular parameters, such as transmission of electronic effects of substituents in organic molecules. W. F. Reynolds and his workers were the first people to successfully study electronic effects in conjugated aromatic system using both ^{1}H- and ^{13}C-NMR chemical shifts [147,148]. Proton magnetic resonance (PMR or ^{1}H-NMR) has also been used to show

correlation between substituent constants and the PMR chemical shifts of various protons in organic molecules; for example in the ring protons of substituted phenols [149], the amino protons of analines [150], the carboxylic protons of mono substituted benzoic acids [151] and the ring protons of various pyridines [152].

Infrared spectroscopy has been applied to substituted aromatic, heterocyclic and alphatic compounds and correlation made between the frequencies of various ligand vibrations and substituent constants. Correlation analysis studies have shown that there is a linear correlation that exists in the symmetric and asymmetric νN-H of anilines [153] and amines [154], νC=O of aliphatic ketones [155] and νO-H of phenols [156], with substituent parameters ζ or ζ*.

In coordination chemistry correlation analysis has been used to explore the relationships between νM-L and substituent constants ζ or ζ* in metal salicylaldimine complexes [157-159].

1.6 The proposed system of investigation

In an effort to evaluate and identify the electronic effect produced by the substituents within the *para*-substituted Schiff bases and their copper(I)/(II) halide complexes linear correlation analyses were conducted based on Linear Free Energy Relationships. The linear analyses were accomplished by varying the electron donating or withdrawing properties of the substituents and by plotting the experimental spectroscopic data of the *para*-substituted Schiff bases against substituent parameters using *Microsoft Excel*. The experimental data were collected from different spectroscopic techniques including nuclear magnetic resonance, infrared and ultraviolet/visible spectroscopy.

The substituent parameters were chosen in a manner so that overall the electronic effects at *para*-position of the substituted Schiff bases may be monitored. The overall electronic effects of the substituents collectively are composed of both an inductive/field and resonance effect [160, 161]. Inductive effect (I) is an effect that depends only on the nature of the bonds and

the field effect describes a through-space transmission effect, and is denoted by (F).[160] Resonance effects (R), also known as the mesomeric effect, involves the distribution of unshared paired electrons either from or to the substituent [162].

The electronic effects were expressed in numerical form by calculating correlation coefficients and fitting trend lines using Linear Free Energy Relationships principles, and the classical example is the Hammett equation. The equation describes the combination of inductive and resonance effect produced by the substituent in a benzene ring on the equilibrium constant as described in section 1. To further analyse the effects dual substituent parameters were used. Dual substituent parameter relationships are known to be more beneficial than single substituent parameter relationships, because they offer information on both inductive and resonance effects separately and they are the extension of Hammett equation. For this study the Hammett [163-165], Swain [166] and Williams & Norrington [167] substituent parameters were used for the investigation of the electronic effects of substituents on Schiff bases, their amine derivatives and their copper complexes.

Table1.1: Hammett substituent parameters, ζ

R	Hammett substituent parameter, ζ [163-165]
4-NO_2	+0.78
4-Cl	+0.23
4-Br	+0.23
-H	0.00
4-CH_3	-0.17
4-OCH_3	-0.27
4-$N(CH_3)_2$	-0.60

Table 1:2 Values of DSP's for the study

Substituent	Swain [166]		Williams and Norrington [167]	
R	$S\zeta_F$	$S\zeta_R$	$WN\zeta_F$	$WN\zeta_R$
4-NO_2	1.00	1.00	1.109	0.155
4-Cl	0.72	-0.24	0.690	-0.161
4-Br	0.72	-0.24	0.727	-0.176
H	0.00	0.00	0.00	0.00
4-CH_3	-0.01	-0.41	-0.052	-0.141
4-OCH_3	0.54	-1.68	0.413	-0.500
4-$N(CH_3)_2$	0.69	-3.81	0.032	-0.863

The correlation coefficient (r) is a value that provides information on the type of electronic effect produced by the substituent in terms of percentages and it indicates the extent to which the spectroscopic property is influenced by the substituent. It can be equal to or less than one, and can be positive or negative.

The value of r (r =1) implies that a large inductive or resonance effect is more dominating between the substituent and the interaction site or between the substituent and the position of interest within the structure. This also indicates an excellent correlation between substituent parameters and spectroscopic data. A negative correlation (r = -1) indicate a negative correlation between the substituent and the interaction site.

Fitting trend-lines to the resulting data series using *Excel* functions results to a linear plot. The slope of the resultant trend-line is an indication of the extent to which the spectroscopic properties is influenced by the substituent.

1.7 References

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2. EXPERIMENTAL

2.1 Physical methods

2.1.1 Mid infrared spectroscopy (MIR)

The mid infrared spectra were recorded on a Perkin-Elmer spectrum 2000 FT-IR spectrometer equipped with a KBr beam splitter and a DTG detector, in a region 4000 – 400 cm^{-1}, with typically 16 scans at an average resolution of 4 cm^{-1}. Samples were run in a KBr disc.

2.1.2 Nuclear magnetic resonance (NMR)

^{1}H and ^{13}C-NMR spectra were obtained on an Avance Bruker AMX 400 MHz spectrometer. All samples were prepared using deuterated solvents. Chemical shifts are reported in parts per million (ppm) relative to an internal standard tetramethylsilane (TMS).

2.1.3 Mass spectrometry

Mass spectrometry: Finnigan Mat LCQ, was performed by the Rhodes University Mass Spectrometry Unit. Both the Electronspray mass spectrometry and Atmospheric Pressure Chemical Ionization were used for mass analysis of the compounds.

2.1.3.1 Electronspray ionization mass spectrometry (ESI-MS)

The interface parameters for electronspray mass spectrometry were set as follows: sheath gas flow rate, 40 psi, auxiliary gas flow rate, 20 units; capillary temperature, 220 ^{o}C; the solutions of the compounds were directly infused with a 250 μL unimetrics at a flow rate of 8.00 μl/min.

2.1.3.2 Atmospheric pressure chemical ionization mass spectrometry (APCI-MS)

Solutions of the compounds were directly infused with a 250 μL unimetrics at a flow rate of 8.00 μl/min and the interface parameters were set as follows: sheath gas flow rate, 40 psi, auxiliary gas flow rate, 0; capillary temperature, 150 ^{o}C.

2.1.4 Electronic spectra (UV/vis solution)

Electronic spectra were recorded on a Varian Cary 500 spectrophotometer. The spectra for the ligands and the complexes were recorded in solution.

2.1.5 Microanalyses

Combustion microanalyses for carbon, hydrogen and nitrogen were performed on Virio Elementar EL111 CHNS Analyzer, (Rhodes University, South Africa) or were obtained from the University of Cape Town, South Africa, with a Fisons Elemental Analyzer 1108 CHNS-O.

2.1.6 Melting point

All melting points were determined using a Gallenkamp melting point apparatus. The results were uncorrected.

2.1.7 Thin-layer chromatography (TLC)

Thin-layer chromatography was performed on silica gel sheets 60F254 (Merck, Darmstadt). The purity of Schiff bases were confirmed by TLC in a mixture of suitable polar or non-polar solvents. The polar solvents used for separation were ethanol and methanol. Ethyl acetate, and hexane and chloroform were used.

2.2 Reagents and instrumentation

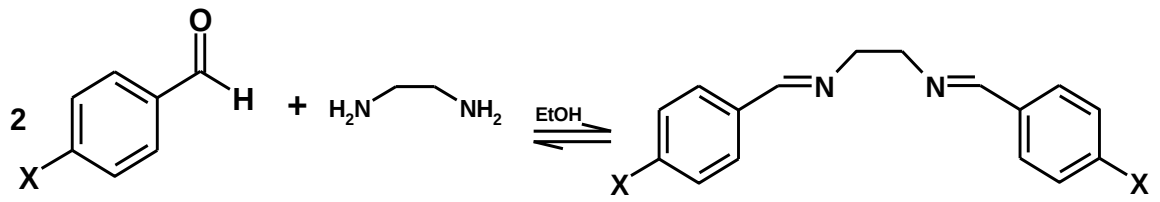
All chemicals and reagents used for the preparation of ligands and complexes were commercial products (Sigma–Aldrich) and used as received unless otherwise noted. Ethylenediamine was distilled over potassium hydroxide under nitrogen and trans-cinnamaldehyde was distilled from anhydrous sodium sulphate before use. The solvents were dried and distilled before use according to the standard procedures [1].

2.3 Synthetic methods

2.3.1 Synthesis of N, N'-(aryl)benzyaldiimine ligands

The Schiff bases were synthesized according to a well-established synthetic procedure [2] which involved the condensation of benzyladehyde or its derivatives with the ethylenediamine in 95 % ethanol, as shown in scheme 2.1. The synthetic scheme in the figure below presents the various Schiff base ligands that were synthesized for the study.

For the synthesis of all the Schiff bases, a 1:2 ratio of amine to aldehyde was used. The Schiff bases were obtained as solid precipitates. Upon recrystallization of the compounds from suitable solvents, clean compounds were obtained and their microanalyses are reported in table 3.1.



No.	1	2	3	4	5	6	7
X	NO_2	Cl	Br	H	OCH_3	CH_3	$N(CH_3)_2$

Scheme 2.1 The *para*-substituted benzylideneethylenediamine ligands (R-BEN) employed in the study

2.3.1.1 Preparation of N, N'-*bis*(4-nitrobenzyl)ethylenediimine

Ethylenediamine (1.4646 g, 24.4 mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of 4-nitrobenzaldehyde (7.3643 g, 48.7 mmol). The mixture was refluxed for 2 hours. The resulting diimine precipitated as a yellow-pink solid. The crude solid was filtered off and washed with ethanol. The Schiff base was then recrystallized from hot ethanol to remove impurities and was left in the fume-hood to evaporate slowly. The product precipitated out as light peach fine crystals. The Schiff base was filtered and washed with cold ethanol (3 x 10 mL). The resulting product was dried at room temperature for 48 hours. The purity was confirmed by TLC in chloroform – ethanol (4: 1). The physical data are reported in table 3.1.

2.3.1.2 Preparation of N, N'-*bis*(4-chlorobenzyl)ethylenediimine

Ethylenediamine (1.5650 g, 26.0 mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of 4-chlorobenzaldehyde (7.320 g, 52.0 mmol). The mixture was refluxed for 2 hours. The resulting diimine precipitated as a white solid. The crude solid was filtered off and washed with methanol. The Schiff base was then recrystallized from hot ethanol to remove impurities and was left in the fume-hood to evaporate slowly. The product precipitated out as shiny white crystals which were collected and washed with cold ethanol

(3 x 10 mL). The shiny white crystals were dried at room temperature for 48 hours. The purity was confirmed by TLC in chloroform – methanol (3:1). The physical data are reported in table 3.1.

2.3.1.3 Preparation of N, N'-*bis*(4-bromobenzyl)ethylenediimine

Ethylenediamine (1.2138g, 20.2mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of 4-bromobenzaldehyde (7.4739 g, 40.4 mmol). The mixture was refluxed for 2 hours. The resulting diimine precipitated as white crystals. The product was filtered off and washed with cold methanol (3 x 10 mL) to remove excess 4-bromobenzaldehyde. The resulting Schiff base was dried at room temperature for 48 hours. The purity was confirmed by TLC in chloroform – methanol (3: 1). The physical data are reported in table 3.1.

2.3.1.4 Preparation of N, N'-*bis*(benzyl)ethylenediimine

Ethylenediamine (2.0170 g, 33.6 mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of benzyaldehyde (7.1248 g, 67.1 mmol). The mixture was refluxed for 20 hours. The volume was reduced using a Rotavapour until yellow oil remained. The resulting diimine was precipitated out by adding hexane in a drop-wise manner with constant stirring. After the addition of about 15 mL hexane, a yellow precipitate formed. The resulting Schiff base was filtered and then recrystallised from hot hexane to remove the impurities and was left in the fume hood to evaporate slowly. The yellow crystals were filtered and dried at room temperature for 48 hours. The purity was confirmed by TLC in ethyl acetate – hexane (4: 1). The physical data are reported in table 3.1.

2.3.1.5 Preparation of N, N'-*bis*(4-methylbenzyl)ethylenediimine

Ethylenediamine (1.8048 g, 30.0 mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of p-methoxybenzaldehyde (7.2169 g, 60.1 mmol). The mixture was refluxed for 2 hours. The resulting diimine precipitated as white crystals. The crude solid was filtered off and washed with methanol. The Schiff base was then recrystallized from hot methanol to remove impurities. The filtrate was left in the fume-hood to evaporate slowly.

The product precipitated out as light yellow crystals which were collected and washed with cold methanol (3 x 10 mL). The light yellow crystals were dried at room temperature for 48 hours. The purity was confirmed by TLC in chloroform – ethanol (4: 1). The physical data are reported in table 3.1.

2.3.1.6 Preparation of N, N'-*bis(*4-methoxybenzyl)ethylenediimine

Ethylenediamine (1.6113 g, 26.8 mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of p-methoxybenzaldehyde (7.301 g, 53.6 mmol). The mixture was refluxed for 2 hours. The resulting diimine precipitated as a yellow solid. The crude solid was filtered off and washed with methanol. The Schiff base was then recrystallized from hot ethanol to remove impurities and was left in the fume-hood to evaporate slowly. The product precipitated out as light yellow crystals which were collected and washed with cold ethanol (3 x 10 mL). The Schiff base was dried at room temperature for 48 hours. The purity was confirmed by TLC in chloroform – methanol (3: 1). The physical data are reported in table 3.1.

2.3.1.7 Preparation of N, N'-*bis*(4-dimethylaminobenzyl)ethylenediimine

Ethylenediamine (1.4818 g, 24.7 mmol) in 20 mL ethanol was added drop-wise to an ethanolic solution of 4-dimethylaminobenzaldehyde (7.3574 g, 49.3 mmol). The mixture was refluxed for 2 hours. The reaction mixture was allowed to cool to room temperature. The resulting diimine precipitated as a yellow solid. The crude solid was filtered off and washed with methanol. The Schiff base was then recrystallized from hot chloroform to remove insoluble impurities and was left in the fume-hood to evaporate slowly. The product precipitated out as a light yellow solid which was collected and washed with anhydrous cold methanol (3 x 10 mL) until the wash was no longer coloured dark red due to the unreacted starting material. The fine light yellow crystals were filtered and dried at room temperature for 48 hours. The purity was confirmed by TLC in ethyl acetate – hexane (4: 1). The physical data are reported in table 3.1.

2.3.1.8 Attempted preparation of N, N'-*bis*(4-dihydroxybenzyl)ethylenediimine

For the preparation of N, N'-*bis*(4-dihydroxybenzyl)ethylenediimine three methods [3-4] were used in an attempt to obtain the Schiff base**.** All three methods were unsuccessful. One problem associated with the synthesis of this Schiff base is that it suffers a degree of hydrolysis. This is because the hydroxyl substituent at the para position of the 4-hydroxybenzaldehyde is more acidic, instead of the formation of iminic bond the hydroxyl substituent acts as acid, in which it breaks the azomethine bond and resulting in the undesired product.

2.3.1.8.1 Method 1

To 7.2783 g (59.6 mmol) of 4-hydroxybenzaldehyde in 10 mL ethanol, was added drop-wise a 15 mL ethanolic solution of ethylenediamine (1.7909 g, 29.8 mmol). To this reaction mixture a quantity of silica (0.1120 g, 1.9 mmol) was added. The mixture was placed under ultrasound irradiation for an hour. The resulting product precipitated as a brown solid. The crude solid was filtered off and washed with ethanol. The product was then recrystallized from hot ethanol to remove impurities and was left in the fume-hood to evaporate slowly. The product precipitated out as light yellow crystals which are collected and washed with ethanol and left to dry out.

2.3.1.8.2 Method 2

In this method, a solvent free synthesis was used for the preparation of N, N'-*bis*(4-hydroxybenzylideneamino)ethane. A 1:2 molar ratio of amine to aldehyde was used. Both the (0.9104 g, 7.5 mmol) 4-hydroxybenzaldehyde and (0.2240 g, 3.7 mmol) of ethylenediamine were mixed together through grinding until a melt product was formed. The resulting product was allowed to dry in the fume hood for 24 hours. The solidified melt was recrystallized from hot ethanol.

2.3.1.8.3 Method 3

The procedure for method 3 is similar to that used for the synthesis of N, N'-*bis*(benzyl)ethylenediimine, but a two fold excess of sodium hydroxide (0.1600 g, 4.0 mmol) was added to the ethanolic solution (10 mL) of 4-hydroxybenzaldehyde (0.4550 g, 4.0 mmol). The solution mixture was stirred at room temperature until the base dissolved completely. 0.1335 g of ethylenediamine in 20 ml ethanol was added drop-wise to the solution mixture. The mixture was refluxed for 2 hours. The resulting brown solution was acidified with methanolic hydrochloric acid (8.33 M) to remove the sodium and to precipitate the Schiff base.

2.3.2 Synthesis of N, N'-(aryl)benzyaldiamine dihydrochloride salt

The synthesis of *para*-substituted benzylethylenediamine dihydrochloride ligands, involved two separate reaction steps. The first step required the reduction [5] of Schiff bases with a five-fold molar excess of solid sodium borohydride in dry methanol. The second step involved the protonation of the amine ligands with concentrated methanolic hydrochloric acid (8.33 M) in methanol medium or 0.1 M of hydrochloric acid of pH=1 in an acetone medium. The concentrated methanolic hydrochloric acid solution was prepared in a similar manner to the preparation described by Sanches-Silva[6] and Taber.[7]

2.3.2.1 Preparation of Methanolic HCl

A separating funnel with 50 mL of concentrated sulphuric acid was inserted, through a glass adaptor, into a 250 ml round bottom flask with 40.0 g of sodium chloride. By drop-wise addition of concentrated sulphuric acid into the sodium chloride, HCl gas was produced and it was transferred into a 250 mL round bottom flask containing methanol (100 mL). The concentration of the resulting solution was determine by potentiometric titration against silver nitrate solution using silver titrate and working electrode. The concentration was found to be 8.33 M methanolic HCl solution.

2.3.2.2 Preparation of N, N'-*bis*(4-nitrobenzyl)ethylenediamine dihydrochloride

To a solution of N, N'-*bis*(4-nitrobenzyl)ethylenediimine (0.1363 g, 0.4 mmol) in 10 ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (0.07902 g, 2.1 mmol). After which the reaction mixture was refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold water was added to the reaction mixture to liberate the secondary amine. The white product was then extracted with chloroform (4 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and an oily product was obtained.

N, N'-*bis*(4-nitrobenzyl)ethylenediamine dihydrochloride salt was prepared by diluting 0.2272 g (0.7 mmol) in 200 mL of acetone. The solution was filtered and allowed to cool down to room temperature. The resulting colourless filtrate was acidified with hydrochloric acid (0.1 M = 15 mL) until pH = 1. During the course of the addition of acid, a fine white crystalline powder precipitated. After the addition of hydrochloric acid, the solution mixture was allowed to stir at room temperature for 1 hour. The resulting fine amine salt was filtered washed with cold acetone (3 x 10 mL) and dried at room temperature for 48 hours. The physical data are given in table 3.2.

2.3.2.3 Preparation of N, N'-*bis*(4-chlorobenzyl)ethylenediamine dihydrochloride

To a solution of N, N'-*bis*(4-chlorobenzyl)ethylenediimine (2.2909 g, 7.5 mmol) in 10ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (1.4195 g 37.5 mmol). After which the reaction mixture was refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold was added to the reaction mixture to liberate the secondary amine. The white product was then extracted with chloroform (4 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and an oily product was obtained.

N, N'-*bis*(4-chlorobenzyl)ethylenediamine dihydrochloride was prepared by diluting 0.7125g (2.30 mmol) of N, N'-*bis*(4-chlorobenzyl)ethylenediamine in 150 mL of acetone. The solution was filtered and allowed to cool down to room temperature. The resulting colourless filtrate was acidified with hydrochloric acid (0.1 M = 15 mL) until pH = 1. During the course of the addition of acid, a fine white crystalline powder precipitated. After the addition of hydrochloric acid, the solution mixture was allowed to stir at room temperature for 1 hour. The resulting fine amine salt was filtered washed with cold acetone (3 x 10 mL) and dried at room temperature for 48 hours. The physical data are given in table 3.2.

2.3.2.4 Preparation of N, N'-*bis*(4-bromobenzyl)ethylenediamine dihydrochloride

To a solution of N, N'-*bis*(4-bromobenzyl)ethylenediimine (3.0 g, 7.6 mmol) in 10 ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (1.4326 g, 37.9 mmol). After which the reaction mixture was refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold water was added to the reaction mixture to liberate the secondary amine. The white product was then extracted with chloroform (4 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and a yellow oily product obtained.

N, N'-*bis*(4-bromobenzyl)ethylenediamine dihydrochloride salt was prepared by diluting 1.0558g (2.7 mmol) of N, N'-*bis*(4-bromobenzyl)ethylenediamine in 250 mL of acetone. The solution was filtered and allowed to cool down to room temperature. The resulting filtrate was acidified with hydrochloric acid (0.1 M = 15 mL) until pH = 1. During the course of the addition of acid, a fine white crystalline powder precipitated. After the addition of hydrochloric acid, the solution mixture was allowed to stir at room temperature for 1 hour. The resulting fine amine salt was filtered, washed with cold acetone (3 x 10 mL) and dried at room temperature for 48 hours. The physical data are given in table 3.2.

2.3.2.5 Preparation of N, N'-*bis*(benzyl)ethylenediamine dihydrochloride

To a solution of the N, N'-*bis*(benzyl)ethylenediimine (1.6190 g, 6.8 mmol) in 15 ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (1.2850 g, 34.0 mmol), after which the reaction mixture was refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold water was added to the reaction mixture to liberate the secondary amine. The colourless product was then extracted with chloroform (3 x 20 mL). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and an oily product was obtained.

N, N'-*bis*(benzyl)ethylenediamine dihydrochloride salt was prepared by diluting N, N'-*bis*(benzyl)ethylenediamine (0.1716g, 1.75 mmol) in 150 mL of acetone. The solution was filtered and allowed to cool down to room temperature. The resulting colourless filtrate was acidified with hydrochloric acid (0.1 M = 15 mL) until pH = 1. During the course of the addition of acid, a fine white crystalline powder precipitated. After the addition of hydrochloric acid, the solution mixture was allowed to stir at room temperature for 1 hour. The resulting fine amine salt was filtered, washed with cold acetone (3 x 10 mL) and dried at room temperature for 48 hours. The physical data are given in table 3.2.

2.3.2.6 Preparation N, N'-*bis(*4-methylbenzyl)ethylenediamine dihydrochloride

To a solution of N, N'-*bis*(4-methylbenzyl)ethylenediimine (2.4256 g, 9.8 mmol) in 10 ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (1.8624 g 49.3 mmol). The reaction mixture was then refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold water was added to the reaction mixture to liberate the secondary amine. The white product was extracted with chloroform (4 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and an oily product was obtained.

N, N'-*bis*(4-methylbenzyl)ethylenediamine dihydrochloride salt was prepared by dissolving 0.3468 g (1.3 mmol) of N, N'-*bis*(4-methylbenzyl)ethylenediamine in cold absolute methanol

(15 mL). The resulting solution was stirred for 30 min and then was filtered off. The filtrate was acidified with methanolic hydrochloric acid (8.33 M) until pH = 1. The solution was allowed to stir at room temperature for 1 hour, resulting in a fine white precipitate. The precipitate was filtered, washed with methanol (2 x 10 ml) and dried at room temperature. The salt was ground to a fine powder and then taken up in minimum amount of cold water, filtered and reprecipitated by evaporation of the solvent in the fume-hood. The precipitate was recrystallized again in warm acetone/ethanol and placed in the cold (5 ^{o}C) to form a crystalline solid. The physical data are given in table 3.2.

2.3.2.7 Preparation of N, N'-*bis*(4-methoxybenzyl)ethylenediamine dihydrochloride

To a solution of N, N'-*bis*(4-methoxybenzyl)ethylenediimine (2.3164 g, 7.8 mmol) in 10 ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (1.4785g, 39.1 mmol). After which the reaction mixture was refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold water was added to the reaction mixture to liberate the secondary amine. The white product was extracted with chloroform (4 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and an oily product was obtained.

N, N'-*bis*(4-methoxybenzyl)ethylenediamine dihydrochloride salt was prepared by dissolving 0.5106g (1.7 mmol) of N, N'-*bis*(4-methoxybenzyl)ethylenediamine in 150 mL of acetone. The light yellow solution was filtered and allowed to cool down to room temperature. The resulting colourless filtrate was acidified with hydrochloric acid (0.1 M = 15 mL) until pH = 1. During the course of the addition of acid, a fine white crystalline powder precipitated. After the addition of hydrochloric acid, the solution mixture was allowed to stir at room temperature for 1 hour. The resulting fine amine salt was filtered, washed with cold acetone (3 x 10 mL) and dried at room temperature for 48 hours. The physical data are given in table 3.2.

2.3.2.8 Attempted preparation of N, N'-*bis(*4-dimethylaminobenzyl)ethylenediamine dihydrochloride

To a solution of N, N'-*bis*(4-dimethylaminobenzyl)ethylenediimine (1.0 g, 3.1 mmol) in 10 ml methanol was slowly added a five-fold molar excess of solid sodium borohydride (0.5830 g, 15.4 mmol). After which the reaction mixture was refluxed for 3 hours. The solvent was distilled off. Then, 20 ml of cold water was added to the reaction mixture to liberate the secondary amine. The white product was then extracted with chloroform (4 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by a Rotavapour and an oily product was obtained.

The hydrochloride salt was prepared by adding the oily product 0.5137g (1.6 mmol) in cold absolute methanol (15 mL). The resulting solution was stirred for 30 min and then was filtered. The filtrate was acidified with methanolic hydrochloric acid (8.33 M) until pH = 1. The solution was allowed to stir at room temperature for 1 hour, resulting in a fine white precipitate. The precipitate was filtered, washed with methanol (2 x 10 ml) and dried at room temperature. The product was ground to a fine powder and then taken up in minimum amount of cold water, filtered and reprecipitated by evaporation of the solvent in the fume-hood. The precipitate was recrystallized again in warm acetone/ethanol and placed in the cold (5 ^{o}C) to form dark brown precipitate. Unfortunately the compound was not the desired product. This was confirmed by microanalysis.

2.3.3 Synthesis of N, N'-(aryl)benzyaldiamine ligands

For the synthesis of the free *para*-substituted benzyaldiamine ligands, a two-fold molar excess sodium acetate was used to ensure a complete stripping of the two molar ratio of hydrochloride acid from the N, N'(aryl)benzyaldamine dihydrochloride ligand and the procedure is illustrated using N, N'-*bis*(4-chlorobenzyl)ethylenediamine dihydrochloride and ethanol as solvent. For some of the diamines methanol was employed (see table 3.3). The physical data of the ligands are given in table 3.3. Since the preparation of N, N'-*bis(*4-dimethylaminobenzyl)ethylenediamine dihydrochloride salt was unsuccessful, the amine of

this was obtained directly from the reduced N, N'-*bis(*4-dimethylaminobenzyl)ethylenediamine, by the recrystallization method (2.3.3.2).

2.3.3.1 Preparation of N, N'-*bis*(benzyl)ethylenediamine ligand

A two-fold molar methanolic (5 ml) solution of (0.1551 g, 2.3 mmol) sodium acetate was added to a stirred methanolic (15 ml) solution of (0.4355 g, 1.1 mmol) N, N'-*bis*(benzyl)ethylenediamine dihydrochloride salt at -10 ^{o}C. The resulting light yellow mixture was stirred for 2 hours in ice-bath; then brought to stir for 30 min at room temperature. The resulting white precipitate was filtered off. The volume of the methanol from the filtrate was reduced by rotator evaporation until an oily precipitate remained. The oily product was then dissolved in chloroform (12 ml), followed by drying over anhydrous sodium sulphate. The solvent was then reduced by rotator evaporation and an oily product was obtained. The resulting amine was dried at room temperature for 3 days. The compounds were obtained as an oily form and are quite air stable.

2.3.3.2 Preparation of N, N'-*bis(*4-dimethylaminobenzyl)ethylenediamine

Since the attempted formation of the salt was unsuccessful, the amine ligand was prepared by recrystallizing 0.8 g of N,N'-*bis(*4-dimethylaminobenzyl)ethylenediamine from hot dichloromethane. The physical data of the ligand is given in table 3.3.

2.3.4 Synthesis of copper(II) halide complexes derived from N, N'-(aryl)benzyaldiamine ligands

For the synthesis of Cu(R-BENH)Br_2 and Cu(R-BENH)Cl_2, cupric chloride dihydrate {(Cu(II)Cl_2.2H_2O)} and anhydrous copper(II) bromide {(Cu(II)Br_2)} were used. The synthesis procedure is generally common for all the complexes. The metal and amine ligand were reacted on a 1:1 basis in dry ethanol. The reactions were carried out at room temperature.

2.3.4.1 Synthesis of the copper bromide complexes

2.3.4.1.1 Preparation of Cu(NO_2-BENH)Br_2, (1B)

A solution of N, N'-*bis*(4-nitrobenzyl)ethylenediamine (0.0252 g, 0.08 mmol) in ethanol (8 mL) was added drop-wise to a warm stirred solution of (0.0188 g, 0.08 mmol) copper(II) bromide in ethanol (10 mL). The drop-wise addition of N, N'-*bis*(4-nitrobenzyl)ethylenediamine resulted in a formation of fine green crystals of the product. The reaction mixture was stirred at room temperature for 30 min. The product was filtered, and washed with cold ethanol. The product was dried at room temperature for 2 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.4.

2.3.4.1.2 Preparation of Cu(Cl-BENH)Br_2, (2B)

A solution of N, N'-*bis*(4-chlorobenzyl)ethylenediamine (0.0064 g, 0.02 mmol) in ethanol (8 mL) was added drop-wise to a warm stirred solution of (0.0461 g, 0.02 mmol) copper(II) bromide in ethanol (10 mL). The drop-wise addition of N, N'-*bis*(4-chlorobenzyl)ethylenediamine resulted in a formation of fine green crystals of the product. The reaction mixture was stirred at room temperature for 30 min. The product was filtered and washed with cold ethanol. The product was dried at room temperature for 2 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.4.

2.3.4.1.3 Preparation of Cu(Br-BENH)Br_2, (3B)

A solution of N, N'-*bis*(4-bromobenzyl)ethylenediamine (0.0347 g, 0.09 mmol) in ethanol (8 mL) was added drop-wise to a warm stirred solution of (0.0194 g, 0.09 mmol) copper(II) bromide in ethanol (10 mL). The drop-wise addition of N, N'-*bis*(4-bromobenzyl)ethylenediamine resulted in a formation of fine green crystals of the product.

The reaction mixture was stirred at room temperature for 30 min. The product was filtered and washed with cold ethanol. The product was dried at room temperature for 2 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.4.

2.3.4.1.4 Preparation of Cu(H-BENH)Br_2, (4B)

A solution of N, N'-di(benzyl)ethylenediamine (0.0406 g, 0.2 mmol) in ethanol (8 mL) was added drop-wise to a warm stirred solution of (0.0378 g, 0.2 mmol) copper(II) bromide in ethanol (10 mL). The drop-wise addition of the ligand resulted in a formation of fine green crystals of the product. The reaction mixture was stirred at room temperature for 30 min. The product was filtered and washed with cold ethanol. The product was dried at room temperature for 2 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.4.

2.3.4.1.5 Preparation of Cu(CH_3-BENH)Br_2, (5B)

A solution of N, N'-*bis*(4-methylbenzyl)ethylenediamine (0.0328 g, 0.1 mmol) in ethanol (8 mL) was added drop-wise to a warm stirred solution of (0.0273 g, 0.1 mmol) copper(II) bromide in ethanol (10 mL). The drop-wise addition of N, N'-*bis*(4-methylbenzyl)ethylenediamine resulted in a formation of fine green crystals of the product. The reaction mixture was stirred at room temperature for 30 min. The product was filtered and washed with cold ethanol. The product was dried at room temperature for 2 days The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.4.

2.3.4.1.6 Preparation of Cu(OCH_3-BENH)Br_2, (6B)

A solution of N, N'-*bis*(4-methoxybenzyl)ethylenediamine (0.1103 g, 0.4 mmol) in ethanol (8 mL) was added drop-wise to a warm stirred solution of (0.0810 g, 0.4 mmol) copper(II)

bromide in ethanol (10 mL). The drop-wise addition of N, N'-*bis*(4-methoxybenzyl)ethylenediamine resulted in a formation of fine green crystals of the product. The reaction mixture was stirred at room temperature for 30 min. The product was filtered and washed with cold ethanol. The product was dried at room temperature for 2 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.4.

2.3.4.2 Synthesis of the copper chloride complexes

2.3.4.2.1 Preparation of $Cu(NO_2\text{-}BENH)Cl_2$, (1C)

The ligand, N, N'-*bis*(4-nitrobenzyl)ethylenediamine (0.0310 g, 0.1 mmol) was dissolved in absolute ethanol (8 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0177 g, 0.1 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, fine blue crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.4.2.2 Preparation of $Cu(Cl\text{-}BENH)Cl_2$, (2C)

The ligand, N, N'-*bis*(4-chlorobenzyl)ethylenediamine (0.0377 g, 0.1 mmol) was dissolved in absolute ethanol (8 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0208 g, 0.1 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, fine blue crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.4.2.3 Preparation of Cu(Br-BENH)Cl_2, (3C)

The ligand, N, N'-*bis*(4-bromobenzyl)ethylenediamine (0.0351 g, 0.09 mmol) was dissolved in absolute ethanol (8 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0151 g, 0.09 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, blue fine crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.4.2.4 Preparation of Cu(H-BENH)Cl_2, (4C)

The ligand, N, N'-*bis*(benzyl)ethylenediamine (0.0180 g, 0.08 mmol) was dissolved in absolute ethanol (10 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0127 g, 0.08 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, fine blue crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.4.2.5 Preparation of Cu(CH_3-BENH)Cl_2, (5C)

The ligand, N, N'-*bis*(4-methylbenzyl)ethylenediamine (0.0333 g, 0.1 mmol) was dissolved in absolute ethanol (10 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0212 g, 0.1 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, fine blue crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.4.2.6 Preparation of $Cu(OCH_3\text{-}BENH)Cl_2$, (6C)

The ligand, N, N'-*bis*(4-methoxybenzyl)ethylenediamine (0.0879 g, 0.4 mmol) was dissolved in absolute ethanol (8 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0494 g, 0.4 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, fine blue crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.4.2.7 Preparation of $Cu(N(CH_3)_2\text{-}BENH)Cl_2$, (7C)

The ligand, N, N'-*bis*(4-dimethylaminobenzyl)ethylenediamine (0.0359 g, 0.1 mmol) was dissolved in absolute ethanol (10 mL) and was slowly added drop-wise to a warm stirred suspension of (0.0246 g, 0.1 mmol) cupric chloride dihydrate in the same solvent (10 mL). Upon addition of the ligand, fine blue crystals of the product immediately formed. The product was further stirred for 30 min. The fine blue crystals were filtered and washed with cold absolute ethanol (3 x 10 mL). The product was dried at room temperature for 3 days. The purity of the isolated complex was checked by elemental analysis, and the physical data are given in table 3.5.

2.3.5 Synthesis of N, N'-*bis*(cinnamaldiimine) ligands

The N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diiminoethane ligand was prepared in the similar manner as described in the literature.[8]

2.3.5.1 Preparation of N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diiminoethane ligand, (21)

To a stirring solution of *trans*-cinnamaldehyde (12.61 mL, 100 mmol) in methanol (100 mL) cooled with an ice bath, was added dropwise 3.35 mL (50 mmol) ethylenediamine. The

mixture was then stirred for an additional 45 min. The reaction mixture was poured into a beaker containing 400 mL of water, and it was allowed to stir for a further 30 min. The resulting product was collected on a coarse fritted glass funnel, washed with water and dried at room temperature for 48 hours. The Schiff base was recrystallized from acetone and the resulting white crystals were collected and washed with cold acetone (10 x 2 mL). The physical data are given in table 3.6.

2.3.5.2 Preparation of N, N'-*bis*(4-dimethylaminocinnamaldehyde)-1, 2-diiminoethane ligand, (22)

The cinnamaldiimine ligand, N, N'-*bis*(4-dimethylaminocinnamaldehyde)-1, 2-diiminoethane was synthesized via Schiff base condensation using 1.8615 g (10.6 mmol) of 4-dimethylaminocinnamaldehyde in 15mL ethanol and 0.3192 g (5.3 mmol) of ethylenediamine in 10 mL of the same solvent. The solution mixture was reflux for 2 hours. The resulting orange crude product was filtered, washed with cold ethanol (3 x 10 mL) and dried at room temperature for 48 hours. The physical data are given in table 3.6.

2.3.6 Synthesis of N, N'-*bis*(cinnamaldiamine) ligand

2.3.6.1 Preparation of N, N'-*bis*(*trans*-cinnamylbenzyl)ethylenediamine ligand, (23)

To a solution of N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diiminoethane (1.0208 g, 3.5 mmol) in 15 mL of methanol was slowly added a five-fold molar excess of solid sodium borohydride (0.5384 g, 14.2 mmol), after which the reaction mixture was refluxed for 3 hour. The solvent was distilled off. Then, 20 ml of cold water was added to reaction mixture to liberate the secondary amine. The colourless product was then extracted with chloroform (3 x 20 ml). The combined extracts were washed with water and dried over anhydrous sodium sulphate. The solvent was removed by rotator evaporation and a colourless oily solid was obtained. The physical data are given in table 3.6.

2.3.7 Synthesis of copper(I) complexes derived from N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diiminoethane ligand

The syntheses were carried out using distilled, dry, degassed solvents. All the chemicals were degassed before use. Reactions were performed under high purity nitrogen atmosphere by purging the system with nitrogen. The synthesis of the bromo and chloro complexes were carried out using anhydrous $CuCl_2$ and $CuBr_2$ in the presence of copper wire, while the iodo complex was prepared directly from anhydrous CuI. The anhydrous $CuCl_2$ was prepared by heating cupric chloride dihydrate in a heating piston. For the entire synthesis 1:1 metal to ligand mole ratio was used. The preparation of Cu(I) compounds were done in an identical manner. The synthesis is described using Cu(I)(CA_2EN)Cl. The physical data are given in table 3:7.

2.3.7.1 Preparation of Cu(I)(CA_2EN)Cl, (2I)

0.1008g (0.6 mmol) of anhydrous $CuCl_2$ was added to 8 mL of distilled acetonitrile, under a stream of purified N_2. A Cu(0) coil was added to the suspension to reproportionate any Cu(II) species that could form upon addition of the ligand, an excess of 2, 2-dimethoxypropane (1.23 mL, 5.9 mmol) was added to the CuCl suspension under nitrogen. After the addition of 2, 2-dimethoxypropane, the solution immediately became in a pale colourless solution after stirring under nitrogen. 0.1705g of N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diiminoethane (5.9 mmol) was added to the colourless solution under nitrogen and an orange solid precipitated immediately. The orange product was filtered under nitrogen using a special glass frit. The compounds are air stable when they are completely dry, but a rapid oxidation to Cu(II) was observed in the presence of moisture. The compounds were stored in a degassed desicator. The physical data are given in table 3:7.

2.3.8 Synthesis of copper(II) complexes derived from N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diaminoethane ligand, Cu(II)(CA_2EN)Cl_2 and (Cu(II)(CA_2EN)Br_2)

The synthesis of dibromoN, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diaminoethanecopper(II) and dichloroN, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diaminoethanecopper(II) were carried out using cupric chloride anhydrous and anhydrous copper(II) bromide under high a purity nitrogen atmosphere. The anhydrous $CuCl_2$ was prepared by heating cupric chloride dihydrate in a heating pistol. The synthesis is described using Cu(II)(CA_2EN)Cl_2, because the preparation of Cu(II)(CA_2EN)Br_2 was unsuccessful, yielding inconsistent results. This is possibly due to the bromide stabilising the reduction of Cu(II) to Cu(I). Thus synthesis of the Cu(II) iodide complex was not attempted.

2.3.8.1 Preparation of Cu(II) (CA_2EN)Cl_2, (4I)

To a 0.1007 g (0.6 mmol) of anhydrous $CuCl_2$ was added 10 mL of distilled acetonitrile, under a stream of purified N_2. An excess of 2, 2-dimethoxypropane (1.23 mL, 5.9 mmol) was added to the stirred $CuCl_2$ suspension under nitrogen. Upon the addition of 2, 2-dimethoxypropane, the solution turned colourless. 0.1705 g of N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diiminoethane (0.6 mmol) was added to the colourless solution under nitrogen and blue crystals precipitated immediately. The compound is air and moisture stable and its physical data is given in table 3.8.

2.3.9 Attempt to synthesize copper(II) complexes derived from N, N'-*bis*(*trans*-cinnamylbenzyl)ethylenediamine ligand

Attempts were made to prepare the amine complexes, Cu(II)(CA_2ENH)Br_2 and Cu(II)(CA_2ENH)Cl_2 in a similar manner to the synthesis described in section 2.2.5 and 2.2.6. Unfortunately the syntheses for both compounds were unsuccessful. The attempted synthesis is described using Cu(II)(CA_2ENH)Br_2.

2.3.9.1 Preparation of Cu(II)(CA_2ENH)Br_2

The complex was prepared by drop-wise addition of ethanolic solution (8 mL) of N, N'-*bis*(*trans*-cinnamaldehyde)-1, 2-diaminoethane (0.1456 g, 0.5 mmol) into a solution of Cu(II)Br_2 in ethanol. Upon the addition of the ligand solution, a green solid product precipitated out. The solution mixture was then stirred for 30 min at room temperature. The resulting green product was filtered, washed with absolute ethanol (10 x 3 mL) and dried at room temperature for 48 hours. The complex was then recrystallized from hot acetone – hexane and in hot ethanol. The microanalysis gave inconsistant results. This is possibly because the complexes undergo dissociation of the ligand in these solvents, leading to contamination of the metal salts on recrystalisation.

2.4 References

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3. RESULTS (PHYSICAL AND CHEMICAL STUDY)

All the results obtained from the techniques used in characterizing the ligands and their complexes are listed in this chapter.

The interpretation of the experimental spectra data (including the IR, ^{1}H- and ^{13}C-NMR, UV/vis and MS in table 3.1-3.22) and the elucidation of the chemical structure of the respective compounds and their complexes are based on known reported structures in literature [1-2]. Since the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligand is not a new compound, the interpretation and the assignment of the proton and carbon chemical shifts for the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligand and its dimethylamine analogue were made by comparing the NMR spectra of the ligand with those reported in literature [3, 4].

3.1 Physicochemical data for ligands and complexes

Table 3.1 Microanalysis and analytical data for the of N, N'-(aryl)benzaldiimine ligands

			Found (Calculated)					Mp	Molar	M^+
No.	Ligand	Molecular formula	%C	%H	%N	Color	Yield (%)	(^oC)	mass	
1	NO_2-BEN	$C_{16}H_{14}N_4O_4$	58.94 (58.89)	4.31 (4.33)	17.17 (17.17)	yellow-pink	97.6	200-202	326.3	328.1
2	Cl-BEN	$C_{16}H_{14}Cl_2N_2$	62.95 (62.97)	4.71 (4.62)	9.23 (9.18)	shinny white	92.6	145-147	305.2	306.4
3	Br-BEN	$C_{16}H_{14}Br_2N_2$	48.67 (48.76)	3.65 (3.58)	7.24 (7.11)	shinny white	88.2	160-161	394.1	396.9
4	H-BEN	$C_{16}H_{16}N_2$	81.18 (81.32)	7.04 (6.83)	11.84 (11.85)	light yellow	80.5	40-42	236.3	237.9

Table 3.1 (continued)

			Found (Calculated)					Mp	Molar	M^+
No.	Ligand	Molecular formula	%C	%H	%N	Color	Yield (%)	(^oC)	mass	
5	CH_3-BEN	$C_{18}H_{20}N_2$	81.33 (81.77)	7.86 (7.63)	10.55 (10.59)	white	78.3	150-152	264.4	266.3
6	OCH_3-BEN	$C_{18}H_{20}N_2O_2$	72.57 (72.95)	6.99 (6.80)	9.44 (9.45)	yellow	73.6	110-111	296.4	298.3
7	$N(CH_3)_2$-BEN	$C_{20}H_{26}N_4$	74.24 (74.49)	8.39 (8.13)	17.13 (17.38)	light cream	65.2	185-186	322.5	324.1

OH-BEN see section 2.3.1.8.

Table 3.2 Microanalysis and analytical data for the N, N'-(aryl)benzaldiamine dihydrochloride salts

No.	Ligand	Molecular formula	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)	Molar mass [a]	M^{+}
8	NO_2-BENH•2HCl	$C_{16}H_{18}Cl_2N_4O_4$•2HCl	47.65 (47.66)	5.22 (5.00)	13.32 (13.89)	light yellow	73	205-207	332.4	333.2
9	Cl-BENH•2HCl	$C_{16}H_{18}N_2Cl_2$•2HCl	50.41 (50.29)	5.44 (5.28)	7.24 (7.33)	shinny white	56	245-246	311.3	311.8
10	Br-BENH•2HCl	$C_{16}H_{18}N_2Br_2$•2HCl	40.97 40.80	4.44 (4.28)	5.87 (5.95)	shinny white	62	240-241	400.	400.1
11	H-BENH•2HCl	$C_{16}H_{20}N_2$•2HCl	61.28 (61.35)	7.17 (7.08)	8.78 (8.94)	shinny white	57	249-250	242.4	243.4
12	CH_3-BENH•2HCl	$C_{18}H_{24}N_2$•2HCl	63.54 (63.34)	7.59 (7.68)	8.33 (8.21)	shinny white	82	219-220	270.4	271.0
13	OCH_3-BENH•2HCl	$C_{18}H_{24}N_2O_2$ •2HCl	57.32 (57.91)	6.51 (7.02)	7.46 (7.02)	shinny white	65	255-257	302.4	303.0

a (LH_2^{2+}) ion

Table 3.3 Microanalysis and analytical data for the N, N'-(aryl)benzaldiamine ligands

No.	Ligand	Molecular formula	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)	Molar mass	M^{+}
14	NO_2-BENH•MeOH	$C_{16}H_{18}N_4O_4$	52.93 (53.00)	5.80 (5.01)	15.74 (15.46)	light orange	62	o	330.3	331.9
15	Cl-BENH•MeOH	$C_{16}H_{18}Cl_2N_2$	56.86 (56.31)	6.27 (5.32)	8.71 (8.21)	yellow	63	o	309.2	310.6
16	Br-BENH	$C_{16}H_{18}Br_2N_2$	47.88 (48.27)	4.70 (4.56)	6.96 (7.04)	yellow	54	o	398.1	400.2
17	H-BENH•MeOH•H_2O	$C_{16}H_{20}N_2$	68.88 (68.78)	7.47 (7.22)	9.07 (10.23)	white	68	56-58	240.3	242.0
18	CH_3-BENH•½EtOH	$C_{18}H_{24}N_2$•½C_2H_5OH	74.63 (74.18)	8.51 (9.01)	9.24 (9.61)	white	72	74-75	268.4	270.5
19	OCH_3-BENH•½EtOH	$C_{18}H_{24}N_2O_2$•½C_2H_5OH	66.36 (66.84)	7.44 (7.48)	8.24 (8.66)	cream	55	94-95	300.4	302.2
20	$N(CH_3)_2$-BENH•MeOH	$C_{20}H_{30}N_4$•CH_3OH	67.35 (67.00)	8.91 (8.46)	15.15 (15.63)	yellow	44	87-89	326.5	327.8

o oils

Table 3.4 Microanalysis and analytical data for the N, N'-(aryl)benzaldiaminedibromidecopper(II) complexes

No.	Complex	Molecular formula	Molar mass	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)
1B	Cu(NO_2-BENH)Br_2	$C_{16}H_{18}Br_2CuN_4O_4$	553.7	34.98 (34.71)	3.38 (3.28)	10.06 (10.12)	green	74	160-161
2B	Cu(Cl-BENH)Br_2	$C_{16}H_{18}Br_2Cl_2CuN_2$	532.6	41.88 (41.08)	4.25 (4.41)	6.31 (6.26)	green	69	192-193
3B	Cu(Br-BENH)Br_2	$C_{16}H_{18}Br_4CuN_2$	621.5	30.51 (30.92)	2.91 (2.92)	4.70 (4.51)	green	57	147-149
4B	Cu(H-BENH)Br_2	$C_{16}H_{20}Br_2CuN_2$	463.7	41.03 (41.44)	4.27 (4.35)	6.30 (6.04)	green	64	163-164
5B	Cu(CH_3-BEHN)Br_2	$C_{18}H_{24}Br_2CuN_2$	491.7	44.99 (44.03)	5.08 (4.93)	5.69 (5.69)	green	81	153-154
6B	Cu(OCH_3-BENH)Br_2	$C_{18}H_{24}Br_2CuN_2O_2$	523.7	40.08 (40.58)	4.75 (4.62)	5.23 (5.35)	green	56	111-112

Table 3.5 Microanalysis and analytical data for the N, N'-(aryl)benzaldiaminedichloridecopper(II) complexes

No.	Complex	Molecular formula	Molar mass	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)
1C	$Cu(NO_2\text{-}BENH)Cl_2$	$C_{16}H_{18}Cl_2CuN_4O_4$	464.79	41.07 (41.35)	3.97 (3.90)	11.99 (12.05)	blue	52	196-197
2C	$Cu(Cl\text{-}BENH)Cl_2$	$C_{16}H_{14}Cl_2CuN_2$	443.7	43.09 (43.31)	4.08 (4.10)	6.25 (6.32)	blue	63	192-193
3C	$Cu(Br\text{-}BENH)Cl_2$	$C_{16}H_{18}Br_2Cl_2CuN_2$	532.6	35.95 (36.08)	3.33 (3.41)	5.33 (5.26)	blue	59	189-190
4C	$Cu(H\text{-}BENH)Cl_2$	$C_{16}H_{16}Cl_2CuN_2$	374.8	50.51 (51.27)	5.38 (5.38)	7.29 (7.47)	blue	68	192-194
5C	$Cu(CH_3\text{-}BENH)Cl_2 \bullet \frac{1}{3}EtOH$	$C_{18}H_{20}Cl_2CuN_2 \bullet \frac{1}{3}C_2H_5OH$	418.2	53.59 (53.67)	6.22 (6.01)	6.36 (6.95)	blue	73	190-191

Table 3.5 (continued)

No.	Complex	Molecular formula	Molar mass	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)
6C	$Cu(OCH_3\text{-}BENH)Cl_2$	$C_{18}H_{20}Cl_2CuN_2O_2$	343.8	50.18 (49.71)	5.53 (5.57)	6.41 (6.44)	blue	74	178-179
7C	$Cu((NCH_3)_2\text{-}BEN)Cl_2 \bullet ½H_2O$	$C_{20}H_{30}Cl_2CuN_4 \bullet ½H_2O$	469.9	51.58 (51.12)	6.57 (6.44)	11.96 (11.92)	blue	67	204-206

Table 3.6 Microanalysis and analytical data for the N, N'-*bis*(cinnamaldiimine) ligands

No.	Ligand	Molecular formula	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)	Molar mass	M^{+}
21	CA_2EN	$C_{20}H_{20}N_2$	83.11 (83.29)	6.87 (6.87)	9.70 (9.72)	white	85	108-109	288.4	290.5
22	$N(CH_3)_2CA_2EN•½H_2O$	$C_{24}H_{30}N_4•½H_2O$	76.01 (76.96)	7.83 (8.07)	14.41 (14.96)	orange	77	193-194	374.5	379.4
23	$CA_2ENH•MeOH$	$C_{20}H_{22}N_2•CH_3OH$	74.55 (74.50)	7.57 (6.88)	8.16 (8.69)	white	62	76-79	290.3	292

Table 3.7 Microanalysis and analytical data for the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethanecopper(I)halide

No	Complex	Molecular formula	Molar mass	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)
1I	Cu(I) (CA_2EN)Br•($4CH_3CN$)	$C_{24}H_{32}N_2BrCu(CN)_4$	596.0	40.38 (40.58)	3.49 (3.88)	5.15 (5.39)	dark orange	71	209-211
2I	Cu(I)(CA_2EN)Cl•(1½ CH_3CN)	$C_{21}H_{24}N_2ClCuCN$	449.0	53.85 (53.51)	4.47 (4.49)	6.43 (6.24)	orange	67	166-168
3I	Cu(I)(CA_2EN)•(½ CH_3CN)I	$C_{20}H_{21}N_2ICu$	499.4	48.01 (48.11)	3.88 (4.08)	5.74 (5.61)	red-orange	88	215-216

Table 3.8 Microanalysis and analytical data for the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethanecopper(II)dihalide

No	Complex	Molecular formula	Molar mass	Found (Calculated) %C	%H	%N	Color	Yield (%)	Mp (^{o}C)
4I	Cu(CA_2EN)Cl_2	$C_{20}H_{20}CuCl_2N_2$	422.9	56.08 (56.80)	4.62 (4.78)	6.78 (6.63)	green	89	156-157

3.2 NMR spectroscopy spectra data for the ligands

Table 3.9 Proton nuclear magnetic resonance data for the N, N'-(aryl)benzaldiimine ligands

No.	Ligand	H-5	H-4	H-2	H-1	X
1	NO_2-BEN	8.28 (m, 2H)	7.90 (m, 2H)	8.41 (s, 1H)	4.09 (s, 2H)	-
2	Cl-BEN	7.62 (m, 2H)	7.35 (m, 2H)	8.22 (s, 1H)	3.95 (s, 2H)	-
3	Br-BEN	7.55 (m, 2H)	7.51 (m, 2H)	8.21 (s, 1H)	3.95 (s, 2H)	-
4	H-BEN	7.70 (m, 2H)	7.39 (m, 2H)	8.29 (s, 1H)	3.98 (s, 2H)	7.71 (m, 2H)

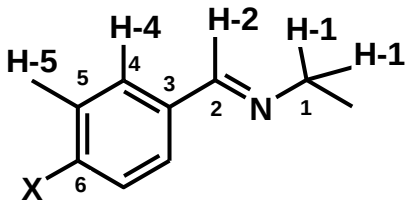

Figure 3.1 Numbering system used for the Schiff bases

Table 3:9 continues

No	Ligand	H-5	H-4	H-2	H-1	X
5	CH_3-BEN	7.19 (m, 2H)	7.58 (m, 2H)	8.25 (s, 1H)	3.95 (s, 2H)	2.36 (s, 3H)
6	OCH_3-BEN	6.87 (m, 2H)	7.61 (m, 2H)	8.18 (s, 1H)	3.79 (s, 2H)	3.86 (s, 3H)
7	$N(CH_3)_2$-BEN	6.67 (m, 2H)	7.57 (m, 2H)	8.16 (s, 1H)	3.87 (s, 2H)	2.99 (s, 6H)

Table 3:10 Carbon nuclear magnetic resonance data for the N, N'-(aryl)benzaldiimine ligands

No.	Ligand	C-6	C-5	C-4	C-3	C-2	C-1	X
1	NO_2-BEN	149.51	124.36	129.21	141.78	160.86	61.91	-
2	Cl-BEN	136.66	128.91	129.31	134.56	161.41	61.51	-
3	Br-BEN	125.00	131.75	129.42	134.91	161.33	61.37	-
4	H-BEN	130.78	128.71	128.24	136.25	162.89	61.79	-
5	CH_3-BEN	140.79	129.22	128.00	133.50	162.52	61.66	21.45
6	OCH_3-BEN	162.38	114.35	130.07	129.58	161.98	62.18	55.78
7	$N(CH_3)_2$-BEN	151.61	111.35	129.29	124.20	162.23	61.85	40.03

Table 3:11 Proton nuclear magnetic resonance data for the N, N'-(aryl)benzaldiamine dihydrochloride salts

No.	Ligand	H-5	H-4	H-2	H-1	NH_2	X
8	NO_2-BEN•2HCl	8.27 (m, 2H)	7.80 (m, 2H)	4.22 (s, 2H)	3.50 (s, 2H)	3.39 (s, 2H)	-
9	Cl-BEN•2HCl	7.55 (m, 2H)	7.36 (m, 2H)	3.52 (s, 2H)	2.72 (s, 2H)	2.89 (s, 2H)	-
10	Br-BEN•2HCl	7.58 (m, 2H)	7.39 (m, 2H)	3.89 (s, 2H)	3.51 (s, 2H)	3.36 (s, 2H)	-
11	H-BEN•2HCl	7.57 (m, 2H)	7.56 (m, 2H)	4.18 (s, 2H)	3.71 (s, 2H)	3.35 (s, 2H)	7.44 (s, 1H)
12	CH_3-BEN•2HCl	7.20 (m, 2H)	7.33 (m, 2H)	3.95 (s, 2H)	2.98 (s, 2H)	3.39 (s, 2H)	2.30 (s, 3H)
13	OCH_3-BEN•2HCl	6.98 (m, 2H)	7.49 (m, 2H)	4.10 (s, 2H)	3.30 (s, 2H)	3.32 (s, 2H)	3.77 (s, 3H)

Table 3:12 Proton nuclear magnetic resonance data for the N, N'-(aryl)benzaldiamine ligands

No.	Ligand	H-5	H-4	H-2	H-1	N-H	X
14	NO_2-BENH	8.18 (m, 2H)	7.50 (m, 2H)	3.90 (s, 2H)	2.77 (s, 2H)	1.95 (s, 1H)	-
15	Cl-BENH	7.28 (m, 2H)	7.23 (m, 2H)	3.74 (s, 2H)	2.73 (s, 2H)	1.73 (s, 1H)	-
16	Br-BENH	7.43 (m, 2H)	7.18 (m, 2H)	3.72 (s, 2H)	2.72 (s, 2H)	1.16 (s, 1H)	-
17	H-BENH	7.31 (m, 2H)	7.26 (m, 2H)	3.78 (s, 2H)	2.78 (s, 2H)	2.28 (s, 1H)	7.21 (s, 1H)
18	CH_3-BENH	7.13 (m, 2H)	7.20 (m, 2H)	3.74 (s, 2H)	2.76 (s, 2H)	2.08 (s, 1H)	2.34 (s, 3H)
19	OCH_3-BENH	6.85 (m, 2H)	7.23 (m, 2H)	3.79 (s, 2H)	2.75 (s, 2H)	2.07 (s, 1H)	3.71 (s, 3H)
20	$N(CH_3)_2$-BENH	6.78 (m, 2H)	7.25 (m, 2H)	3.75 (s, 2H)	2.82 (s, 2H)	1.61 (s, 1H)	2.99 (s, 3H)

Table 3:13 Carbon nuclear magnetic resonance data for the N, N'-(aryl)benzaldiamine ligands

No.	Ligand	C-6	C-5	C-4	C-3	C-2	C-1	X
14	NO_2-BENH	147.53	124.09	129.03	148.42	53.54	49.21	-
15	Cl-BENH	132.42	128.29	129.22	138.65	52.94	48.43	-
16	Br-BENH	120.79	131.56	129.91	139.58	53.34	48.82	-
17	H-BENH	127.17	128.57	128.35	140.12	53.86	48.51	127.17
18	CH_3-BENH	136.30	128.85	127.91	136.91	53.29	48.27	20.87
19	OCH_3-BENH	158.74	113.88	129.46	132.36	53.28	48.51	55.38
20	$N(CH_3)_2$-BENH	150.25	113.19	129.04	129.52	53.87	49.17	41.27

Table 3:14 Proton and Carbon nuclear magnetic resonance data for the N, N'-*bis*(cinnamaldiimine) ligands

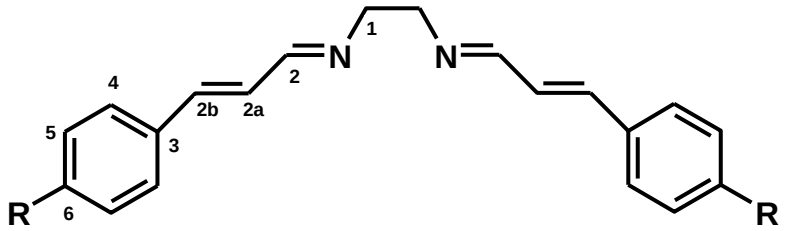

Figure 3.2 Numbering system used for the N, N'-*bis*(cinnamaldiimine) ligands

No		R	1	2	2a	2b	3	4	5	6	X
21	^{1}H	H	3.85 (s, 2H)	8.05 (d, 1H)	6.94 (d, 1H)	6.89 (d, 1H)	-	7.34 (d, 2H)	7.46 (d, 2H)	7.46 (d, 2H)	-
	^{13}C		61.55	164.01	127.05	141.64	135.52	127.87	128.60	128.93	-
22	^{1}H	$4N(CH_3)_2$	3.79 (s, 2H)	7.99 (d, 1H)	6.72 (d, 1H)	6.66 (d, 1H)	-	7.35 (d, 2H)	6.85 (d, 2H)	-	2.98 (s,3H)
	^{13}C		61.38	164.21	123.35	141.76	123.11	128.08	111.49	150.41	39.73

3.3 Electronic spectra data for the ligands

Table 3:15 UV/visible spectral data for the N, N'-(aryl)benzaldiimine ligands, (Extinction coefficient in parentheses (log ε, l/mol cm))

No.	R	Solvent	π→π*(benzene)	π→π* (imine)	CT	n→π* (imine)	others
1	4-NO_2	EtOH	216 (3.03) 218 sh	237 (2.67) 238	282 (3.65)	321 (2.50)	324 (2.42)
2	4-Cl	EtOH	210 (3.68)	masked	254 (2.82)	284 (2.96) 294 (2.65)	293 (2.69)
3	4-Br	EtOH	212 (3.45)	masked	258 (2.85)	285 (2.75)	292 (2.55)
4	H	EtOH	204 (3.85)	211 (3.65)	247 (4.00)	274 (2.78)	-
5	4-CH_3	EtOH	208 (3.44)	masked	256 (3.73)	288 (2.60)	294 (2.45)
6	4-OCH_3	EtOH	216 (3.43)	masked	271 (4.00)	287 (3.36)	297 (3.19), 302 (2.96)
7	4-$N(CH_3)_2$	EtOH	203 (3.50)	215 (3.07)	235 (3.15)	336 (4.08)	408 (2.44)

The UV spectra of the N, N'-(aryl)benzaldiamine dihydrochloride ligands due to the poor solubility of the salts. (No. 8-13)

Table 3:16 UV/visible spectral data for the N, N'-(aryl)benzaldiamine ligands

(Extinction coefficient in parentheses (log ε, l/mol cm))

	Assignment:		$n \rightarrow \zeta^*$ transition	$\pi \rightarrow \pi^*$ transition		
No.	Compound	Solvent	200-240 nm	250-300 nm	305-350 nm	360-700 nm
14	4-NO_2	Ethanol	214 (3.92)	271 (4.00)	-	-
		$CHCl_3$	-	-	313 (3.50)	448 (2.00)
15	4-Cl	EtOH	222 (4.26)	271 (2.75)	-	-
		$CHCl_3$	-	264 (2.82)	-	438 (1.43)
16	4-Br	EtOH	221 (4.40)	272 (2.85)	-	-
		$CHCl_3$	-	262 (3.45)	-	433 (1.82)
17	H	EtOH	212 (4.15)	260 (2.93)	-	-
		$CHCl_3$	-	268 (3.51)	333 (2.58)	-

Table 3.16 continues

	Assignment:		$n \rightarrow \zeta^*$ transition	$\pi \rightarrow \pi^*$ transition		
No.	R	Solvent	200-240 nm	250-300 nm	305-350 nm	360-700 nm
18	4-CH_3	EtOH	214 (4.17)	270 (2.71)	-	-
		$CHCl_3$	-	261 (3.87)	332 (2.66)	-
19	4-OCH_3	EtOH	214 (4.17)	268 (2.71)	-	-
		$CHCl_3$	-	258 (3.87)	332 (2.66)	-
20	4-$N(CH_3)_2$	EtOH	210 (2.54)	264 (3.0)	311 (3.62)	
		$CHCl_3$		266 (4.38)	315 (4.00), 351(3.89)	-

3.4 Electronic spectral data for the N, N'-(aryl)benzaldiaminedihalidecopper(II) complexes

Table 3:17 UV/visible spectral data for the N, N'-(aryl)benzaldiaminedibromidecopper(II) complexes

(Extinction coefficient in parentheses (log ε, l/mol cm))

Assignment:			$n \rightarrow \zeta^*$ transition	$\pi \rightarrow \pi^*$ transition	CT (M → L)	CT (M → L)	d → d transition
No	R	Solvent	200-240 nm	250-300 nm	305-350 nm	360-500 nm	505-900 nm
1B	4-NO_2	Ethanol	214, (3.99)	271, (4.01)	308, (3.91)	479, (3.70)	872, (2.33)
		$CHCl_3$		271, (4.02)	-	485, (3.63)	850, (2.20)
2B	4-Cl	Ethanol	224 (4.16)	274 (3.62)	311, (3.77)	465 (2.81)	699,(2.81)
		$CHCl_3$		272, (4.08)	308, (3.93)	464, (2.90)	708 (2.66)
3B	4-Br	Ethanol	228 (4.21)	277, (3.64)	308, (3.80)	466, (2.84)	735, (2.86)
		$CHCl_3$		279, (4.10)	301, (3.99)	468, (3.07)	755, (2.95)
4B	H	Ethanol	212 (4.05)	271 (3.58)	308 (3.79)	456 (2.76)	728 (2.77)
		$CHCl_3$	-	273, (4.01)	307, (3.94)	465, (2.90)	686, (2.63)
5B	4-OCH_3	Ethanol	231 (4.17)	277 (3.80)	314 (3.70)	469 (2.77)	686 (2.78)
		$CHCl_3$		277, (4.03)	307, (3.87)	464, (3.04)	686, (2.77)
6B	4-CH_3	Ethanol	221 (4.04)	276 (3.63)	308, (3.72)	477 (2.70)	740, (2.77)
		$CHCl_3$		279, (3.77)	308, (3.82)	469, (2.81)	694, (2.60)

Table 3:18 UV/visible spectral data for the N, N'-(aryl)benzaldiaminedichloridecopper(II) complexes

(Extinction coefficient in parentheses (log ε, l/mol cm))

	Assignment:		$n \rightarrow \zeta^*$ transition	$\pi \rightarrow \pi^*$ transition	CT (M $\rightarrow$ L)	CT (M $\rightarrow$ L)	d $\rightarrow$ d transition
No	R	Solvent	200-240 nm	250-300 nm	305-350 nm	360-500 nm	505-900 nm
1C	4-NO_2	Ethanol	211 (3.99)	267 (3.05)		-	859 (2.63)
		$CHCl_3$	-	272 (3.76)	308 (3.54)	-	698 (2.22)
2C	4-Cl	Ethanol	226 (4.07)	271 (3.91)	308 (3.86)	-	860 (3.06)
		$CHCl_3$	-	265 (3.82)	306 (3.90)	-	757 (2.78)
3C	4-Br	Ethanol	225 (4.05)	277 (3.73)	448 (3.43)		880 (2.43)
		$CHCl_3$		268 (3.74)	473 (3.56)	-	866(2.11)
4C	H	Ethanol	272 (3.95)	281 (3.73)	308 (3.68)	-	857 (3.14)
		$CHCl_3$	-	270 (3.76)	308 (3.64)	-	656 (2.58)
5C	4-CH_3	Ethanol	221 (4.00)	275 (3.81)	308 (3.72)	-	619 (3.04)
		$CHCl_3$	-	271 (3.84)	308 (3.67)	-	684 (2.31)
6C	4-OCH_3	Ethanol	232 (4.07)	277 (3.88)	308 (3.63)	-	621 (3.01)
		$CHCl_3$	-	275 (3.92)	308 (3.58)	-	719 (2.18)
7C	4-$N(CH_3)_2$	Ethanol	-	262 (4.19)	316 (3.67)	405 (3.29)	562 (2.7)
		$CHCl_3$	-	270 (5.01)	317 (4.78)	456 (4.72)	-

3.5 Electronic spectral data for the copper(I) and copper(II) complexes with N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane

Table 3:19 UV/visible spectral data for the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethanecopper(I)halide and copper(II) dihalide

(Extinction coefficient in parentheses (log ε, l/mol cm))

No	Assignment: Complex	Solvent	π→π*(benzene) 250 - 300 nm	π→π* (imine) 305 - 350 nm	CT	n→π* (imine) 360 - 400 nm	CT (M → L) 410 – 500 nm	d→d transition 500 -900 nm
21	CA_2EN	DCM	249 (3.50)	masked	311 (4.82)	339 (3.76)	-	
22	$N(CH_3)_2$-CA_2EN	DCM	251 (3.67)	masked	317 (4.75)	mask		
1I	Cu(I)(CA_2EN)Br	DCM	252 (3.85)	masked	321 (4.04)	-	442 (2.98)	-
2I	Cu(I)(CA_2EN)Cl	DCM	250 (3.86)	masked	320 (4.00)	-	448 (2.90)	-
3I	Cu(I)(CA_2EN)I	DCM	250 (3.87)	masked	320 (4.02)	-	449 (2.91)	-
4I	Cu(II)(CA_2EN)Cl_2	DCM	249 (3.75)	masked	313 (3.81)	389 (3.57)	-	741 (2.22)

3.6 Mid-infrared spectral data for the N, N'-(aryl)benzaldiimine ligands

Table 3:20 The mid-infrared spectral data for the N, N'-(aryl)benzaldiimine ligands

R	νC=N
4-NO_2	1649
4-Cl	1644
4-Br	1643
H	1614
4-CH_3	1608
4-OCH_3	1614
4-$N(CH_3)_2$	1636

3.7 Mid-infrared spectral data for the N, N'-(aryl)benzaldiamine dihydrochloride salts

Table 3:21 The mid-infrared spectral data for the N, N'-(aryl)benzaldiamine dihydrochloride salts

R	νNH_2^+	δNH_2^+
4- NO_2	2519	1598
4- Cl	2548	1589
4- Br-	2503	1598
H	2501	1587
4- CH_3	2500	1605
4- OCH_3	2597	1600

3.8 Mid-infrared spectral data for the N, N'-(aryl)benzyaldiamine ligands and their copper(II) halide complexes

Table 3:22 The mid-infrared spectral data for the copper(II) N, N'-(aryl)benzaldiaminebromide and chloride complexes

R	νN-H	$\nu H\text{-}N_{(CuBr)}$	$\nu H\text{-}N_{(CuCl)}$
$4\text{-}NO_2$	3387	3209	3219
4-Cl	3380	3196	3215
4-Br	3357	3203	3213
H	3372	3212	3212
$4\text{-}CH_3$	3269	3207	3208
$4\text{-}OCH_3$	3359	3212	3212
$4\text{-}N(CH_3)_2$	3365	3210	3214

3.9 Mid-infrared spectral data for the N, N'-*bis*(cinnamaldiimine) ligands and their copper(I) and copper(II) halide complexes

Table 3:23 The mid-infrared spectral data for the N, N'-*bis*(cinnamaldiimine) ligands and their copper(I) and copper(II) halide complexes

No	Compound	νC=N
21	CA_2EN	1615
22	$N(CH_3)_2$-CA_2EN	1620
1I	Cu(I)(CA_2EN)Br	1625
2I	Cu(I)(CA_2EN)Cl	1627
3I	Cu(I)(CA_2EN)I	1627
4I	Cu(II)(CA_2EN)Cl_2	1618

3.1 References

1. E. Pretsch, P. Bühlman, C. Affolter, "*Structure determination of organic compounds*: *Table of spectral data*", 3rd ed, Springer, Berlin, 2000.
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4. DISCUSSION (PHYSICAL AND CHEMICAL STUDY)

4.1 Elemental analyses

4. 1.1 Micro-analyses of Schiff base ligands and their copper(II) halide complexes

The proposed structure for the N, N'-(aryl)benzyaldiimine based ligands (the imines, amines and amine salts) and their copper complexes are based upon the elemental analysis as shown in table 3.1, 3.2 and 3.3 and upon spectrometry data discussed below. In some cases a trace of water or other solvents was found in the crystal lattice. From the elemental analysis results, the ratio between the ligand and the metal ion was found to be 1:1, and the results show good agreement with proposed structures.

4. 1.2 Micro-analyses of N, N'-*bis*(cinnamaldiimine) ligands and their copper(I) halide and copper(II) dihalide complexes

The data from the microanalysis for N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane showed good agreement with the proposed structure, while the microanalysis for N, N'-*bis*(4-dimethylaminocinnamaldehyde)-1, 2-diiminoethane showed the presence of water. Both the microanalysis of copper(I) and copper(II) complexes of N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane confirmed the 1:1 metal : ligand ratio. The data for the microanalyses is summarized in tables 6 and 7.

4.2 Mass spectrometry studies of Schiff base ligands

For this study electrospray mass spectrometry (ESI-MS) and atmospheric pressure chemical ionization (APCI-MS) were used for the characterization of the stoichiometry of the ligands in solution. ESI-MS uses a soft ionization technique to generate ions or to transform molecules in solution into ions, and the ions produced are negative. It generates less fragmentation and is suitable for polar and ionic compounds.

APCI is a method used in mass spectrometers to form ions from molecules. This method is very useful for non-polar substances and is a less soft ionization technique than ESI-MS. It was developed and optimized for Positive and Negative Ion Chemical Ionization. This ionization technique can produce multiple charged molecules $[M + nH]^{n+}$, depending on the type of solvent used.

Both ESI and APCI were found to be useful for the study of *para*-substituted Schiff base ligands, and they both confirmed the expected molecular weights of the obtained compounds.

4.2.1 APCI-MS studies of the N, N'-(aryl)benzaldiimine ligands

The solutions of N, N'-(aryl)benzaldiimine ligands in chloroform were characterized with atmospheric pressure chemical ionization, which confirmed the structure of the expected compounds. The observed parent ion m/z values for N, N'-(aryl)benzaldiimine ligands are listed in table 3.1. The m/z values for the parent ions of all the N, N'-(aryl)benzaldiimine ligands showed a high mass ions due to $[M + 2H]^+$ and this is due to the presence of the two imine groups within the N, N'-(aryl)benzaldiimine ligand. To illustrate the behaviour of the Schiff bases the mass spectra obtained for N, N'-*bis*(4-dimethylaminobenzyl)-1, 2-diiminoethane, N, N'-*bis*(4-chlorobenzyl)-1, 2-diiminoethane and N, N'-*bis*(4-bromobenzyl)-1, 2-diiminoethane are shown in figure 4.2.1, 4.2.2 and 4.2.3.

For the mass spectrum studies of the N, N'-*bis*(4-dimethylaminobenzyl)-1, 2-diiminoethane is note that the expected parent ion m/z value for the ligand, $\{(N(CH_3)_2\text{-BEN})\}$ is [M + 4H] due to the additional two available $(CH_3)_2N$ groups of the ligand, but only $[M + 2H]^+$ is observed. This indicates that the protonation of the $(CH_3)_2N$ group of the Schiff base, $\{(N(CH_3)_2\text{-BEN})\}$ is not stable in the mass spectrometer.

The mass spectrum of N, N-*bis*(4-dimethylaminobenzyl)-1, 2-diiminoethane $\{N(CH_3)_2\text{-BEN}\}$ (Fig 4.2.1), shows a molecular ion (M^{2+}) peak at m/z 324 and the presence of another species at m/z 186. The fragment at m/z 186 came from cleavage of the amine ligand.[1, 2] It has been shown that in APCI nitrogen-aromatic compounds such as imines are reduced to the corresponding amines.[1, 2] The degree of the reduction was found to be dependent on the compound, the nature of the solvent and the temperature of the nebulizer probe. The reduction of the imines it is known to be more prominent in protic solvents such as methanol, water and in acid solutions. These complicate the APCI-MS spectra. This process can be limited by using dried acetonitrile or methylene chloride solvent.

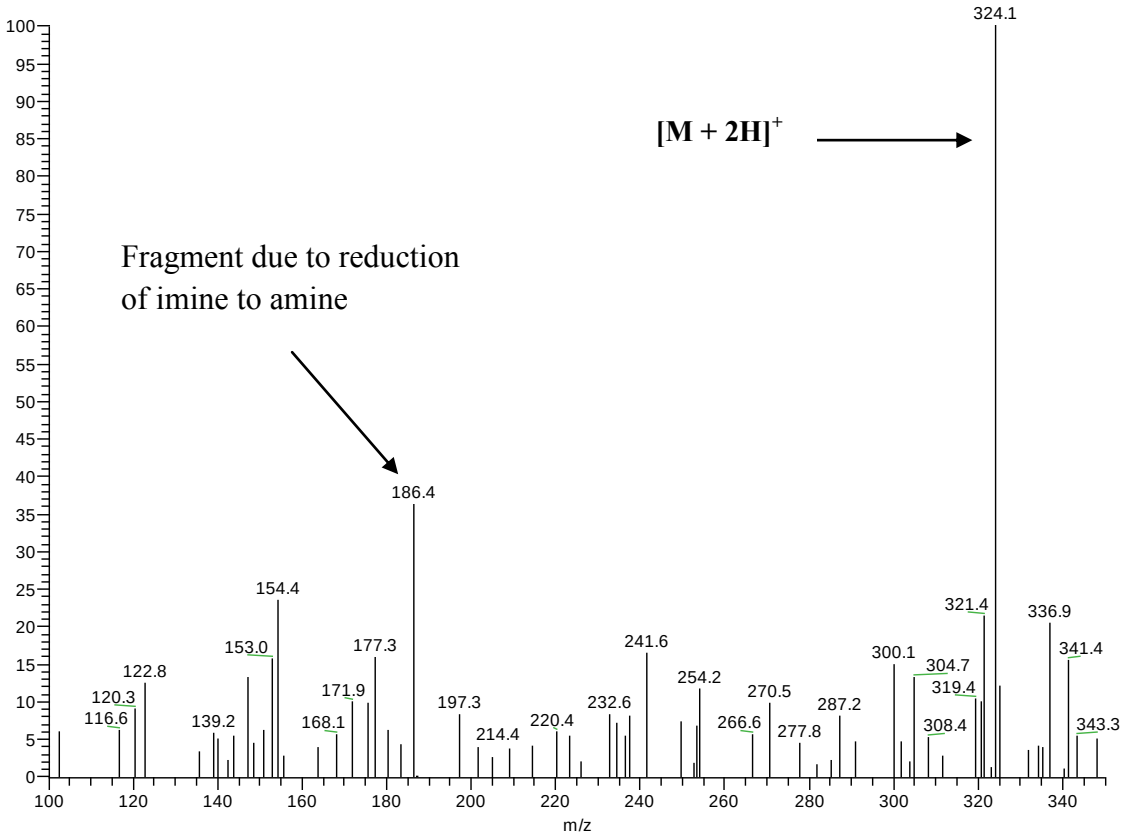


Figure 4.2.1 APCI-MS spectrum obtained for $N(CH_3)_2$-BEN in chloroform solution

The mass spectra of the Cl and Br analogues are shown in figure 4.2.2 and 4.2.3. From the mass spectrum of the Schiff base, Cl-BEN, the signal at m/z 306 corresponds to $[M + 2H]^+$ for two ^{35}Cl. The signal at m/z 308 is due to ^{35}Cl and ^{37}Cl for $[M + 2H]^+$. At m/z 310 the weak signal corresponds to $[M + H]^+$ for the two ^{37}Cl. From the mass spectrum of the Cl-BEN can be concluded that the ratio is 9:6:1 due to the relative heights of the 306. 4, 308. 4 and 310.4 lines. The pattern of the three peaks in the spectrum of Cl-BEN confirms clearly that the ligand contains two chlorides with the natural chlorine isotope distribution of ^{35}Cl and ^{37}Cl (75.77 % and 24.23 %, respectively) [3].

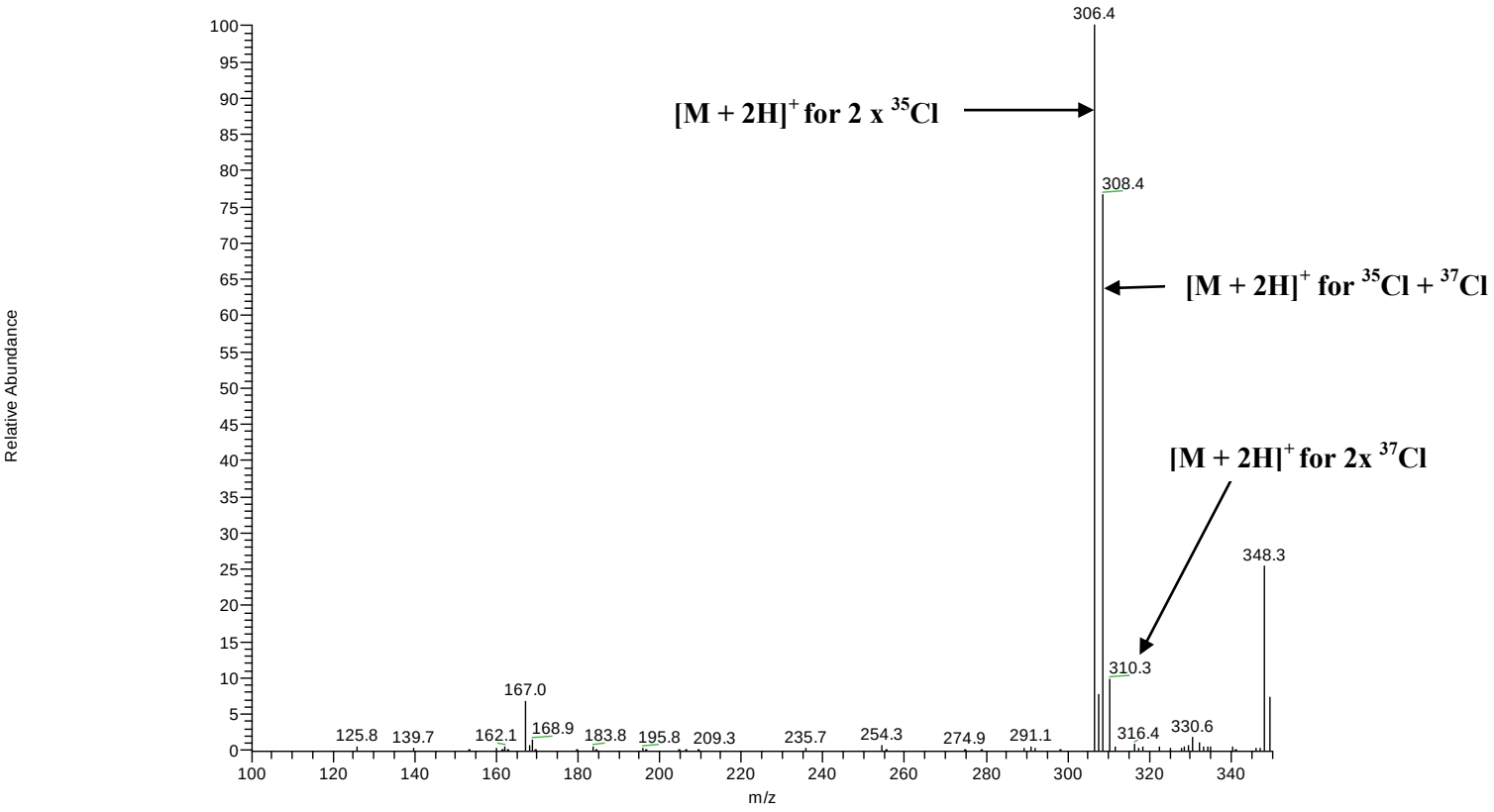


Figure 4.2.2 APCI-MS spectrum obtained for Cl-BEN in chloroform solution

The mass spectrum of Br-BEN, show a mass ion at m/z 393.9 due to $[M + 2H]^+$ for two ^{79}Br, the alternative explanation for this is signal may be due to $[M]^+$ for ^{79}Br and ^{81}Br. At m/z 394.8 the parent ion corresponds to $[M + H]^+$ for ^{79}Br and ^{81}Br. The ion peak at m/z 395.9 corresponds to $[M + 2H]^+$ for ^{79}Br and ^{81}Br, with the alternative explanation $[M]^+$ for two ^{81}Br. The latter interpretation is unlikely give the absence of a $[M]^+$ for two ^{79}Br. The strong signal at m/z 396.9 is due to $[M + H]^+$ for two ^{81}Br. The signal at m/z 398.1 corresponds to $[M + 2H]^+$ for two ^{81}Br. The relative heights of the peaks observed in the mass spectrum of Br-BEN demonstrate clearly that the Schiff base consists of the mixture of ^{79}Br and ^{81}Br, the apparent abundance of ^{81}Br is a reflection of two bromines in the molecule [3]. The natural abundance for ^{79}Br and ^{81}Br are 50.52 % and 49.48 % respectively [3].

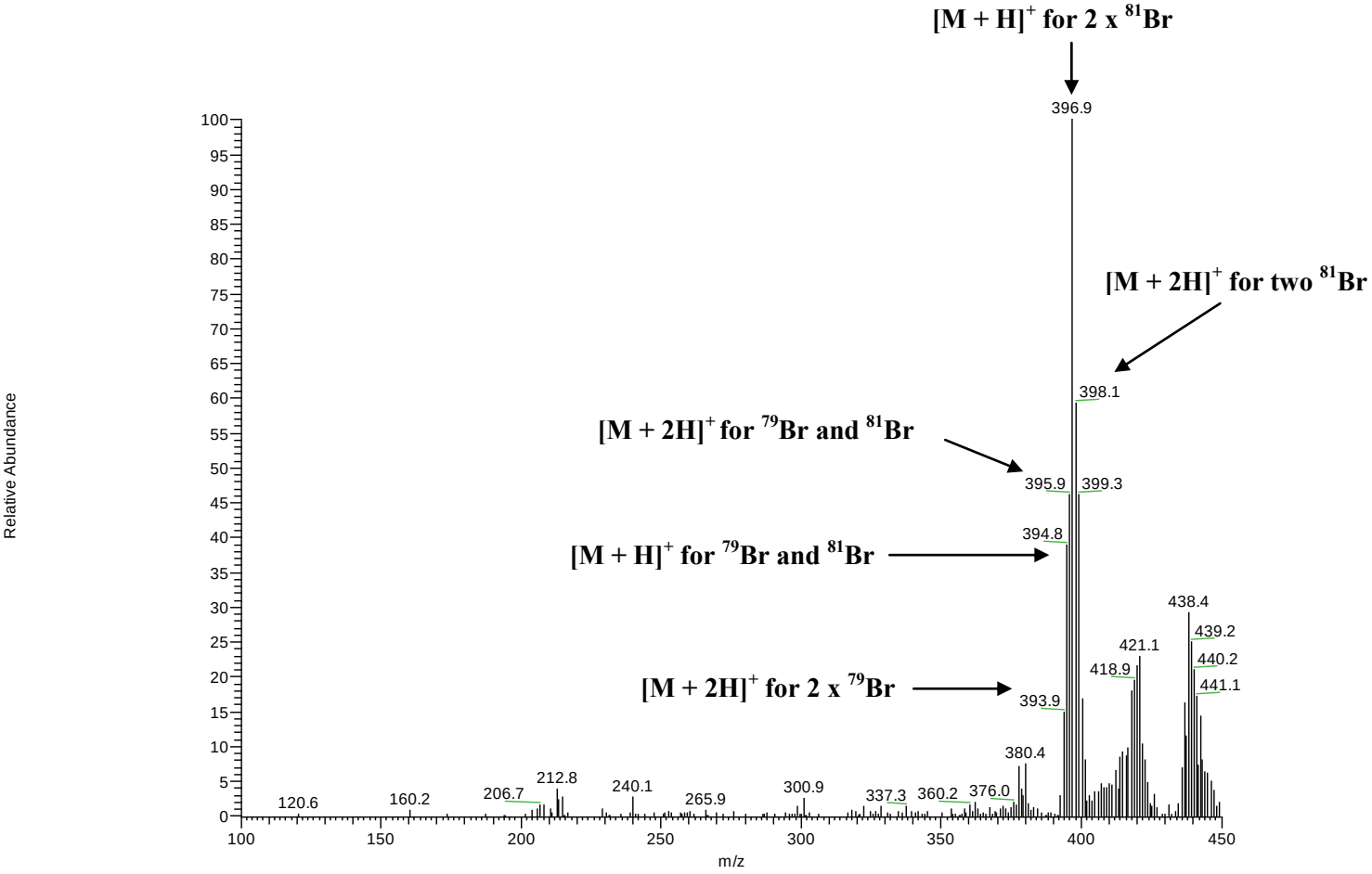


Figure 4.2.3 APCI-MS spectrum obtained for Br-BEN in chloroform solution

4.2.2 APCI-MS and ESI studies of the N, N'-(aryl)benzaldiamine dihydrochloride salts

The mass spectra of the N, N'-(aryl)benzaldiamine dihydrochloride ligands were analysed with atmospheric pressure chemical ionization and with electronspray ionization in deionised water solutions. The mass spectra of the N, N'-(aryl)benzaldiamine dihydrochloride salts are shown in figures 4.2.4, 4.2.5 and 4.2.6. The m/z values for the parental ion of all the amine ligand salts showed higher mass ions due to $[M + H]^+$. The results obtained from the mass spectra of the ligands confirmed the structure of the expected ligands. The observed parent ion m/z values for all the N, N'-(aryl)benzaldiamine dihydrochloride ligands are listed in table 3.2.

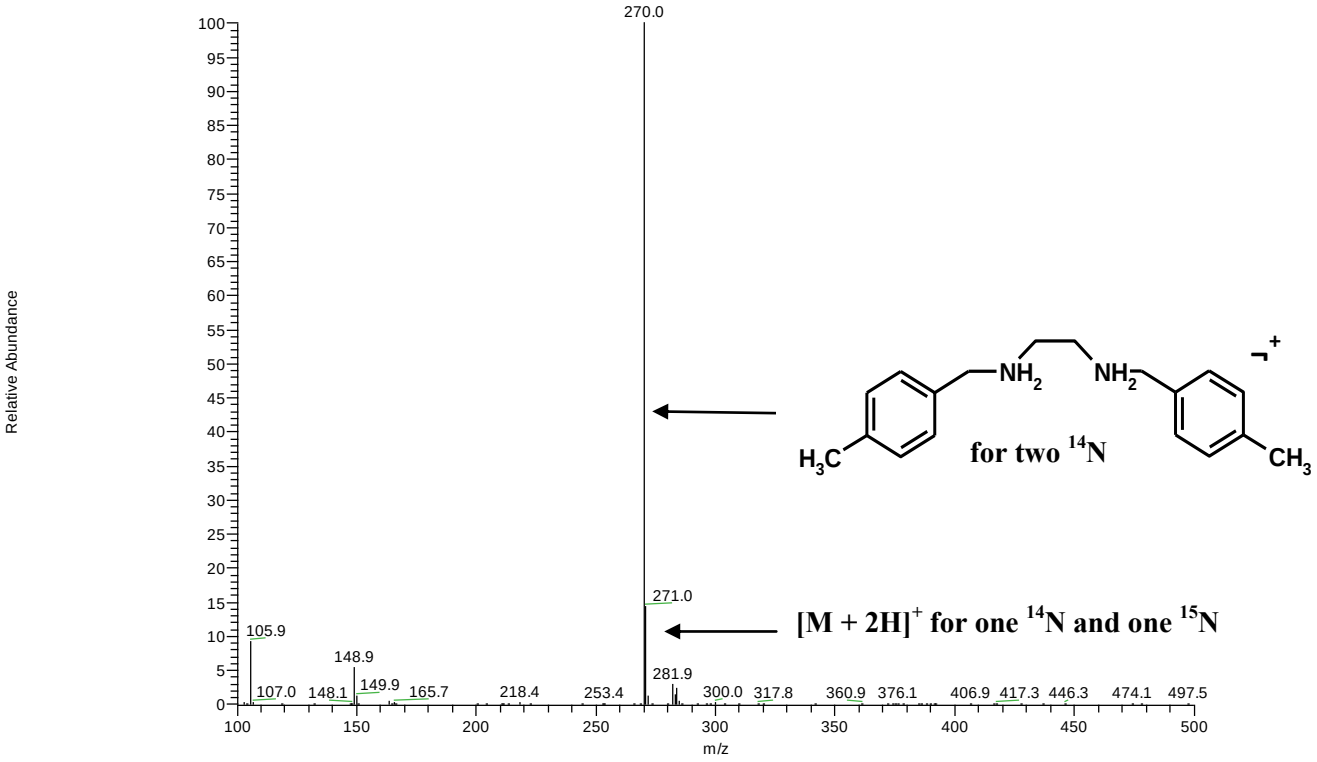


Figure 4.2.4 APCI spectrum obtained for (CH_3)-BENH•2HCl in water

The mass spectrum of the N, N'-*bis*(4-methylbenzyl)-1, 2-diaminoethane dihydrochloride ligand is shown in figure 4.2.4. The mass spectrum shows a base peak at m/z 270 which corresponds to $[M + 2H]^+$ for two ^{14}N, and at m/z 271 a higher mass ion is observed and the signal corresponds to $[M + 2H]^+$ for ^{14}N and possibly ^{15}N. The natural abundance of ^{14}N and ^{15}N are 100 and 0.4 %.

The bromide and chloride analogues of the N, N'-(aryl)benzaldiamine dihydrochloride ligands were characterized with electronspray ionization for two reasons:

(i) For better mass spectral resolution for both bromide and chloride analogues.

(ii) For an easy comparison between the N, N'-(aryl)benzaldiamine dihydrochloride and N, N'-(aryl)benzaldiamine ligands.

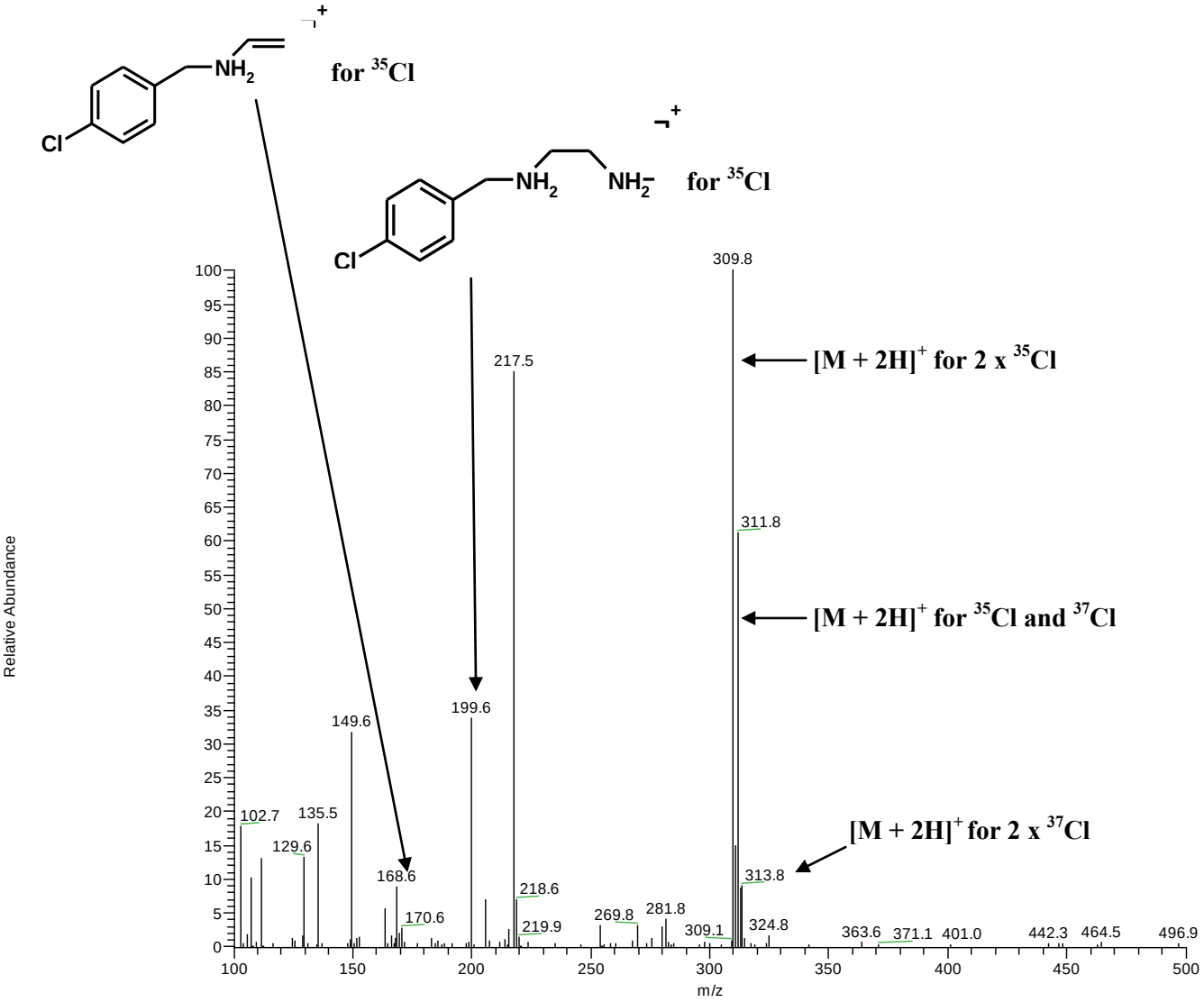


Figure 4.2.5 ESI spectrum obtained for Cl-BENH•2HCl in water

The mass spectrum of N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethane dihydrochloride (fig 4.2.5) shows a strong signal or parent ion at m/z 309.8 that corresponds to $[M + 2H]^+$ for 2 x ^{35}Cl. The signal at m/z 311.8 represents $[M + 2H]^+$ for ^{35}Cl and ^{37}Cl, while the weak signal at m/z 313.8 corresponds to $[M + 2H]^+$ for two ^{37}Cl. The signals at m/z 199.8 and at m/z 168.6 are the result of the fragmentation of the molecule. The relative heights of the peaks due to the isotopes pattern shows a 9:6:1 ratio, typical for a molecule with two chlorines [3].

From the electronspray ionization mass spectrum of the N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane dihydrochloride (fig 4.2.6), the amine salt shows a typical bromide isotope pattern. At m/z 398.4 a parent ion which corresponds to $[M + 2H]^+$ for two ^{79}Br is observed. The signal at m/z 400.1 represents $[M + 2H]^+$ for ^{79}Br and ^{81}Br as has been discussed above the alternative explanation for the signal is $[M + 2H]^+$ for two ^{79}Br. The signal at m/z 402.1 is due to $[M + 2H]^+$ for two ^{81}Br. The isotope pattern of the N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane dihydrochloride ligand indicates the natural isotopes distribution of any compound containing a single Br group in an approximately 1:1 ratio as observed for the N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane analysis discussed above.

The signals at m/z 122.1 and 312.5 correspond to the fragmentation of the ligand as presented in the figure below (fig 4.2.6)

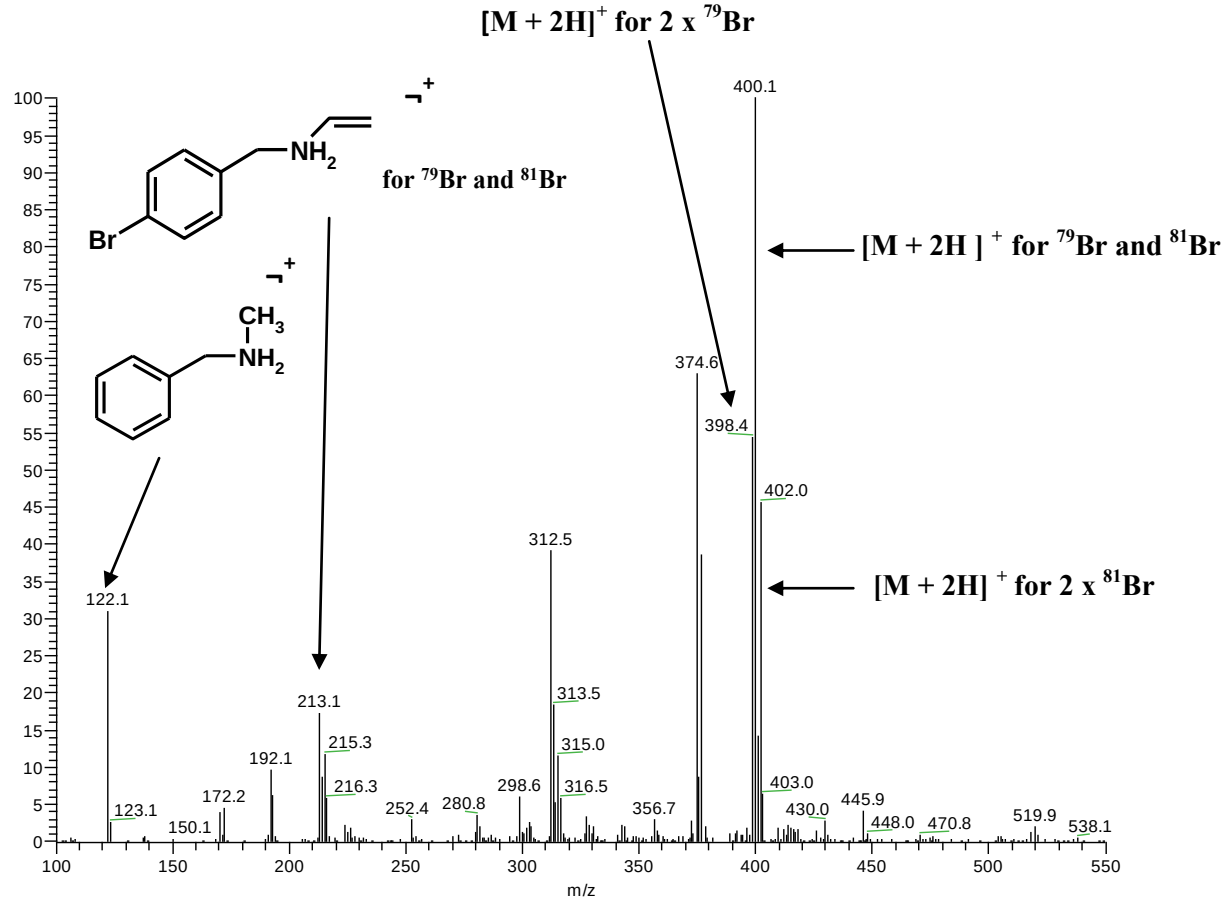


Figure 4.2.6 ESI spectrum obtained for Br-BENH•2HCl in water

4.2.3 ESI-MS studies of N, N'-(aryl)benzaldiamine ligands

The N, N'-(aryl)benzaldiamine ligands were all characterized with electrospray ionization mass spectrometry in methanol. The ESI mass spectra of the N, N'-(aryl)benzaldiamine ligands showed a very strong signal due to the molecular ion peak for all the N, N'-(aryl)benzyaldamine ligands. The parent ion m/z values for the ligands were the $[M + 2H]^+$ ion, and are listed in table 3.3. The mass spectra of N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethane and N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane are shown in figures 4.2.7 and 4.2.8.

The mass spectrum of N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethane shows a mass ion at m/z 310.6 which corresponds to $[M + 2H]^+$ for two ^{35}Cl. At m/z 312 a signal due to $[M + 2H]^+$ for ^{35}Cl and ^{37}Cl is observed and the alternative explanation for this signal is $[M]^+$ for two ^{37}Cl. The alternative explanation is unlikely given the absence of $[M]^+$ for two ^{35}Cl and $[M]^+$ for ^{35}Cl and ^{37}Cl. The signal at m/z 313.5 corresponds to $[M + H]^+$ for two ^{37}Cl. At m/z 314 the signal is due to [M + H] for two ^{37}Cl. This pattern indicates the presence of two halogens (^{35}Cl : ^{37}Cl of 75.77 : 24, 23).

It can be concluded, due to the isotope patterns, that the parent ion for the Cl-BEN•2HCl in water (fig 4.2.5) is similar to that of the Cl-BENH in methanol (fig 4.2.7). But it is observed that the manner in which the fragmentation in the mass spectrum of Cl-BEN•2HCl in water occurs is more complicated and complex below m/z 250 when compared to the Cl-BENH in methanol. This is because of the nature of the solvent used for each analysis, and the intense signals observed in the Cl-BEN•2HCl spectrum are the indication of stabilisation of the fragmentations due to the use of water as solvent.

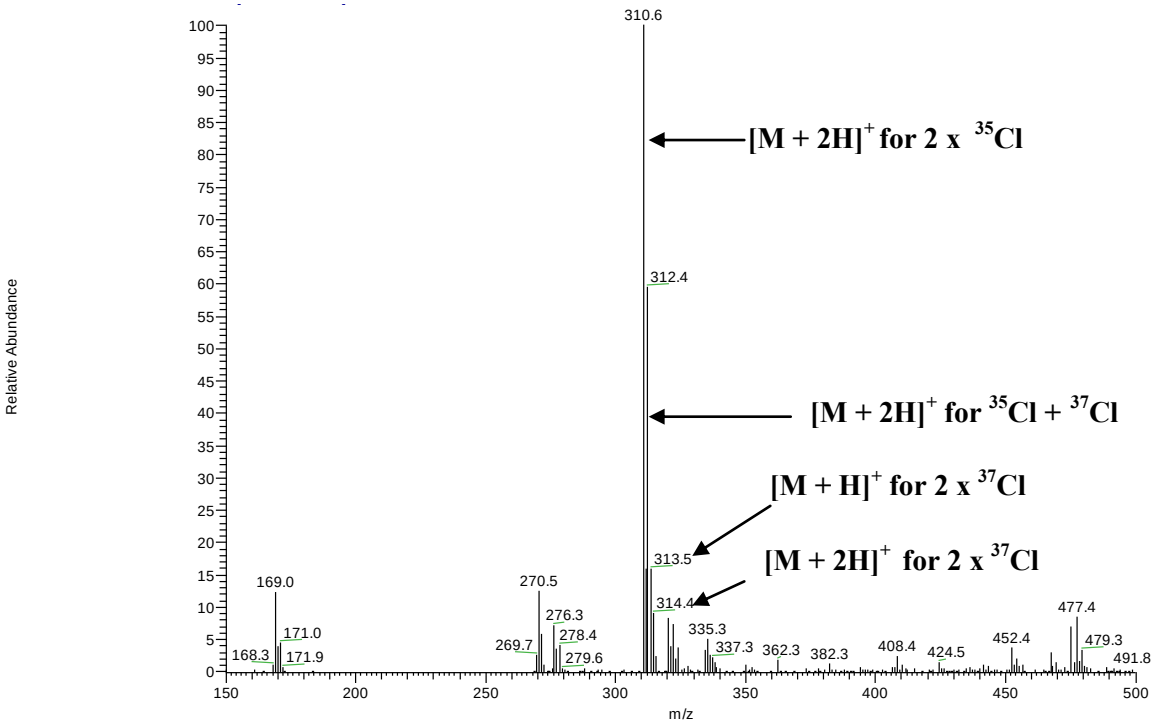


Figure 4.2.7 ESI spectrum obtained for Cl-BENH in methanol

The mass spectrum of the N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane shows three signals which correspond to the isotope pattern at m/z 398.3, m/z 400.2 and m/z 402.1. The signal at m/z 398.3 represents $[M + 2H]^+$ for two ^{79}Br and the alternative explanation is $[M]^+$ for ^{79}Br and ^{81}Br. The molecular peak at m/z 400.2 corresponds to $[M + 2H]^+$ for ^{79}Br and ^{81}Br and the alternative explanation for this signal is $[M]^+$ for two ^{81}Br. However the alternative explantions are unlikely, given that there is no signal at m/z 396 due to $[M]^+$ for two ^{79}Br. The parent ion at m/z 402.1 is due to $[M + 2H]^+$ for two ^{81}Br. From the mass spectrum of the amine ligand it can be concluded from the relative heights of the peaks that the ratio of the isotope pattern is 9:6:1, typical of dibrominated molecule [3].

The fragments at m/z 169.8 and m/z 212.7 correspond to the cleavage of the N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane as shown in figure 4.2.8.

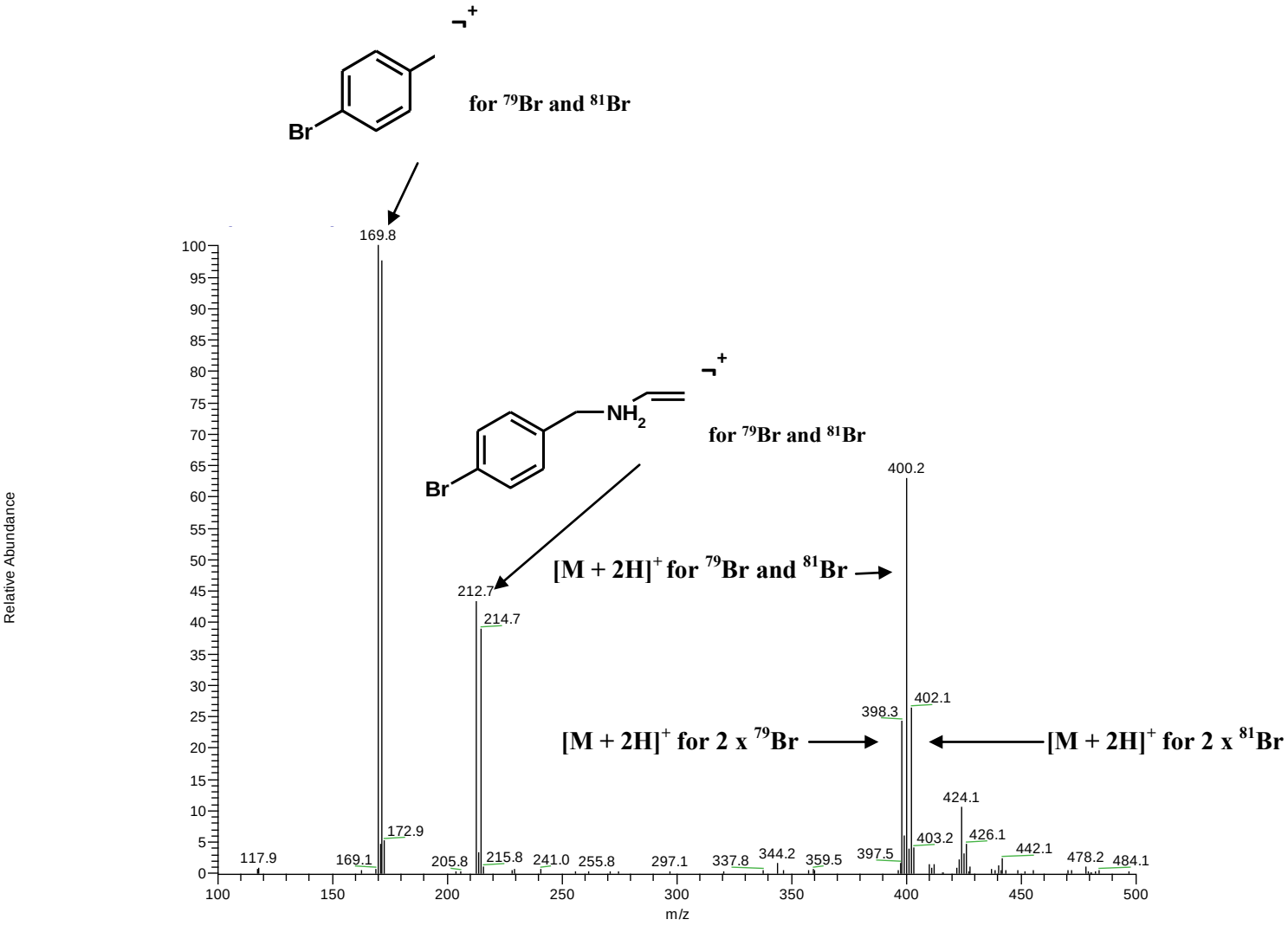


Figure 4.2.8 ESI spectrum obtained for Br-BENH in methanol

4.2.4 Comparison between the mass spectral patterns of the ligands N, N'-(aryl)benzaldiamine ligands and N, N'-(aryl)benzaldiamine dihydrochloride salts

From the mass spectrometry studies of N, N'-(aryl)benzyaldiamine ligands and N, N'-(aryl)benzyaldiamine salts (tables 3.2 and 3.3) it may be concluded that base peak for the imines and the amine ligands were [M + H] and $[M + 2H]^+$. This shows that these ligands easily pick up protons. This is due to the lone pair electrons on the nitrogen atom of the molecule. The studies indicate that the base peak of the amine salts is the already existing [M

+ 2H]$^+$ of the amine salts. This implies that the N, N'-(aryl)benzaldiamine salts are very stable in the mass spectrometer compared to the N, N'-(aryl)benzyaldiamine ligands.

4.2.5 Comparison between the mass spectral patterns of the N, N'-(aryl)benzaldiamine dihydrochloride salts analogues

The distinct difference observed between the fragmentation pattern in the mass spectra of the N, N'-*bis*(4-bromobenzyl)-1, 2-diaminoethane dihydrochloride (fig 4.2.6) and N, N'-*bis*(4-chlorobenzyl)-1, 2-diaminoethane dihydrochloride ligands (fig 4.2.5) may be associated with the differences in the electron clouds of the two halogen atoms, chlorine and bromine. Bromine is more polarasible compared to the chlorine as its electron shell is larger than that of chlorine. This will alter the stability of the ions produced in the mass spectrometer, so explaining the difference in their respective patterns.

The ESI mass spectra of the amine ligands in methanol solutions, Cl-BENH and Br-BENH (fig 4.2.7 and 4.2 8) exhibit some differences in the fragmentation pattern. In the mass spectrum of Br-BENH in methanol, two sharp peaks at m/z 169.8 and m/z 212.7 are observed, while in the mass spetrum of Cl-BENH no intense signals are observed in that region. This is the result of the bromo analogue being more polarisible than the chloro analogue.

4 .3 ^{1}H- and ^{13}C-NMR studies

4.3.1 Linear Free Energy Relationship and NMR chemical shifts

NMR chemical shifts have been used to exploit and evaluate the electronic effect (inductive, resonance, steric and polar effects) produced by the substituents, because of the important information they provide to study perturbations in electronic density, especially with ^{1}H- and ^{13}C-NMR. Electron density is the measure of the probability of an electron released by a

substituent (donating or withdrawing groups) being present at a specific location within the molecule.

The effects of the substituents may be monitored using ^{1}H- and ^{13}C-NMR substituent chemical shifts based on the principles of linear free energy relationships (LFER) comprising the single substituent parameters (SSP) or dual substituent parameters (DSP). This is achieved by correlating the substituent parameters (SSP or DSP) with the ^{13}C- or ^{1}H-NMR shifts to obtain a correlation coefficient and the resultant trend. The slope of the trend-line indicates the extent to which the spectroscopic properties are influenced by the substituent.

Single substituent parameters can be ascribed by the classical Hammett equation while the dual substituent parameters are used in determining both the inductive and resonance effect transmitted by the substituent within the molecule. The Hammett equation [4, 5] is given in equation 1. The equation represent a combination of inductive and resonance effects.

$$\log(k / k_0) = \rho\zeta \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Dual substituent parameters, such as Swain [6] and Williams & Norrington [7] allow the separation and identification of the relative contributions of inductive and resonance electronic influence by the substituent on chemical reactivities and physical properties. These dual substituent parameters are an example of the extension of the Hammett equation and are described using equation 2.

$$\text{Log}(k / k_0) = \rho_I\zeta_I + \rho_R\zeta_R \quad \ldots\ldots\ldots\ldots\ldots \quad (2)$$

A negative ρ value is an indication of a positive charge within the ring and positive values indicate resonance stabilization. When the signs of ρ_I and ρ_R are opposing each other, Taft [8]

explains this as an indication of a charge migration going from reactant to the transition state, for example a positive charge moving towards the substituent.

4.3.2 ^{1}H- and ^{13}C-NMR studies of N, N'-(aryl)benzaldiimine ligands

In this section, the attention will be on the effect produced by substituents, this will be done by using the slope of the resultant trend line.

The spectra were all run in deuterated chloroform. The ^{1}H- and ^{13}C-NMR spectral data for the assignment of the carbon and proton signals was followed using figure 4.1. Chemical shifts for the Schiff bases together with the relevant assignment are provided in tables 3:9 and 3:10. The data obtained supports the structures presented in scheme 2:1.

From the spectroscopic data obtained from the ^{13}C-NMR studies of the N, N'-(aryl)benzaldiimine ligands, given in table 3.10, it can be concluded that the electron-donor substituents {4-CH_3, 4-OCH_3 and 4-$N(CH_3)_2$} on the benzene ring of the Schiff base cause an increase of electron density at C-5 and C-3 (upfield shifts; see chapter 3, table 3.10). The same electron donor substituents decrease the electron density at C-6 (downfield shifts) as shown in table 4.1. The spectroscopic data from the ^{1}H-NMR studies (table 3.11) indicate that the electron donor substituents at *para*-positions of the benzene ring of the Schiff base cause an increase of electron density at H-5, H-2, and H-1(except for the 4-CH_3). The same substituents cause a decrease of electron density at H-4. This means that the sequence of the electron density for the hydrogen atom is as follows: H-5 >> H-4, H-2 >> H-4, H-2 >> H-1 and H-1 > H-4.

The manner in which the electron donor substituents influence the chemical shifts of the ring carbon and ring protons of the N, N'-(aryl)benzaldiimine ligands was found to be similar to the behaviour of the ring protons and ring carbons of the Titanocene benzoates [9].

Table 4.1 Trends of the electron donor substituents on the N, N'-(aryl)benzyaldiimine ligands

	6	5	4	3	2	1
^{1}H	–	↑	↓	–	↑	↑
^{13}C	↓	↑	↓	↑	↑	↓

↑ = Upfield shift, ↓ = Downfield shift

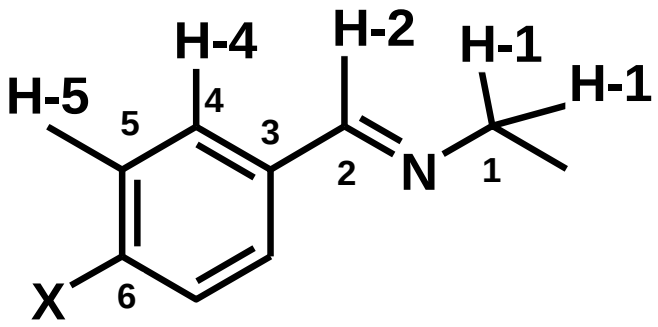


Figure 4.3.1 Numbering system used for the Schiff bases

Early work has shown that there is no simple relationship that exists between the proton or carbon chemical shifts and the substituents, this cannot easily be explained by the relationship that exists between the chemical shifts and the local electron densities [10].

From the above observation it can be deduced that the electronic effect subjected onto the carbon and hydrogen atoms of the N, N'-(aryl)benzaldiimine ligands by the donor substituent may not be clearly understood by using Hammett parameters only, this shows the need for the use of dual parameters, because there is no simply general relationship that exists between the ^{1}H- and ^{13}C-NMR chemical shifts and the local electron density .

The opposite trends were observed for electron-acceptor substituents as compared to those of electron-donor substituents. Since the Hammett parameters [3, 4] use the combined inductive and resonance effect, dual substituent parameters such as those of Swain [5] and of Williams & Norrington [6] may be suitable to measure the separately the contributions of inductive and resonance effect on the N, N'-(aryl)benzaldiimine ligands.

The Hammett constants are derived from the protonation of a substituted benzoic acid and Swain constants are also based on the aromatic system. Both these parameters are applicable in monitoring the effect of the substituents on the carbon atoms of aromatic ring of the Schiff base ligands. The Williams & Norrington parametes are based on the aliphatic system and should be more applicable to understand the electronic effect on the side chain of the Schiff base ligands.

According to the size of the correlation coefficient obtained between the correlation of the ^{1}H-NMR chemical shifts and the three substituent parameters {(Hammett (ζ_{ρ}), Swain (ζ_{R}) and Williams & Norrington (ζ_{R}))}, the results indicate that there is a positive resonance correlation at positions H-5, H-2 and H-1 (see table 4.2), this implies that the conjugation of the electrons from the substituent move up to the nitrogen atom (see table 4.2 and figure 4.3.2).

In addition, looking at the sign of the constants ρ from table 4.2, similar observations are observed. All the parameters, Hammett (ζ_{ρ}), Swain and Williams & Norrington suggest a conjugation of the electrons up to the nitrogen atom for the correlation of protons.

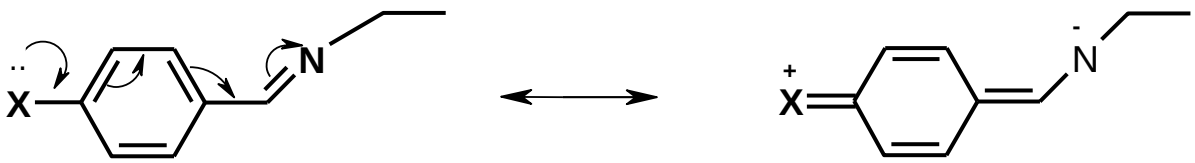


Figure 4.3.2 The delocalisation of electrons to the imine nitrogen

Table 4.2 Correlation coefficients for protons derived from the H-NMR data of N, N' -(aryl)benzyaldiimine ligands and various substituents parameters

Parameters	Correlation coefficient			
	H-5	H-4	H-2	H-1
Hammett (ζ_ρ)	0.9478	0.3334	0.7988	0.7826
Swain (ζ_I)	0.6414	0.4611	0.1303	0.1629
Swain (ζ_R)	0.9048	0.1577	0.7822	0.7617
Williams & Norrington (ζ_I)	0.6652	0.4573	0.4812	0.4661
Williams & Norrington (ζ_R)	0.9162	0.1543	0.8295	0.8142

Table 4.3 Correlation coefficients for carbons derived from the ^{13}C-NMR data of N, N'-(aryl)benzyaldiimine ligands and various substituents parameters

Parameters	Correlation coefficient					
	C-6	C-5	C-4	C-3	C-2	C-1
Hammett (ζ_ρ)	-0.0214	0.6389	-0.0119	0.9575	-0.6715	-0.2499
Swain (ζ_I)	0.2552	-0.2616	0.7491	0.1085	-0.8969	0.0009
Swain (ζ_R)	-0.4584	0.8027	-0.3057	0.9747	-0.3705	-0.2967
Williams & Norrington (ζ_I)	-0.0019	0.2091	0.5376	0.6063	-0.9644	-0.1215
Williams & Norrington (ζ_R)	0.4795	0.7999	-0.4154	0.9771	-0.2817	-0.2812

While for the carbon atoms of the N, N'-(aryl)benzaldiimine ligands no positive resonance correlation is observed up through the side chain using the three substituent parameters {(Hammett (ζ_ρ), Swain (ζ_R) and Williams & Norrington (ζ_R))}, see table 4.3. The only positive resonance correlation observed for the carbon atoms is at C-5 and C-3, this is expected due the distance between the substituents and positions five and three. The

correlation analysis shows a negative inductive effect at C-2, and this was better described by Williams & Norrington parameters. This is not suprising, because the parameters are derivered from aliphatic system. The results for the carbon chemical shifts indicate that the phenyl ring is not parallel to the imine bond, and that there is no conjugation into the side chain. Clearly the apparent conjugation indicated by the proton spectral must be due to the through space interaction.

Using both the size and sign of the correlation coefficient obtained from the correlation between the proton chemical shifts and the substituent parameters, evidence of the conjugation observed in the proton spectrum, may be associated with the flexibility of the molecule. A model of the system shows that the rotation of the N, N'-(aryl)benzaldiimine ligand about the methylene bridge brings H-1 and H-2 under the benzene ring, see figure 4.3.3. This would allow the H-2 and H-1 to be affected by the electron cloud of the benzene ring and increasing the inductive effect through space, as shown in figure 4.3.3. From the statements mentioned above it can be concluded that there is no electron delocalization from the substituent up to the imine group. This shows that the phenyl group is not parallel with the azomethine functional group [11]. The absence of the through space inductive effect within the carbon atoms is due to the distance between the carbon atoms (C-2 or C-1) and the electron cloud generated by the benzene ring. This system should possibly be examined more through molecular modelling studies as it might give greater insight into what is happening here.

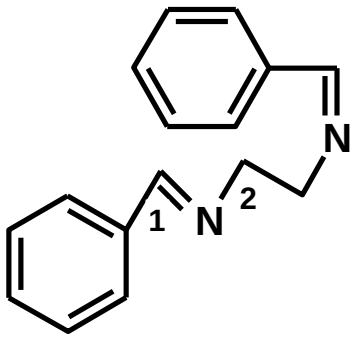


Figure 4.3.3 The rotation of the imine ligand about the methylene

4.3.3 ^{1}H- and ^{13}C-NMR studies of N, N'-(aryl)benzaldiamine ligands

The spectra were all run in deuterated chloroform. The ^{1}H- and ^{13}C-NMR spectral data for the assignment of the carbon and proton signals was followed using figure 4.1. Chemical shifts for the N, N'-(aryl)benzaldiamine ligands together with the relevant assignment are provided in table 3:12.

The correlation analysis between the hydrogen atoms and substituent parameters, shows that the use of Hammett parameter decreases the resonance correlation as from position 5 (H-5) up to N-H. Similar observations were found with Swain and Williams & Norrington parameters (see table 4.4). This implies that the reduction of the imine bond decreases the possibility of the suggested through space inductive effect observed in the N, N'-(aryl)benzaldiimine ligands.

Table 4.4 Correlation coefficients for protons derivered from the ^{1}H-NMR data of N, N'-(aryl)benzaldiamine ligands and various substituents parameters

Parameters	Correlation coefficient				
	H-5	H-4	H-2	H-1	N-H
Hammett (ζ_{ρ})	0.9278	0.5838	0.5468	-0.5519	-0.0070
Swain (ζ_{I})[b]	0.4031	0.4932	0.3861	-0.1248	-0.5718
Swain (ζ_{R})[c]	0.8216	0.4016	0.4026	-0.5698	0.1977
Williams & Norrington (ζ_{I})	0.7429	0.5746	0.5179	-0.5050	-0.3722
Williams & Norrington (ζ_{R})	0.8276	0.4363	0.4265	-0.4559	0.2676

Looking at the signs of the constants ρ and the size of the correlation coefficient, using the three substituent parameters, the correlation of the protons for the N, N'-(aryl)benzaldiamine ligands suggest that there are two different effects stabilising the aromatic ring and the side chain. The analyses from the three parameters (the signs of the constants ρ) indicate that there is conjugation of electrons within the ring, but not up to the nitrogen atom (same signs for ρ_I and ρ_R). These observations are in agreement with the results obtained when using the size of the correlation coefficient. The size of correlation coefficient, indicates that at H-5 there is a pronounced resonance effect (r = 0.8216 and r = 0.8276), this was better described using Swain (ζ_R) and Williams & Norrington (ζ_R) parameters. While a moderate inductive effect is observed at H-2 and H-1 (r = 0.5179 and r = -0.5050), this was described better with Williams & Norrington (ζ_I) parameters. This is not surprising given that Williams & Norrington (ζ_I) parameters are a better model to understand the effect of the substituents on the side chain of the molecule. Again Swain (ζ_I) parameters show that at nitrogen atom (N-H) there is a negative inductive effect (r = -0.5718). From the above statement it can be concluded that the benzene ring is not co-planar with the amine bond.

The correlation analysis for the carbon atoms show a good correlation between C-3 and Hammett parameters, a similar effect is observed between C-3 and Swain (ζ_R) and Williams & Norrington (ζ_R) parameters (see table 4.5). Again the analysis indicates that there is a moderate positive resonance correlation between C-5 and the three parameters {Hammett, Swain (ζ_R) and Williams & Norrington (ζ_R)}. The signs of the constants ρ and the magnitude of correlation coefficient for all the three substituent parameters suggest two different effects are exerted in benzene ring and side chain. Swain (ζ_R) and Hammett (ζ_ρ) parameters suggest that the conjugation moves up to C-3 (r = 0.9536, r = 0.9153). These observations are in agreement with the results found when using Williams & Norrington (ζ_R) parameters (r = 0.9253 for C-3). At position C-1 an inductive effect is observed (r = 0.7202, Swain (ζ_I)). The Hammett parameters suggest that the delocalization of the electrons from the substituents only occurs within the benzene ring. This implies that there is no conjugation of the electrons from the substituent up to the nitrogen atom, and thus indicates no parallelism between the benzene ring and the amine bond, but there is resonance within the ring.

Table 4.5 Correlation coefficients for carbons derivered from the ^{13}C-NMR data of N, N'-(aryl)benzaldiamine ligands and various substituents parameters

Parameters	Correlation coefficient					
	C-6	C-5	C-4	C-3	C-2	C-1
Hammett (ζ_ρ)	-0.3242	0.6054	0.1542	0.9536	-0.3443	0.08766
Swain (ζ_I)	0.2869	-0.2632	0.7558	0.2402	-0.1814	0.7202
Swain (ζ_R)	-0.4752	0.7671	-0.1249	0.9153	-0.3294	-0.2122
Williams & Norrington (ζ_I)	0.0069	0.1790	0.6288	-0.6653	-0.4091	0.4206
Williams & Norrington (ζ_R)	-0.4900	0.7717	-0.2353	0.9253	-0.2144	-0.1906

4.3.4 ^{1}H-NMR studies of N, N'-(aryl)benzaldiamine dihydrochloride salts

The spectra were all run in deuterated dimethylsulfoxide. The ^{1}H-NMR spectra data for the proton signals was followed using figure 4.3.1. Chemical shifts for the N, N'-(aryl)benzaldiamine dihydrochloride ligands together with the relevant assignment are provided in table 3.11.

Table 4.6 Correlation coefficients for protons derivered from the ^{1}H-NMR data of N, N'-(aryl)benzaldiamine dihydrochloride salts and various substituents parameters

Parameters	Correlation coefficient				
	H-5	H-4	H-2	H-1	N-H_2
Hammett (ζ_ρ)	0.9701	0.6590	0.0743	0.1944	-0.0482
Swain (ζ_I)	0.5626	0.4159	-0.1516	-0.0307	-0.2546
Swain (ζ_R)	0.9406	0.5686	0.1601	0.2499	0.0925
Williams & Norrington (ζ_I)	0.6817	0.4920	-0.0961	0.0351	-0.1997
Williams & Norrington (ζ_R)	0.8775	0.5640	0.2438	0.3001	0.1555

The correlation analysis studies of the proton chemical shifts of the N, N'-(aryl) benzyaldiamine dihydrochloride salts show a good correlation (see table 4.6) between H-5 and the three parameters {Hammett (ζ_ρ), Swain (ζ_R) and Williams & Norrington (ζ_R)}. This is expected because of the short distance between the substituent and the benzene ring. A moderate positive resonance correlation is also observed at the H-4 for the three parameters.

Looking at the signs of the values of ρ and the magnitude of the correlation coefficient, all three parameters are in agreement that the resonance effect is more pronounce within the benzene ring (r = 0.9701, r = 0.9406 and r = 0.8775 for H-5 and r = 0.6590, r = 0.5686 and r = 0.5640 for H-4). Hammett parameters suggest that the conjugation of electrons from the substituent move up to H-2 (positive signs of the values of ρ). Both Swain and Williams & Norrington parameters contradict Hammett parameters (signs of ρ_I and ρ_R). These two parameters suggest that the conjugation of the electrons do not reach side chain, H-2. This is expected, because Hammett parameters give a combination of the two electronic effects, resonance and inductive effect, while the Swain and Williams & Norrington parameters separate the two effects.

From the both the size of the correlation coefficient and the signs of the values of ρ, it can be concluded that the benzene ring is not parallel to the amine salt bond and there is no through space inductive effect which is observed among the imines. The reduction or disappearance of the through space inductive effect might, when compared to the free amines, be restricted by the solvent effect (deuterated dimethyl sulfoxide). The presence of solvent might have hindered the effect of the electron cloud of the benzene ring onto the H-1 and H-2.

4.3.5 ^{1}H- and ^{13}C-NMR studies of N, N'-*bis*(cinnamaldiimine) ligands

The spectra was run in deuterated chloroform. The ^{1}H- and ^{13}C-NMR spectral data for the assignment of the carbon and proton signals was followed using figure 4.3.4. Chemical shifts for the N, N'-*bis*(cinnamaldiimine) ligands together with the relevant assignment are provided in table 3:14.

Due to the absence of a series of substituted N, N'-*bis*(cinnamaldiimine) ligands, no correlation analyses were made. However, from the experimental data in table 3.14 it can be concluded that the presence of the electron donor substituent {4-$N(CH_3)_2$} at the para-position of the Schiff base decreases the electron density of carbon and hydrogen atoms at positions, H-4, C-2, C-2b and C-4. This is expected, because of the possible overlapping of the orbitals containing lone pair of electrons on the azomethine group with the π-orbitals of the π system of the alkene group. The trend effect of the substituent {4-$N(CH_3)_2$} is presented in table 4.7

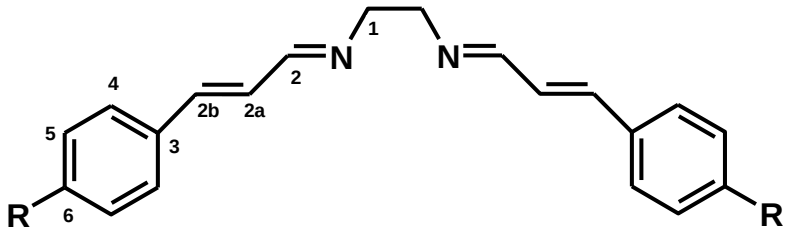


Figure 4.3.4 Numbering system used for the N, N'-*bis*(cinnamaldiimine) ligand

Table 4.7 Trends of of the electron donor substituent on the N, N'-*bis*(4-dimethyl aminocinnamaldehyde)-1, 2-diiminoethane

		6	5	4	3	2b	2a	2	1
$N(CH_3)_2$-CA_2EN	^{1}H	—	↓	↓	—	↑	↑	↑	↑
	^{13}C	↓	↑	↓	↑	↓	↑	↓	↑

↑ = Upfield shift, ↓ = Downfield shift

4.3.6 Comparison between ^{13}C-NMR studies of CA_2EN and BEN ligands.

From the nuclear magnetic resonance studies of the Schiff bases, both the $N(CH_3)_2$-CA_2EN ligands and $N(CH_3)_2$-BEN ligands, it can be concluded, that the presence of the conjugated double bond within the system results in an increase of an electron density at C-6, C-4 and C-2 for the $N(CH_3)_2$-CA_2EN ligand and hence the signals of these are shifted downfield.

While at C-5, C-3 and C-1 positions the electron density decreases and these carbon atoms are observed in the upfield region.

The change in chemical shift for the ligands are give in table 4.8. The alkene group (position 2b) highly affect the side chain of the Schiff base ligand and C-4. As observed in table 4.8, C-2 of the Schiff base, CA_2EN appears downfield; while the same carbon for Schiff base, $N(CH_3)_2$-CA_2EN is observed upfield. Similar findings were observed at C-1. The large shift of 0.86 and 0.84 for C-4 and C-2 reflect the conjugation experienced by the imine carbon and C-4, especially when compared to the smallest shifts (0.23) expected for C-1.

Table 4.8 Change in substitutent chemical shift values for CA_2EN and BEN ligands

No	Ligand	C-6	C-5	C-4	C-3	C-2	C-1
7	$N(CH_3)_2$-BEN	20.83	-17.36	1.05	-12.05	-0.66	0.06
22	$N(CH_3)_2$-CA_2EN	21.81	-17.11	0.21	-12.41	0.20	-0.17
	(ΔSCS)	0.02	0.25	0.84	0.44	0.86	0.23

Change SCS (ΔSCS) = $SCS_{(subst.)}$ - $SCS_{(unsubst.)}$

4.4 Electronic spectral studies

The Ultraviolet and visible spectrometer is an important analytical instrument in the modern day laboratory. It is used to understand the behaviour of molecular electrons when they are exposed to light having an energy that matches possible electronic transition within the organic and inorganic molecules.

The spectra of the Ultraviolet-visible-NIR consist of three different regions, the ultraviolet region (200 – 380 nm), the visible region (ranging from blue through to red, 430 nm to 750 nm) and the near infrared region (800 nm – 2000 nm), as shown in figure 4.4.1.

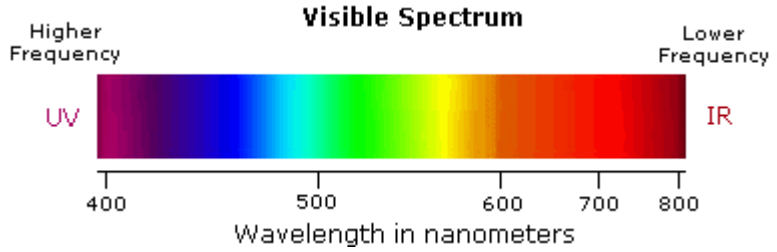


Figure 4.4.1 The Ultraviolet-visible-NIR spectrum

The UV-vis spectroscopic studies can be conducted in solid or solution state. In solution state different solvents may be used and these solvents may have little or major effect on the electronic spectra of samples. The effect of solvent on the electronic spectra of the organic and inorganic molecules is well established [12]. The nature of the solvent plays a major role in the position of the wavelength of a molecular electronic absorption band. Polar solvents such as ethanol (protic) can stabilise cations using the unshared electron pairs, and can stabilise anions by hydrogen bonding. In the case of aprotic solvents (for example chloroform), a large frequency shift can be observed on the electronic spectra of samples, due to the $n \rightarrow \sigma^*$ transition of the chloroform.

For the electronic spectral studies of the ligands and their metal complexes two solvents were used, depending on the solubility of the ligands and their metal complexes. This was done to enable easy comparison of absorption bands. The section is divided into two parts; the first part will involve the assignment of the absorption bands. The last part will focus on the elucidation of the effect of the substituent in the UV/vis spectrum of the ligands and their metal complexes.

4.4.1 The electronic spectra of the ligands and copper complexes

The solution electronic spectra of (concentration 1×10^{-4} to 1×10^{-5} mol/L) of Schiff base ligands, the amines derived from the reduction of the Schiff base ligands and the copper complexes were studied in various organic solvents of different polarities: chloroform ($CHCl_3$), ethanol (EtOH), acetonitrile (CH_3CN) and dichloromethane (DCM). The purpose of this section is to study the spectral behaviour of the Schiff bases and their complexes using

different solvents. It has been observed that the molecular structure of the compounds and the nature (polarity) of the solvent contribute to the spectral behaviour.

4.4.1.1 The electronic spectra of the N, N'-(aryl)benzaldiimine ligands

This section will focus on the interpretation of electronic spectra and the effect produced by the substituents on the HOMO and LUMO orbitals of the N, N'-(aryl)benzaldiimine ligands. This will be done by monitoring the shifts of the electronic transitions in the electronic spectra of the ligands.

N, N'-(aryl)benzaldiimine ligands were examined spectroscopically from 200 nm up to 900 nm in ethanol solution. Representative ultraviolet absorption spectra of the Schiff bases in ethanol are shown in figures 4.4.2 and 4.4.3. The visible region was omitted from figures 4.4.2 and 4.4.3 because there were no maximum absorption bands observed at the longer wavelength region. The corresponding data are also summarized for the N, N'-(aryl)benzaldiimine ligands in table 3.12.

The electronic spectra of the N, N'-(aryl)benzaldiimine ligands in ethanol showed dissimilarities in absorption bands of all the imines, this is due to the influence of the various substituents at the *para*-position of the benzene ring and the effect of the solvent. For the N, N'-(aryl)benzaldiimine ligands, four to five absorption bands are expected, since the ligand has two different types of π electrons, lone pairs and ζ electrons. The numbers of absorption bands for each electronic spectrum of the Schiff bases depend on the nature of the substituent at the *para*-position.

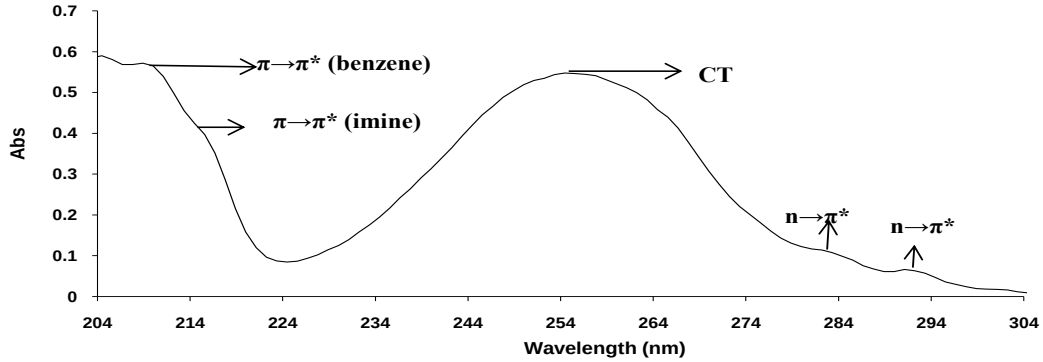
The absorption bands expected for the N, N'-(aryl)benzaldiimine ligands, include two $\pi \rightarrow \pi^*$ transitions, $n \rightarrow \pi^*$ transitions and intramolecular charge transition [13, 14]. The whole spectrum is expected in the ultraviolet region.

In the electronic spectra of the Schiff bases in ethanol, the first $\pi \rightarrow \pi^*$ transition is due to excitation of the π electrons of the aromatic ring, and the other $\pi \rightarrow \pi^*$ transition is due to the presence of unpaired electrons in the azomethine group [13, 14]. Schiff bases also exhibit a charge transfer transition. Since it has been observed that the polar solvents enhanced bathochromic shifts [15], the focus will on be on the electronic effect of the substituent in ethanol.

The electronic spectra of N, N'- *bis*(4-chlorobenzyl)-1, 2-diiminoethane, N, N'- *bis*(benzyl)-1, 2-diiminoethane and N, N'- *bis*(4-methylbenzyl)-1, 2-diiminoethane ligands in ethanol are shown in figure 4.4.2 respectively. As observed from the spectra of Cl-BEN, H-BEN and CH_3-BEN ligands in ethanol, the absorption bands ($\pi \rightarrow \pi^*$ transition, CT and $n \rightarrow \pi^*$ transition) of the Cl and CH_3 analogues suffered bathochromic shifts when compared to the absoption bands of H-BEN in ethanol solution. This is not surprising, because polar solvents enhances bathochromic shifts. This indicate that the HOMO state of these absorption bands are destabilized relative to LUMO state. This indicate that the effects exerted by these groups (4-Cl and 4-CH_3) on the absorption bands of the N, N'-(aryl)benzyaldiimine system in ethanol solution are similar.

The spectrum of the nitro-substituted Schiff base in ethanol is given in figure 4.4.3 and several absorption bands are observed. These absorption bands consist of the three $\pi \rightarrow \pi^*$ transitions, two $n \rightarrow \pi^*$ transitions, two $n \rightarrow \sigma^*$ transitions and two charge transfer bands (within the Schiff base, the nitro functional group). The three $\pi \rightarrow \pi^*$ transitions are due to the azomethine group, benzene ring and the extra conjugated double bond from 4-NO_2 subtituent. The $n \rightarrow \pi^*$ transitions are the result of the lone pair of electrons from 4-NO_2 subtituent and the azomethine group [13, 14, 16, 17].

(a)



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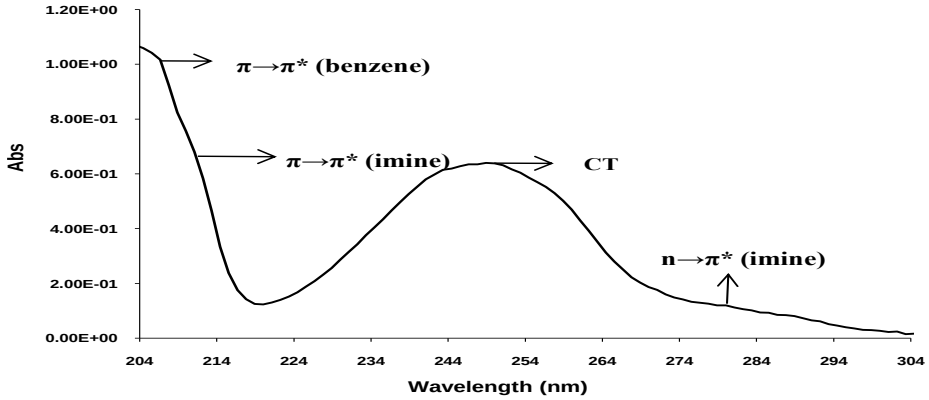

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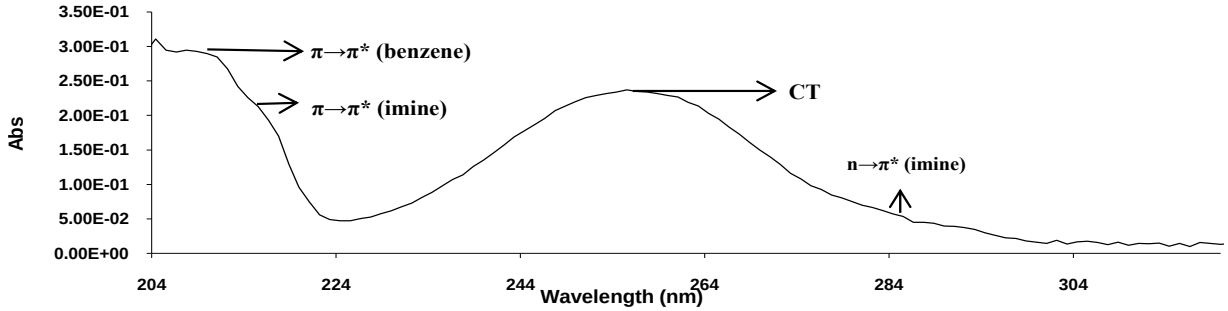

Figure 4.4.2 Ultraviolet absorption spectra of ligands, (a) Cl-BEN, (b) H-BEN and (c) CH_3-BEN in EtOH

In the electronic spectra of N, N'- *bis*(4-nitrobenzyl)-1, 2-diiminoethane ligand, the three $\pi \rightarrow \pi^*$ transitions due to the benzene ring, nitro-substituent and azomethine group are observed between 216 nm to 238 nm region. While one charge transfer band is observed around 282 nm and the other one is masked. The two $n \rightarrow \pi^*$ transitions due to the nitro substituent and imine group are observed in the 321 nm to 324 nm region. The two $n \rightarrow \sigma^*$ transitions absorb in the far-ultraviolet region (10-200 nm), as the result of this they can not be observed.

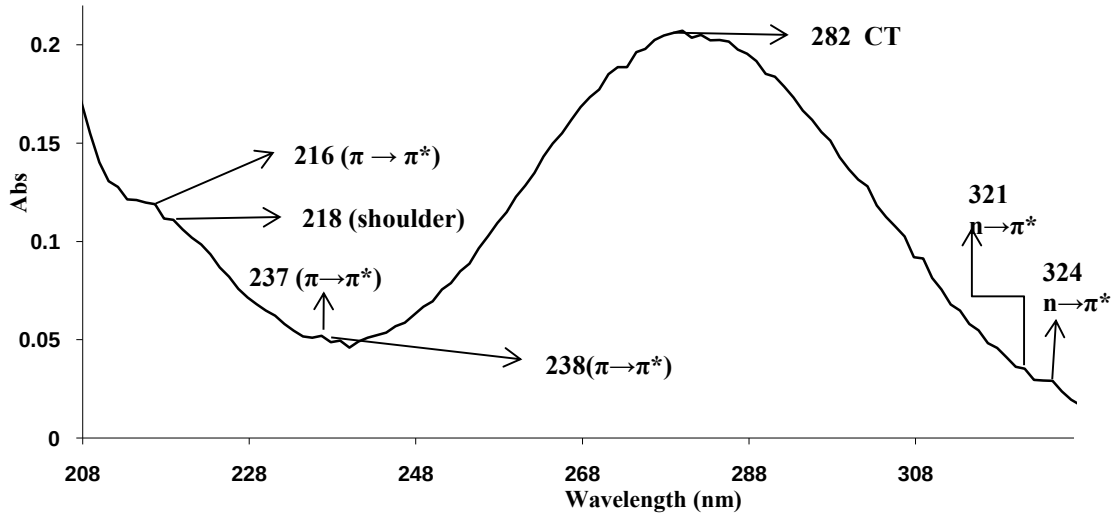

Figure 4.4.3 Ultraviolet absorption spectrum of NO_2-BEN in EtOH

Some general conclusions from the spectra of all the ligands can be made. From the analysis of the spectroscopic data collected in table 3.12 of the Schiff bases in ethanol, it can be concluded that the absorption bands in the wavelength range 202 – 216 nm are due to the excitation of the π electrons of the benzene ring [15]. The results indicate that these bands are sensitive to both the nature of the substituent attached to the benzene ring and the polarity of the solvent. The data show that the presence of the electron acceptor groups at the *para* position of the Schiff base and the use of polar solvent shifts the $\pi \rightarrow \pi^*$ transitions (benzene) to longer wavelength. This implies that both the solvent and the electron-acceptor groups stabilize the excited state π* (LUMO) relative to the ground state (HOMO) [15, 16]. Electron-donor substituents {4-CH_3 and 4-OCH_3, but not for 4-$N(CH_3)_2$} shift the absorption bands towards longer wavelength (fig 4.4.4), relatively destabilizing the excited state π* (LUMO), this results in a smaller energy gap between the π orbital to π* orbitals of the benzene ring.

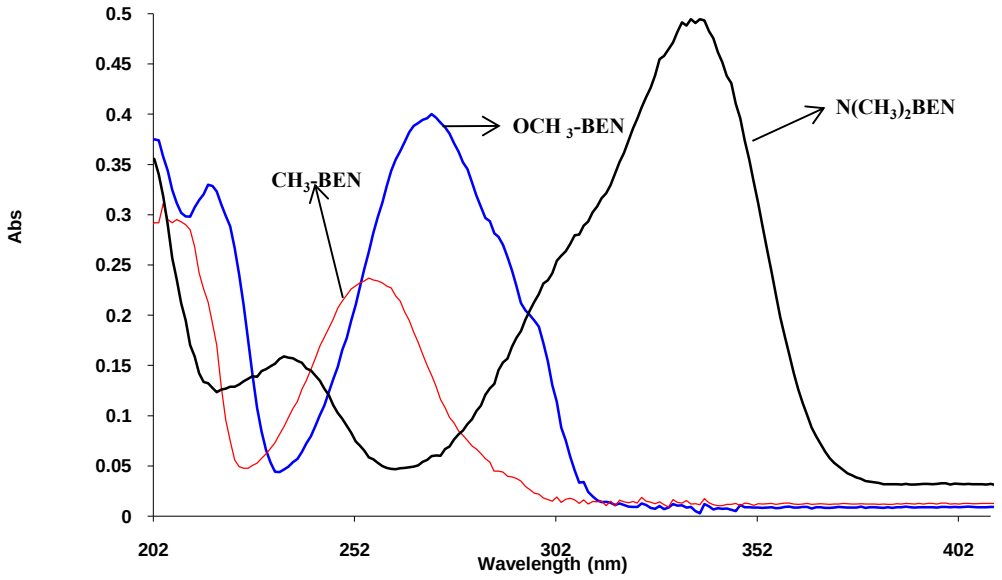

Figure 4.4.4 Ultraviolet absorption spectra of ligands of CH_3-BEN, OCH_3-BEN and $N(CH_3)_2$-BEN in EtOH

The weak absorption bands between 211 to 237 nm in ethanol solution (fig 4.4.4) may be assigned to the $\pi \rightarrow \pi^*$ transition of the azomethine group [18]. The electronic spectroscopic data show that the electron-donor substituents decreases the energy gap between the π and π^* orbital of the imine group destabilizing the HOMO relative the LUMO.

The strong absorption bands within the range 247 to 336 nm are due to the charge transfer bands [15]. These bands are more sensitive to solvents and also to the nature of substituent. Since the spectroscopic data of these absorption bands are non-linear (fig 4.4.4 and table 3.15), no correlation was conducted.

The bands located in the range 283 to 289 nm correspond to $n \rightarrow \pi^*$ transition due to the azomethine group. The effect exerted by donor and withdrawing substituents on $n \rightarrow \pi^*$ transition are non-linear (fig 4.4.4 and table 3.15) and no correlation analysis was conducted on these transitions.

Since the spectroscopic data obtained from the electronic spectra of the N, N'-(aryl)benzaldiimine ligands in ethanol solution was non-linear (except for the π→π* transition of the benzene ring fig 4.4.5), no further studies were made for these absorption bands using correlation analysis and the non-linearlity of the experimental data for CT and n→π* transition are shown in figures 4.4.6 and 4.4.7. The figures show that the benzene ring (fig 4.4.5) is behaving as expected. There is a difference of about 12 wave-numbers between the most electron donating and the most electron withdrawing group. The π→π* transition of benzene ring is not significantly affected by the subtituents and they behave as expected (figure 4.4.5).

The plot of charge transfer transitions (fig 4.4.6) shows that there is a difference of about 75 wavenumbers between the most electron donating and most electron withdrawing group, while the plot of n→π* transition shows a red shift for both the most electron donating and the most electron withdrawing substituent(fig 4.4.7). The red shift of the n→π* transition might be related to the behaviour of the charge transfer for the imines in ethanol.

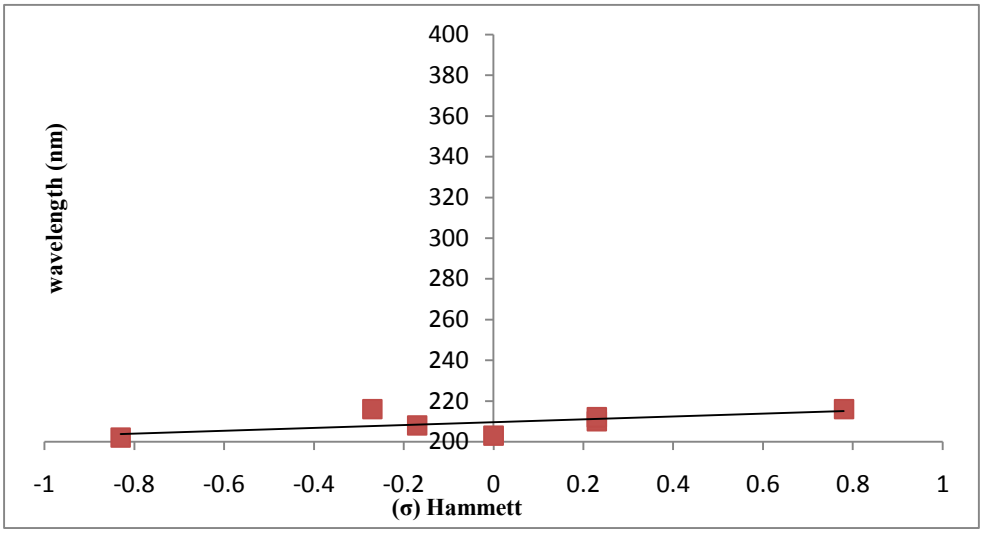

Figure 4.4.5 Plot of wavelength (nm) versus Hammett σ values for π→π* transition of benzene ring for Schiff bases in EtOH solution

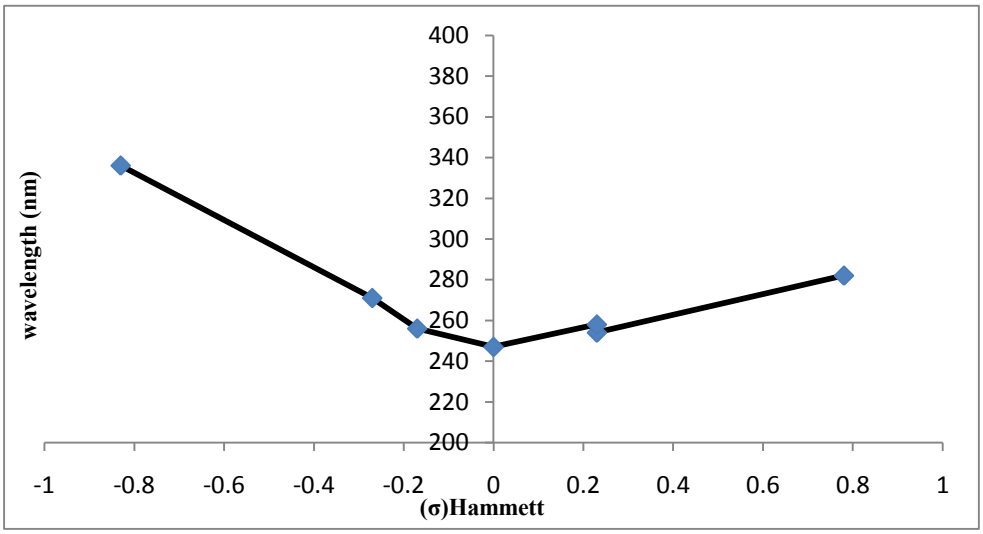

Figure 4.4.6 Plot of wavelength (nm) versus Hammett σ values for charge transfer transitions for Schiff bases in EtOH solution

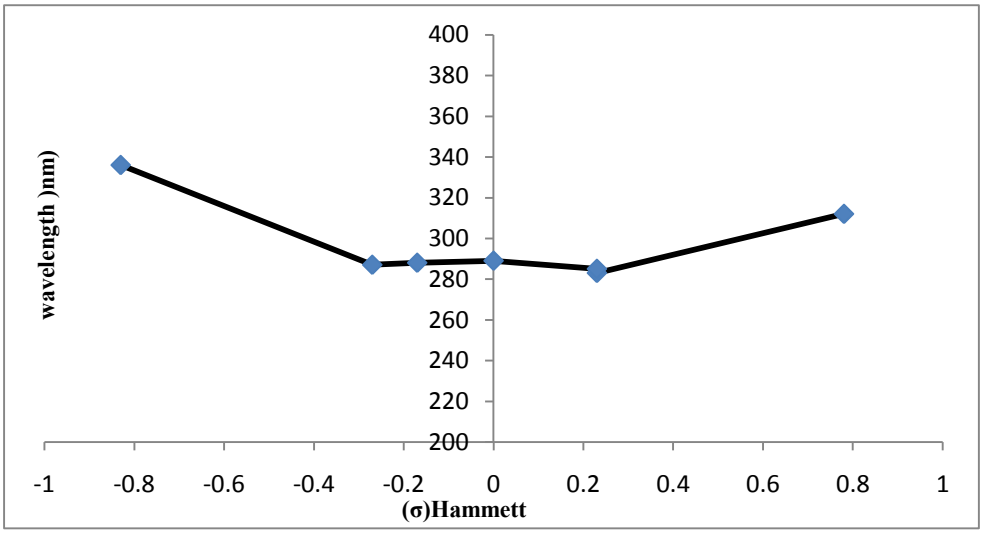

Figure 4.4.7 Plot of wavelength (nm) versus Hammett σ values for n→π* transition for Schiff bases in EtOH solution

4.4.1.2 The electronic spectra of the N, N'-(aryl)benzaldiamine ligands and their copper(II) halide complexes

This section focuses on the interpretation of the electronic spectra, and the effect of the substituents on the spectra. The results obtained are then used to determine the likely geometry of the complexes. This was done by comparing the spectra of the free ligands with the spectra of the copper(II) complexes. The discussion has been restricted to those complexes whose composition have been confirmed by microanalyses.

The electronic spectral studies of the ligands (R-BENH) and their copper(II) dihalide complexes {($Cu(R\text{-}BENH)X_2$)} were recorded in the 200 nm - 900 nm range in ethanol and chloroform solutions respectively. The corresponding electronic spectroscopic data including the molar absorption coefficients (ε) for ligands and copper(II)-halide complexes are summarized in tables 3.16 and 3.17. The abbreviation g.c.i stands for grating change in the instrument. This is the point where the instrument changes grating, resulting in a change in the absorbance intensity readings. For all the complexes this point was observed between 350 nm to 353 nm.

The UV-vis spectra of amine ligands and their copper(II)-halide complexes show few absorption bands in the visible and ultraviolet region. For the amine ligands, three absorption bands are expected. The $\pi \rightarrow \pi^*$ (benzene), $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions and all the bands should appear in the ultraviolet region. Since the $\sigma \rightarrow \sigma^*$ transition absorbs at the far ultraviolet region which is masked by the solvent, for this study only two absorption bands will be focused on; the $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions.

The $\pi \rightarrow \pi^*$ transition is due to the π-electrons of the benzene ring and the $n \rightarrow \sigma^*$ transition is the results of the excitation of the lone pair of electrons of the free primary amine [13, 19]. The electronic spectra of the ligands, in ethanol and chloroform, showed two absorption bands at about 212 and 440 nm respectively [8]. Furthermore in all the electronic spectra of the N, N'-(aryl)benzaldiamine ligands in both ethanol and chloroform solutions, the $\pi \rightarrow \pi^*$ transition due to the azomethine group disappears when compared to the N, N'-

(aryl)benzaldiimine ligand. This confirms the formation of the amine bond to all the N, N'-(aryl)benzaldiimine ligands.

In the electronic spectra of the amine ligands, the absorption bands below 240 nm have high extinction coefficients in ethanol solutions, and are associated with $n \rightarrow \sigma^*$ transitions [19], because the $n \rightarrow \sigma^*$ transitions require a greater deal of energy than $\pi \rightarrow \pi^*$ transition and they can only absorb in the ultraviolet region. The absorption bands observed within the range of 260 – 272 nm in ethanol is corresponds to the $\pi \rightarrow \pi^*$ transition.

In chloroform these two absorption bands are shifted towards the longer wavelength, with the absorption band between 262 nm and 313 nm attributed to the $n \rightarrow \sigma^*$ transition of the amine group. The band between 332 nm and 448 nm corresponds to the $\pi \rightarrow \pi^*$ transition.

From the values obtained in the electronic spectra of all the ligands, it can be concluded that the energy required for each transition within the ligands is substituent depended and is affected by the nature of solvent used. As can be seen in electronic spectra of chloroform solutions, the absorption bands were even shifted to the near visible region.

4.4.1.2.1 Bromo complexes

For a copper(II) complex in a distorted tetrahedral environment there is the possibility of three types of electronic transitions, $d \rightarrow d$ trasitions; internal ligand transitions and charge transfer transitions (both metal to ligand and ligand to metal).

The UV-vis spectra of N, N'-*bis*(benzyl)-1, 2-diaminoethanedibromocopper(II) complexes in ethanol and chloroform solutions, showed five absorption bands between 231 – 852 nm. The $d \rightarrow d$ transitions are La Porte forbidden transitions (they occur within the d orbitals of the metal ion and are not allowed by the selection rules) and so are very weak and difficult to identify. These transitions are expected below 900 nm; for these copper complexes they are

found between 686 nm and 872 nm. The internal ligand charge transfer and transitions are observed below 550 nm.

In the spectra of the bromo complexes the bands observed within the range 213 - 279 nm in ethanol and chloroform solutions are ascribed to the $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions. Since the ligands, N, N'-(aryl)benzaldiimine ligands are transparent in the visible spectrum, the new absorption bands in the visible region are due to formation of the coordination compound.

The spectra of the bromo complexes show a similar pattern in the visible region of all the complexes; they consist of the absorption band at the near ultraviolet region within the range of 301 – 314 nm. Based on the facts above, the absorption bands correspond to the $N \rightarrow$ Cu(II) LMCT [20, 21]. These absorption bands are the results of a single orbitally allowed charge transfer transition, arising from the amine group [22].

The absorption bands in the range 461 – 485 nm in both ethanol and chloroform solutions they may be assigned to $Br \rightarrow$ Cu(II) LMCT , as result of the movement of non-bonding π electrons of the bromine atom from the bonding orbital of the bromide to the antibonding orbital of the copper metal [23].

The stereochemistry of the bromide complexes is suspected to be predominately distorted tetrahedral, because tetrahedral copper(II) absorbs primarily in the red and near infrared. The tetrahedral CuN_4 chromophores absorption occurs below 1000 nm, and they exhibit a single transition ($^2E \rightarrow {}^2T_2$) at relative low energy between 625 to 769 nm [24-27]. The influence of the solvent and the substituent on the likely structure are discussed in more details below.

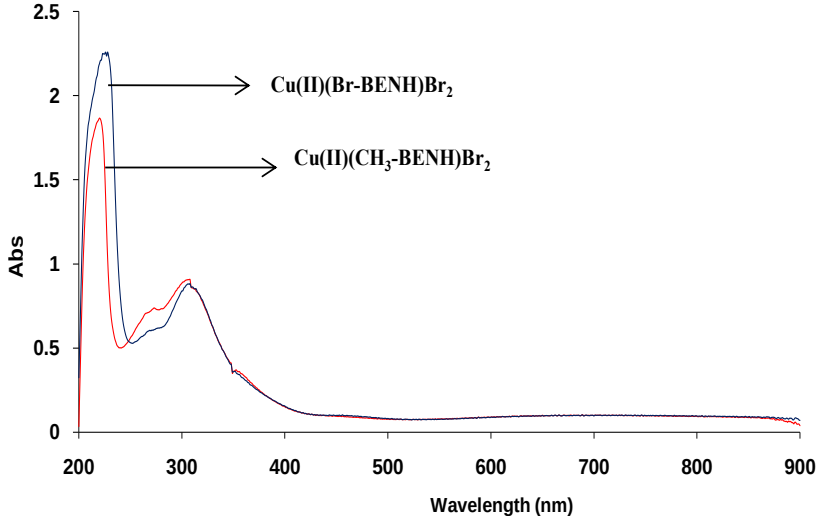

Figure 4.4.8 Uv-vis spectra of $Cu(II)(CH_3\text{-}BENH)Br_2$ and $Cu(II)(Br\text{-}BENH)Br_2$ in EtOH

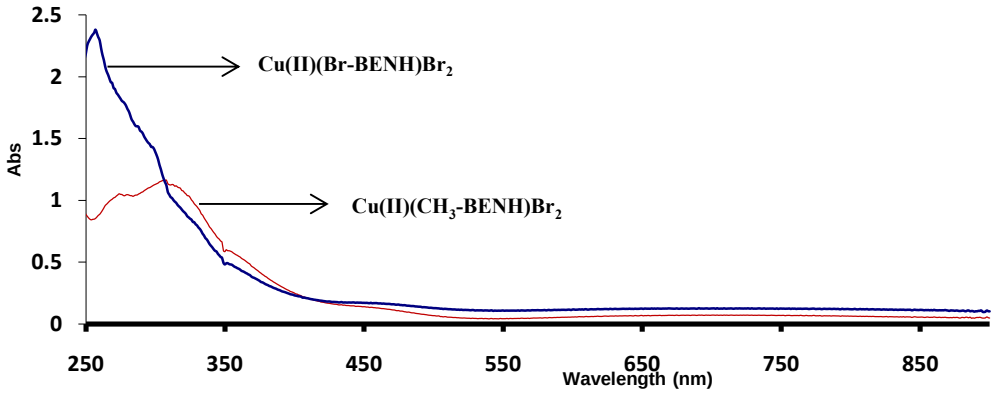

Figure 4.4.9 Uv-vis spectra of complexes, $Cu(II)(CH_3\text{-}BENH)Br_2$ & $Cu(II)(Br\text{-}BEN)Br_2$ in $CHCl_3$

4.4.1.2.2 Chloro complexes

According to the data from the electronic spectra of the chloro complexes in ethanol and chloroform solutions in table 3.18 and the overlap electronic spectra as given in figure 4.4.10 four bands were observed between 211 – 874 nm. The spectra showed absorption bands

between 211 - 232 nm, 265 – 281 nm, 306 – 308 nm and 621 – 874 nm, respectively corresponding to the n → σ* transition, π → π* transition, N → Cu(II) LMCT and d → d transitions. The stereochemistry of the complexes is suspected to be predominately tetrahedral, with only one absorption band observed in the visible region [24-27]. The influence of the solvent and the substituent on the likely structure are discussed in more detail below.

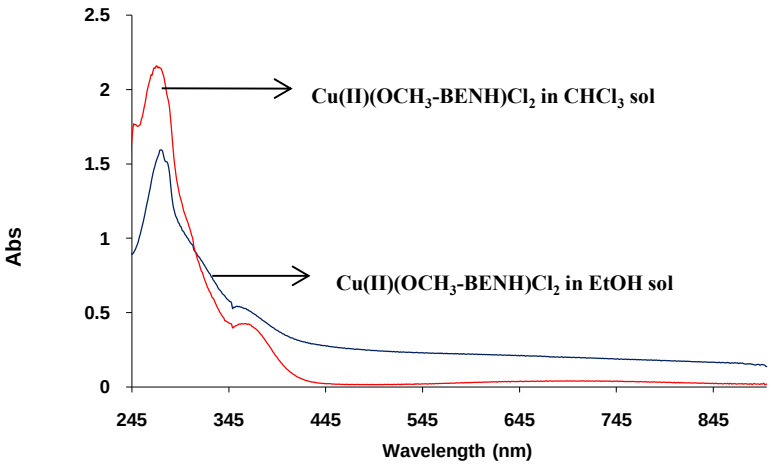

Figure 4.4.10 Uv-vis spectra of Cu(II)(OCH_3-BENH)Cl_2 in EtOH and $CHCl_3$

4.4.2 Correlation analysis studies for the UV-vis data of the N, N'-(aryl)benzaldiimine ligands, N, N'-(aryl)benzaldiamine ligands and their copper(II)-halide complexes

This section will focus on the correlation analysis of the imines, amine ligands and copper(II)-halide complexes whose composition have been confirmed by microanalyses. For the imine ligands the analysis will be conducted by correlating the π → π* transition of the benzene ring with the three substituent parameters. While for the amine ligands and their copper(II)-halide complexes Hammett parameters will be used, because this model gave a better correlation for the analysis of the amines and the copper(II)-halide complexes.

4.4.2.1 N, N'-(aryl)benzaldiimine ligands

Table 4.9 Correlation of $\pi \rightarrow \pi^*$ transition for N, N'-(aryl)benzaldiimine ligands with various substituent parameters in ethanol solution

Parameters	$\pi \rightarrow \pi^*$ transition In EtOH
Hammett (ζ_ρ)	-0.54140
Swain (ζ_I)	0.43527
Swain (ζ_R)	-0.76523
Williams & Norrington (ζ_I)	-0.11070
Williams & Norrington (ζ_R)	-0.73340

The correlation analysis (table 4.9) between the three substituent parameters and $\pi \rightarrow \pi^*$ transitions of the benzene ring for Schiff bases in ethanol solution, suggest that there is a negative resonance effect within the $\pi \rightarrow \pi^*$ transitions of the benzene ring for the N, N'-(aryl)benzaldiimine ligands. This was described better using Swain (ζ_R) and Williams & Norrington (ζ_R) parameters. This is in agreement with proton and carbon NMR studies of the free N, N'-(aryl)benzaldiimine ligands, whereby the resonance effect is highly dominating in the benzene ring of the free imine ligands.

4.4.2.2 N, N'-(aryl)benzaldiamine ligands

From the UV-vis experimental data of the amine ligands, both in ethanol and chloroform solutions two absorption bands were found in the ultraviolet region. The band in the lower energy region ($\pi \rightarrow \pi^*$ transition) was found to be more sensitive to the electronic properties

of the substituent (table 3.16), with these bands shifting towards or away from the lower energy region.

The electron donor and the electron withdrawing substituents in ethanol solutions both seem to exhibit similar effects on the $\pi \rightarrow \pi^*$ transition of the N, N'-(aryl)benzyaldiamine ligands when compared to unsubstituted analogue (H-BEN), see figure 4.4.11. In ethanol these substituents increase the electron density of the benzene ring and decrease the $\pi \rightarrow \pi^*$ transition energy gap resulting in a red shift. This destabilizes the HOMO of the π – orbitals of the benzene ring relative to the LUMO.

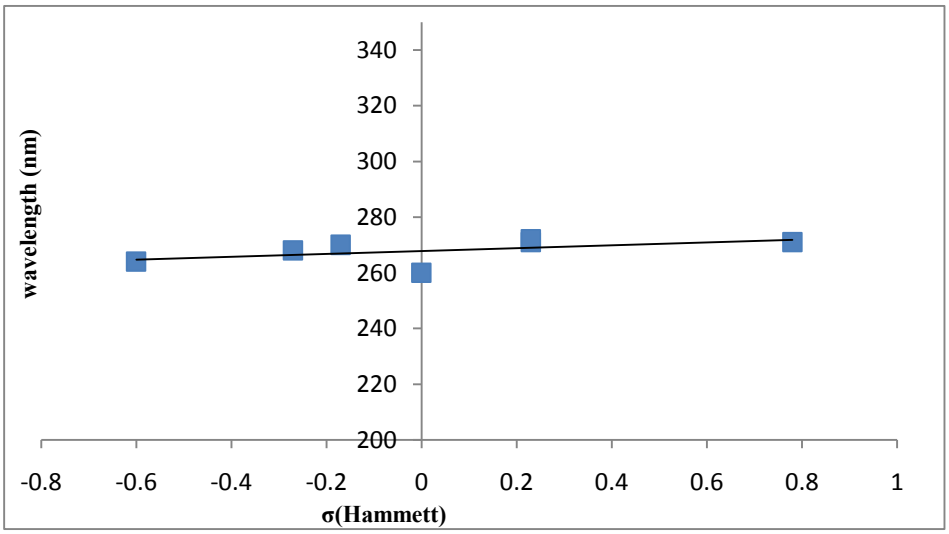

Figure 4.4.11 Plot of wavelength (nm) versus Hammett σ values for $\pi \rightarrow \pi^*$ transition of N, N'-(aryl)benzaldiamine ligands in EtOH solution

Since the spectroscopic data for the $\pi \rightarrow \pi^*$ transition of the N, N'-(aryl)benzaldiamine ligands in chloroform solution was non-linear (see figure 4.4.12), no correlation analyses were conducted. The absence of correlation within the data is expected, because chloroform is an aprotic solvent. Aprotic solvents have lone pairs and they posses $n \rightarrow \zeta^*$ transitions which result in large frequency shifts in the electronic spectra.

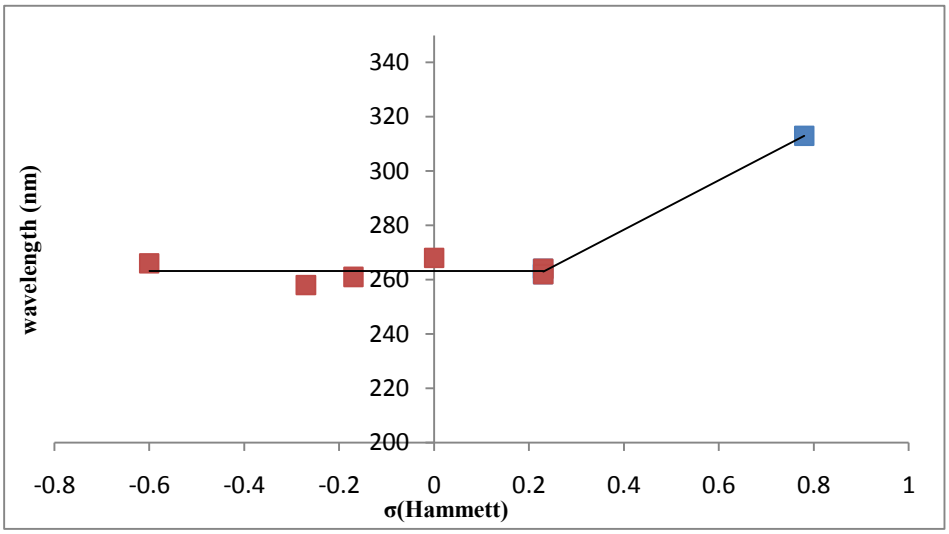

Figure 4.4.12 Plot of wavelength (nm) versus Hammett σ values for π → π* transition of N, N'-(aryl)benzaldiamine ligands in $CHCl_3$ solution

In chloroform solution, both the electron donating and electron withdrawing substituents (except for 4-NO_2) appear to decrease the electron density at the benzene ring, thereby increasing the $\pi \rightarrow \pi^*$ transition energy gap, resulting in a blue shift, (this is presented in figure 4.4.12). The figure shows some similarity for both the electron donor and electron withdrawing substituents, in the manner in which the substituents influence the spectroscopic data. The blue shift stabilizes the HOMO relative to the LUMO. The nitro group often has an anomalous value using the Hammett substituent parameter [28]. The anomalous behaviour of the nitro group substituent may reflect a coupling of the π → π* benzene, with either the π → π* or the CT of the NO_2 group [15], or it may reflect coupling with the n → ζ* transitions of the solvent. The contrast to the spectra of ethanol and chloroform shows a solvent effect is most likely responsible.

Since the behaviour of the $\pi \rightarrow \pi^*$ transition in $CHCl_3$ is non-linear, correlation analysis has been done only for EtOH. The analysis shows poor correlation with the Hammett parameter and opposing behaviour for the inductive and resonance parameters of the other two (see figure 4.4.11 and table 4.9). Swain parameters show a better correlation in EtOH when (ζ_I) is used rather than (ζ_R).

Table 4.10 Correlation of $\pi \rightarrow \pi^*$ transition for N, N'-(aryl)benzaldiamine ligands with various substituent parameters in ethanol and chloroform solutions

Parameters	$\pi \rightarrow \pi^*$ transition In EtOH
Hammett (ζ_ρ)	-0.02377
Swain (ζ_I)	0.60061
Swain (ζ_R)	-0.46109
Williams & Norrington (ζ_I)	0.49151
Williams & Norrington (ζ_R)	-0.61013

The plot in figure 4.4.11 indicates a linear relationship with a small scatter, this suggest that there is no dramatic shift in the $\pi \rightarrow \pi^*$ transitions of N, N'-(aryl)benzaldiamine ligands due to the nature of the substituent, while in chloroform (see figure 4.4.12) a non-linear relationship is observed. From both figures 4.4.11 and 4.4 12 it can be concluded that the bands are sensitive to the nature of the solvent as seen from the slopes. For the electron withdrawing groups the polar solvent, ethanol, stabilises the cationic charge in the benzene ring, resulting in the red shift for the $\pi \rightarrow \pi^*$ transitions of N, N'-(aryl)benzaldiamine ligands, while in the chloroform these bands suffered a slight blue shift.

4.4.2.3 Bromo complexes

For the bromo complexes the data for the 4-$N(CH_3)_2$ analogue is missing in figure 4.4.13 and 4.4.14, due to the unsuccessful synthesis for the complex, Cu(II)(OCH_3-BENH)Br_2.

The presence of metal ion in N, N'-(aryl)benzaldiamine ligands causes a slight shift in the absorption bands of the $\pi \rightarrow \pi^*$ transitions for the bromo complexes in ethanol and chloroform solutions. The red shift caused by the donor and acceptor substituents in ethanol

solution, indicate that the energy gap between the $\pi -$ orbitals of the benzene is smaller and thus stabilize the LUMO relative to the HOMO.

The donor substituents in chloroform solution cause the $\pi \rightarrow \pi^*$ transitions of the bromide complexes to shift towards longer wavelength (red shift) and the withdrawing substituents (except for 4-Br) results in a blue shift. This implies that the presence of the donating group at the para position of the complexes decrease the energy gap between the π – orbitals of the benzene ring and stabilize the LUMO relative to the HOMO. For the withdrawing substituent the opposite effect is observed. From the spectroscopic data of the $\pi \rightarrow \pi^*$ transitions of the bromide complexes (see figure 4.4.14) a notable change in the NO_2 analogue is observed, which is now linear with other substituents in chloroform, as opposed to the free ligand (see figure 4.412).

The trend of the effect of the substituent and solvent on the bromo complexes is reflected in figures 4.4.13 and 4.4.14. These figures show a straight line for both solvents (EtOH and $CHCl_3$). This indicate that in both ethanol and chloroform solutions, substituents are producing a similar effects on the $\pi \rightarrow \pi^*$ transitions of the benzene ring and that while there is a shift in the electronic spectra due to the substituents using Hammett parameters, it is not dramatic with the complexes.

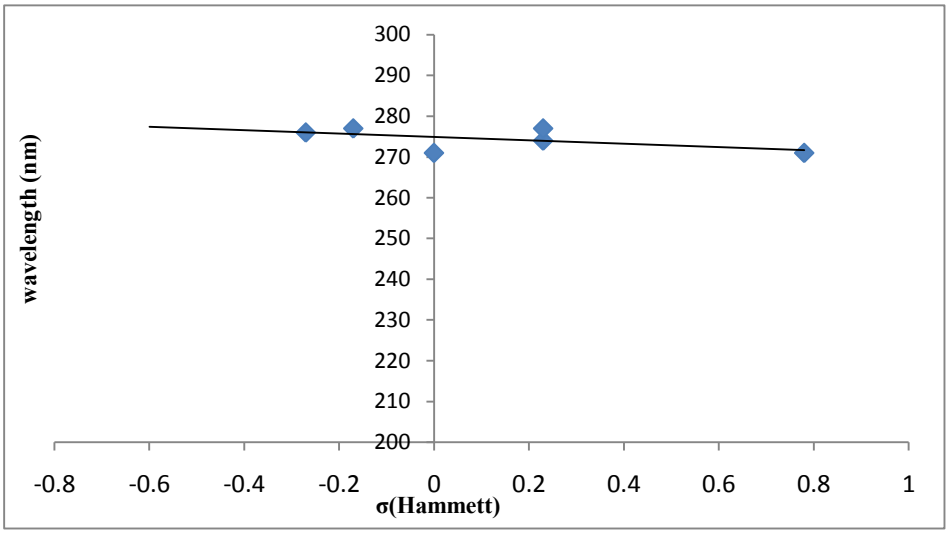

Figure 4.4.13 Plot of wavelength (nm) versus Hammett σ values for $\pi \rightarrow \pi^*$ transition of $Cu(R\text{-}BENH)Br_2$ in EtOH solution

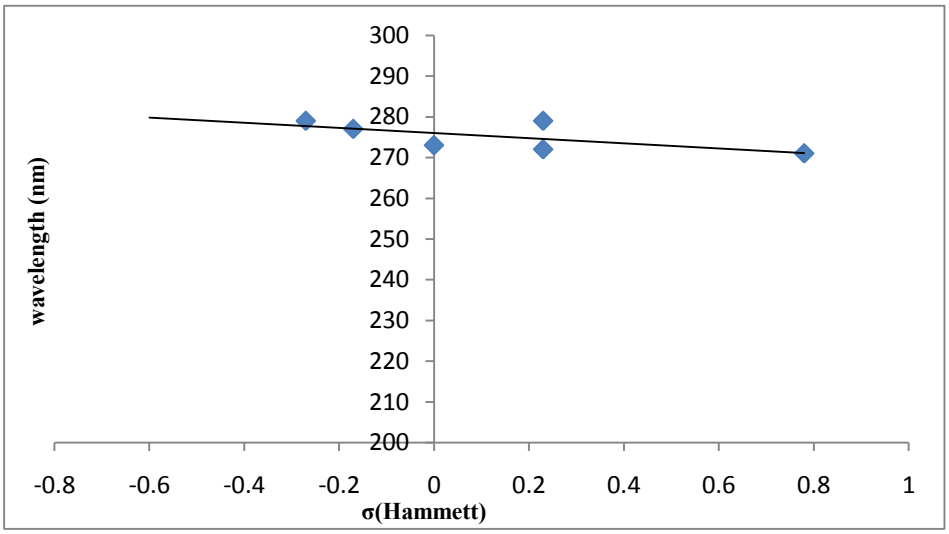

Figure 4.4.14 Plot of wavelength (nm) versus Hammett σ values for π→π* transition of Cu(R-BENH)Br_2 in $CHCl_3$ solution

The effect of the metal ion on the ligand orbitals compared with the free amines (ethanol solution) is shown in figure 4.4.15. The figure shows no parallelism between the plot of the free ligand and of the copper bromide complex in ethanol solution. This suggests that for the copper bromide complexes there is a slight metal contribution to the π → π* transition for the electron donating substituents in ethanol. In chloroform (figure 4.4.16) the mixing between the π – orbitals of the free ligand and of the metal orbitals is more influenced by the donor substituents, but the nitro substituent shows a significant blue shift. This suggests that there is a change, on complexation in the coupling experienced by the NO_2 substituted ligand. This is identifiable by the behaviour of the d - d transitions discussed below.

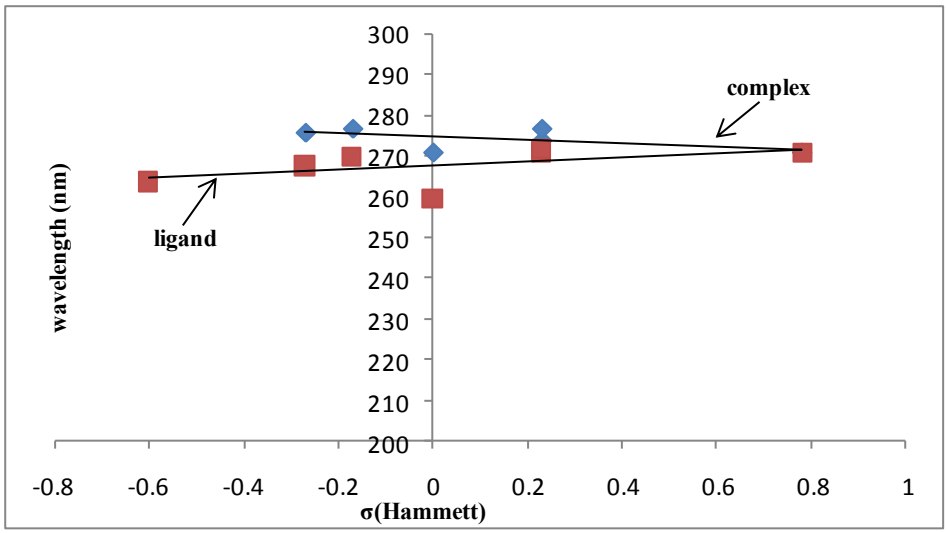

Figure 4.4.15 Plot of wavelength (nm) versus Hammett σ values for π→π* transition of Cu(R-BENH)Br_2 and of the free ligand in EtOH solution

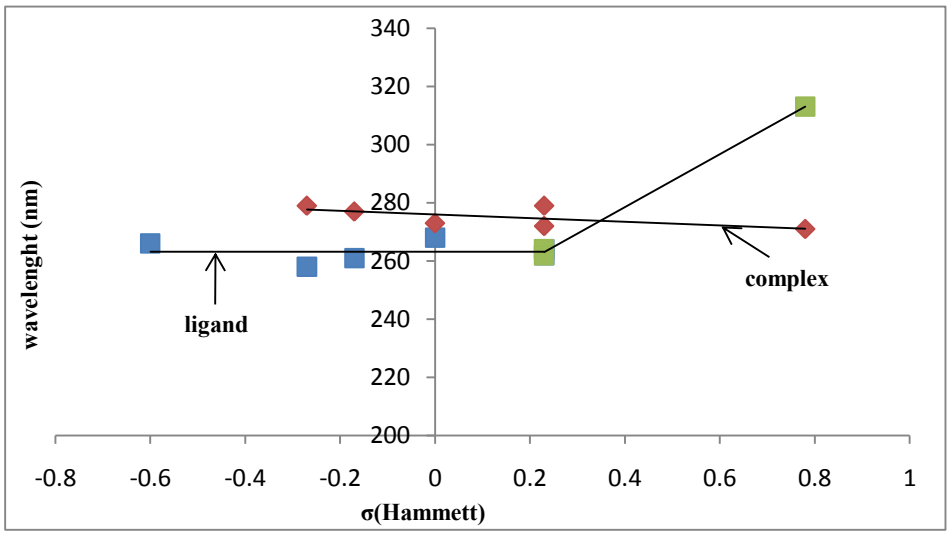

Figure 4.4.16 Plot of wavelength (nm) versus Hammett σ values for π→π* transitions of Cu(R-BENH)Br_2 and of the free ligand in $CHCl_3$ solution

The plot (figure 4.4.17) of the Hammett parameters for the bromo complexes against the d → d transitions show that there is a lack of linearlity within the data of the d → d transition, especially for the nitro analogue. The behaviour of the complex in ethanol is similar to that of the free ligand in chloroform. The lack of linearlity within the data of the d → d transition

of the complexes and nitro analogue might imply that the nitro group is not isostructural compared to the other bromo complexes or this may be due to a change in coupling within the electronic states. A possible explanation for the lack of linearlity may be due to the strong resonance effect of the nitro group, which often results in the Hammett substituent constant having an anomolous value.

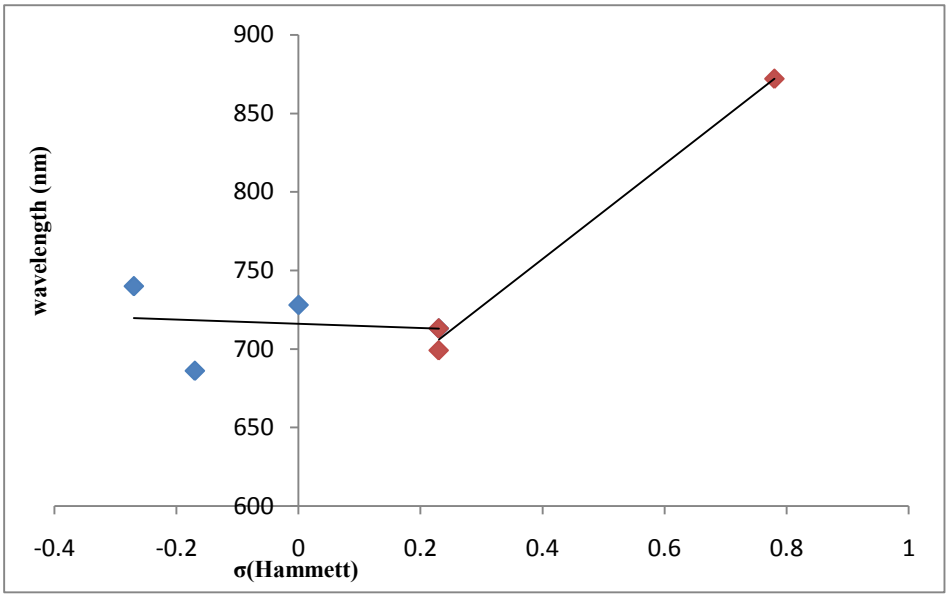

Figure 4.4.17 Plot of wavelength (nm) versus Hammett σ values for d→d transition of Cu(R-BENH)Br_2 in EtOH solution

The effect of the electron donor and electron acceptor substituents on the d − orbitals of the bromide complexes in chloroform solution is illustrated in figure 4.4.18. The figure shows that the electron donor substituents cause a slight blue shift for the d → d transition of the bromo complexes (compared with figure 4.4.17), while the electron withdrawing groups cause a clear blue shift on the d → d transition. When constrasted with figure 4.4.17 this suggest that the polar solvents stabilise the electron withdrawing substituents more in ethanol resulting in a blue shift.

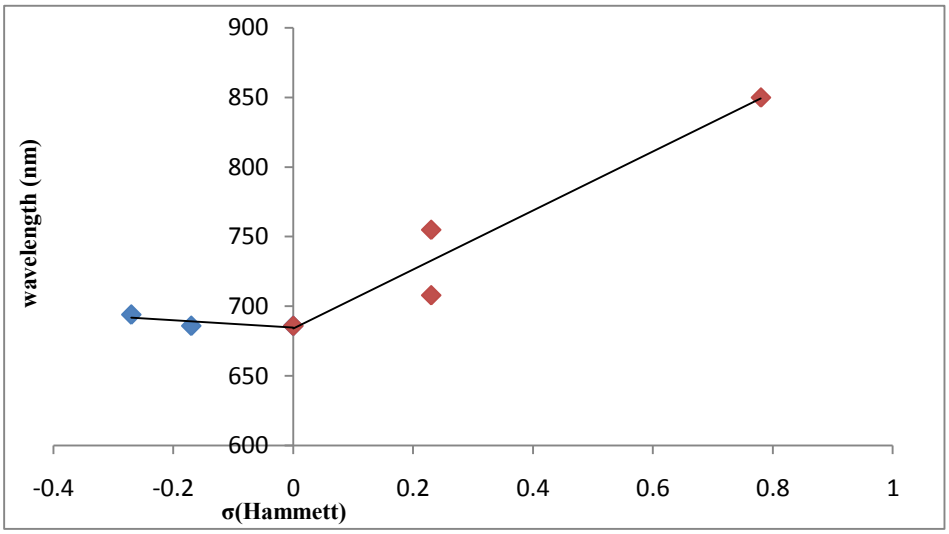

Figure 4.4.18 Plot of wavelength (nm) versus Hammett σ values for d→d transition of Cu(R-BENH)Br_2 in $CHCl_3$ solution

4.4.2.4 Chloro complexes

The electronic effect transmitted (figure 4.4.19) by the donor substituents on the benzene ring of the chloro complexes in ethanol solution results in less mixing between the π orbitals of the free ligand and the metal orbitals compared to the bromo complexes.

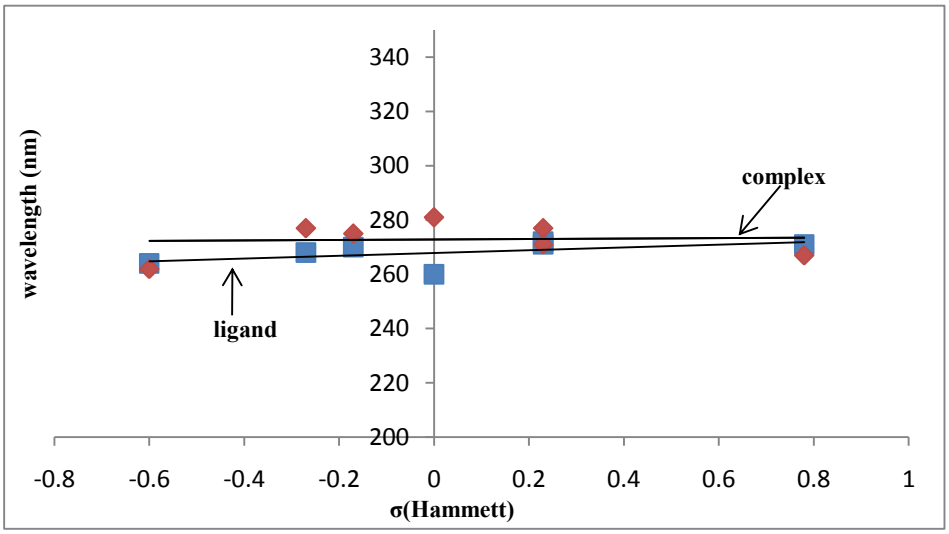

Figure 4.4.19 Plot of wavelength (nm) versus Hammett σ values for π→π* transition of Cu(R-BENH)Cl_2 and of the free ligand in EtOH solution

In chloroform solution (figure 4.4.20) both the electron donor and the electron acceptor substituents contribute to the slight mixing of the π orbitals of the free amine ligand and the metal orbitals cause a bathochromic shift on the $\pi \rightarrow \pi^*$ transition of the benzene ring, this suggests that the HOMO and the LUMO state of the benzene ring contain metal character. This is shown in figure 4.4.20. The experimental data obtained from the analysis of the $\pi \rightarrow \pi^*$ transition of the benzene ring for chloride complexes indicates that the bands are slightly sensitive to the nature of the solvent and there is a minor shift in the electronic spectra due to the substituents.

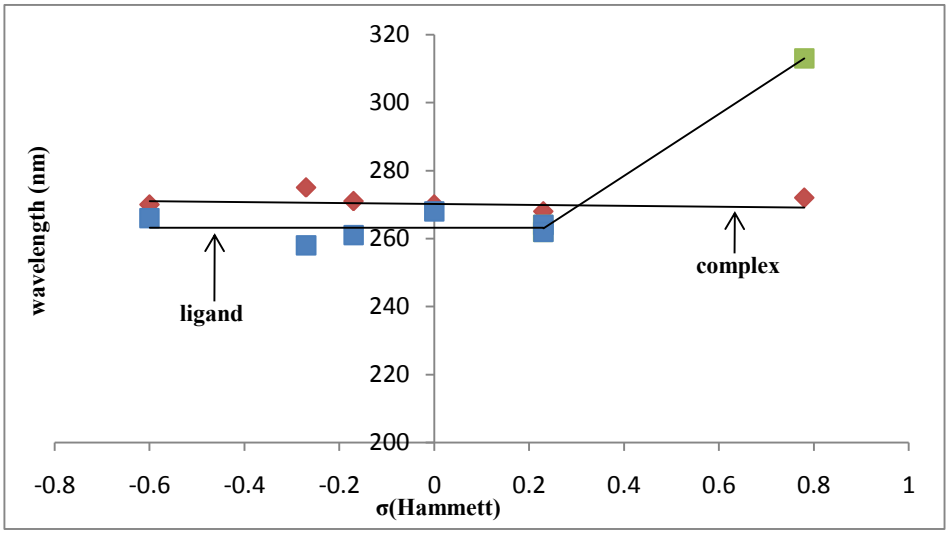

Figure 4.4.20 Plot of wavelength (nm) versus Hammett σ values for π→π* transition of Cu(R-BENH)Cl_2 and of the free ligand in $CHCl_3$ solution

Figure 4.4.21 represents the correlation of Hammett parameters with the d → d transition of the chloro complexes in ethanol. As observed in the plot (figure 4.4.21) there is a difference of about 300 wavenumbers between the most electron donating and the most electron withdrawing substituent. This suggests a change in coordination sphere which means that the ethanol may be coordinated to the complex resulting in a tetragonal coordination for the donor analogues (with a larger crystal field splitting), while for the withdrawing groups a distorted tetrahedral geometry may be exist (yielding smaller crystal field splitting).

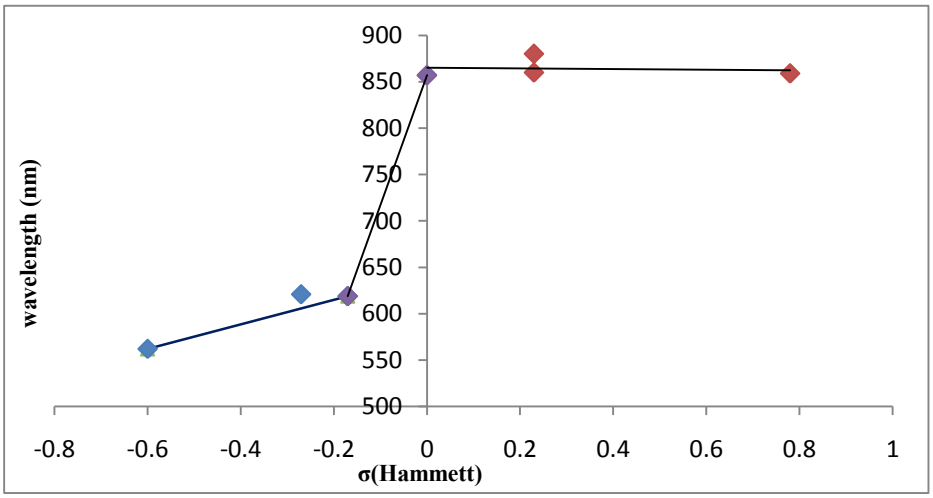

Figure 4.4.21 Plot of wavelength (nm) versus Hammett σ values for d → d transition of Cu(R-BENH)Cl_2 in EtOH solution

From the spectroscopic data obtained for the characterization of the chloro complexes in chloroform, in a noncoordinating solvent the plot, figure 4.4.22 shows a non perfect linear plot. But there is some degree of linearlity between the Hammett substituent parameters and d-d transitions of the chloro complex in chloroform, with the exception for the bromo analogue. It is likely that all except the bromo analogue are probably distorted tetrahedral, while the bromo analogue (based of crystal field splitting consideration) is likely to be tetrahedral.

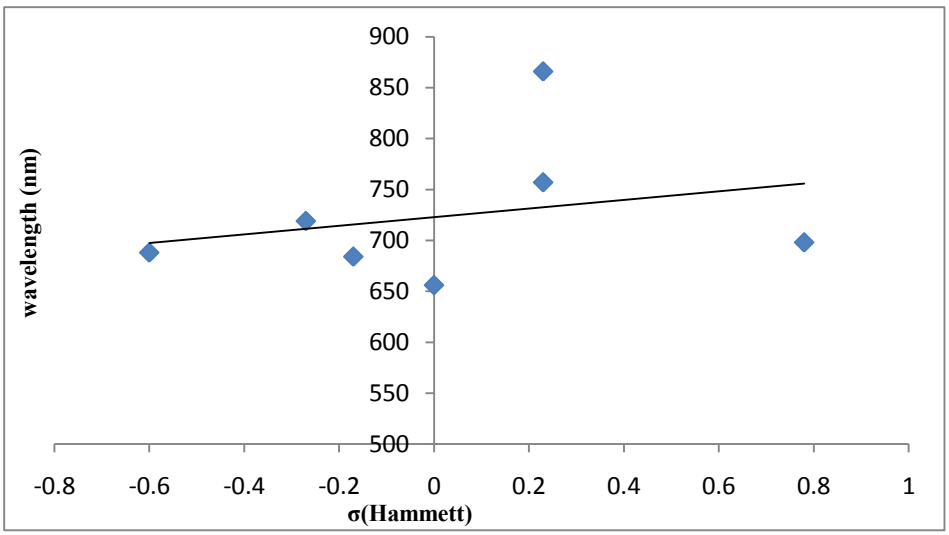

Figure 4.4.22 Plot of wavelength (nm) versus Hammett σ values for d → d transition of Cu(R-BENH)Cl_2 in $CHCl_3$ solution

4.4.3 The electronic spectra of the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligands and their copper(I)-halide and copper(II) halide complexes

The Ultraviolet-visible spectra of the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligands and their complexes were recorded in dichloromethane solution in the range of 200 nm to 900 nm region. This section will focus on the effect produced by the substituent $\{(N(CH_3)_2)\}$ on the *para*-position of the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligand and the influence of the metal ion on the free ligand, CA_2EN. The data obtained for the characterization of N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligands and their metal complexes are listed in table 3.19. The electronic spectra obtained for CA_2EN ligand in dichloromethane solution (figure 4.4.23), show extreme broading of the absorption bands.

The absorption spectrum of CA_2EN in dichloromethane solution shows one intense band at 311 nm, one broad band at 249 nm, one weak band at 339 nm, one very undistinguishable band between 262 nm and 308. All these bands are observed in the ultraviolet region [29]. The absorption at 249 nm ($\varepsilon = 3.50$) corresponds to a $\pi \rightarrow \pi^*$ transition of the benzene ring. The absorption band observed at 339 nm in dichloromethane, solution is most probably due to the $n \rightarrow \pi^*$ transition of imine group [14], the broad band between 262 nm and 308 nm masked the $\pi \rightarrow \pi^*$ transition of the imine group. The absorption band at 311 nm ($\varepsilon = 4.80$) corresponds to the CT band [14].

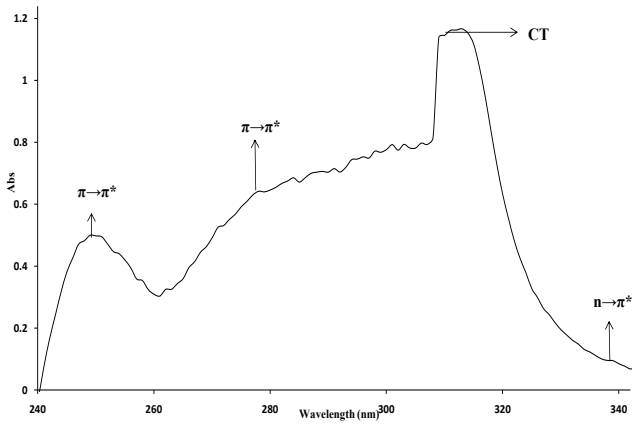

Figure 4.4.23 Ultraviolet spectrum of CA_2EN ligand in DCM

The spectroscopic data obtained from the characterization of N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligands (table 3.19 and figure 4.4.24) , show that the presence of the electron donor substituent{$N(CH_3)_2$} at the *para* position of N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane shifts the $\pi \rightarrow \pi^*$ transition of the benzene ring towards longer wavelength. This decreases the energy gap between the π^* and π of benzene ring, as a result the LUMO state of the $\pi -$ orbitals is stabilized relative to the HOMO state. The same shift is observed for the charge transfer transition.

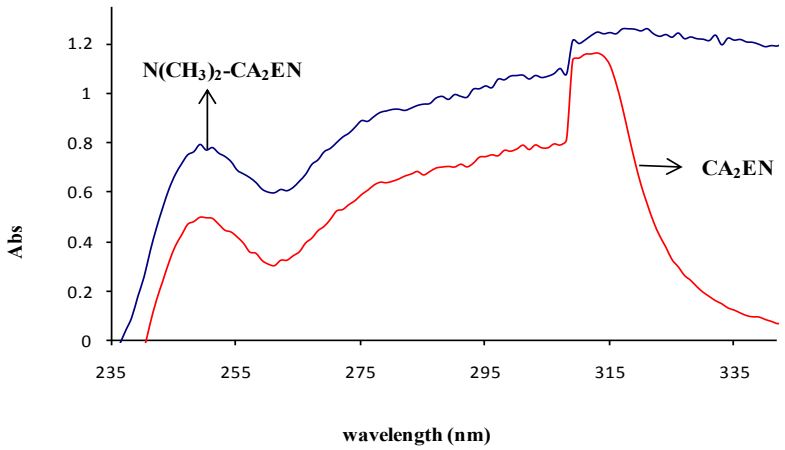

Figure 4.4.24 Ultraviolet spectra of CA_2EN and $N(CH_3)_2$-CA_2EN ligand in DCM

4.4.3.1 Copper(I) and copper(II) halide complexes of N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligand

The electronic spectra of the copper(I) and copper(II) complexes have been recorded in the 200 nm to 900 nm range in dichloromethane solution. The electronic spectra data are listed in table 3.19 and the electronic spectra are overlapped in figure 4.4.25 and 4.4.26.

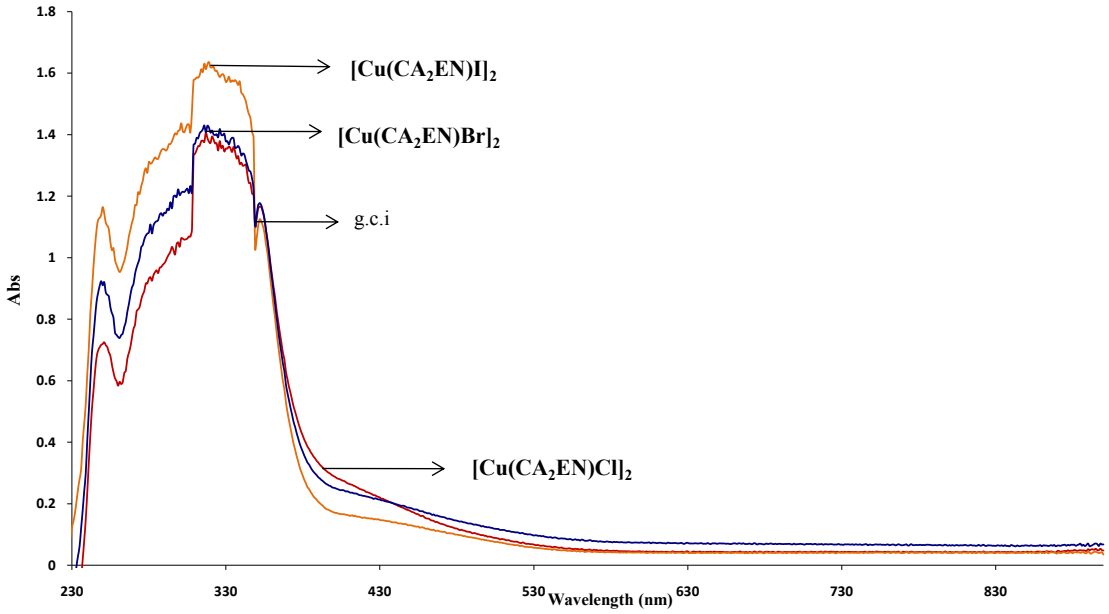

Figure 4.4.25 UV-vis spectra of $[Cu(CA_2EN)X]_2$ complexes in DCM

Since no d → d transitions are expected for the d^{10} Cu(I) complexes, the UV-vis absorption bands are assigned to metal to ligand charge transfer (MLCT) or π → π* transition due to the ligand [30]. The absorption spectra of the complexes in dichloromethane feature one new shoulder in the visible region. This shoulder is observed within the range 432 nm and 449 nm. Since this shoulder is not observed in the electronic spectrum of the free ligand the band may be assigned to MLCT [30]. It shows slight halogen sensitivity.

While in electronic spectrum of $Cu(CA_2EN)Cl_2$, figure 4.4.26 one extremely weak broad absorption band at 741 nm and one shoulder at 393 nm are observed. The broad band at 741 nm correspond to the d → d transition within the orbitals of the copper(II) metal ion, since this band was not observed in $[Cu(I)(CA_2EN)Cl]_2$. Since copper(II) d → d transitions typically have a molar extinction coefficient of 10 (ε = 2) the shoulder at 393 may be assigned to MLCT [30].

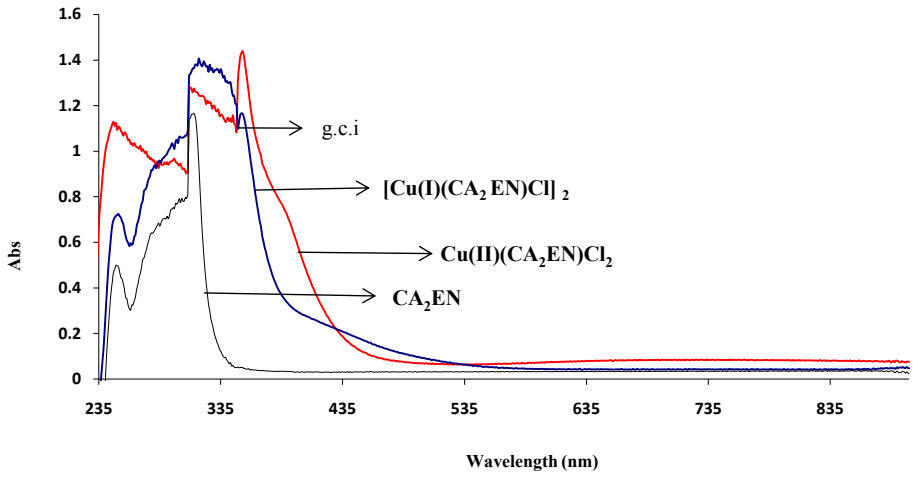

Figure 4.4.26 UV-vis spectra of $[Cu(I)(CA_2EN)Cl]_2$, $[Cu(II)(CA_2EN)Cl_2$ and CA_2EN in DCM

From the experimental data, it can be concluded that on complexing with the Cu(I)Br the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligand undergoes a slightly shift for the π → π* transition (benzene) towards longer wavelength. This decreases the energy gap of the π –

orbitals of the benzene ring, this indicates less mixing between $\pi -$ orbitals of the benzene ring and the metal obrtitals and giving the $\pi -$ orbitals slight metal character.

4.5 Infrared spectroscopy

Infrared spectroscopy is one of the most popular spectroscopic techniques used by chemists. This instrument deals only with molecules that have functional groups that only absorb light (photons) on low energy side (beyond red in the spectrum). The beam or photons associated with an infrared spectrum excite electrons due to the small energy these photons have, but the photons induce vibrational excitation of covalent bonded atoms and groups resulting in molecular vibrations.

The infrared region of the electromagnetic spectrum can be divided into three subsets, far-infrared, near-infrared and mid infrared. The mid-infrared region (4000 cm^{-1} to 400 cm^{-1}), is the region associated with the changes in vibrational energies within the molecule. The far-infrared region determines the vibrational modes for heavy metals such as inorganic molecules. The energy at near-infrared region is useful for the analysis of molecular overtone and combination vibrational modes.

4.5.1 Infrared spectral studies

The infrared spectrum of the N, N'-(aryl)benzaldiimines are rich in fundamental vibrations. For the parent imine (X=H), as well as for the halogen substituents having 34 atoms, there are 96 modes of vibrations, which due to the two fold symmetry equates to 47 pairs of fundamentals, plus two for the C-C bond of the methylene bridge. For the polyatomic substituents, there are an additional 3N fundamentals (N= the number of additional atoms). For the amine parent, there are an additional 12 modes (six for each reduced imine), and for the salts, a further 6 (three for each tertiary amine).

In the absence of a complete vibrational analysis of the molecules (beyond the scope of this work), the identification of suitable group frequencies to use in the characterisation of the

ligands was restricted to attempting to identify suitable C-N-H modes within the diimines, the diamines and their salts against a background of the substituted benzene moiety associated with the aromatic ring. The work by Varsányi and Szöke [31] is seminal in establishing the behaviour of the vibrational coupling within the benzene ring due to the substituent. According to the classification of Varsányi and Szöke [31], given that the Ar-C of the methylene bridge is considered light, the substituents X= NO_2, OH, Me, OMe, $N(CH_3)_2$ are 1, 4 di-light substituents, while the substituents X=Cl, Br are 1-light -4- heavy substituents.

This causes profound differences in the vibrational coupling experienced by the different molecules [31], for example the νC-X (Wilson mode 7a) which occurs between 1270-1100 cm^{-1} (1, 4 di-light) or between 400-240 cm^{-1} (1-light-4-heavy) strongly couples with the ring breathing mode (Wilson mode 1), which in turn occurs between 860-720 cm^{-1} (1, 4 di-light) and between 1100-1050 cm^{-1} (1-light-4-heavy). The other νC-X (Wilson mode 13) which occurs between 1300-1100 cm^{-1} (for both 1, 4 di-light and1-light -4- heavy substituents) couples with the Star of David ring breathing mode (Wilson mode 12) which in turn occurs between 860-760 cm^{-1} (1, 4 di-light) and between 480-680 cm^{-1} (1-light-4-heavy). The variation between the two sets of substituents is even more pronounced below 1000 cm^{-1}, particularly those involving the out-of plane vibrations [31]. Not only is the frequency substituent sensitive, but so too is the intensity of the benzene vibrations, as well as the associated substituent internal vibrations. For example, with increasing Hammett σ function both the frequency and the intensity of the symmetric and asymmetric stretch NH_2 increases (with the symmetric having a steeper slope); but the behaviour of the OH stretch is opposite [31]. In solution this is further complicated in that these properties are solvent sensitive; polar solvents decrease the frequency, but increase the intensity of the νNH_2 vibrations [31].

In addition to the aromatic ring, the vibrations of the methylene bridge needed to be considered, which was done by referring to the isotope labelled studies of metal complexes with ethylenediamine.

4.5.2 Group frequencies of the N, N'-(aryl)benzaldiimines

An ideal characteristic group frequency, the νC=N of an imine, occurring at about 1645 cm^{1}, is very prominent as it occurs in a region where there are few alternative assignments, and it is widely reported within the literature (and is also the reason why the Schiff base imines were initially considered for the present study). The in-plane bend δ_{ip}C-C=N (about 635 cm^{-1} [30]) and out-of-plane δ_{op}C-C=N (about 720 cm^{-1} [31]) occur in a region that is vibrationally rich, dependant on whether light or heavy. The former region includes both in-plane (modes 6b and 12) and out-of-plane (mode 4) benzene modes, the latter includes the in-plane benzene modes (modes 1, 12 and 6a), as well as a number of possible substituent internal vibrations [31], and also the CH_2 rock of the methylene bridge (ρCH_2) [32, 33].

Within the present study only the νC=N could be identified for all the substituents and a correlation analysis performed.

Table 4.11 Correlation of νC=N for N, N'-(aryl)benzaldiimine ligands with various substituent parameters

Parameters	Correlation factor for νC=N
Hammett (ζ_ρ)	0.4687
Swain (ζ_I)	0.8897
Swain (ζ_R)	0.1506
Williams & Norrington (ζ_I)	0.7811
Williams & Norrington (ζ_R)	0.1105

Correlation studies suggest that inductive effect is more pronounced at the νC=N, this effect is the results of the electrons being withdrawn with increasing value of ζ, meaning more negative charge is drawn away from the N into the ring by the electron withdrawing substituents and sp^2 hybrid state is more stable and νC=N is increased [31].

The correlation analysis shows that the inductive effect is a better descriptor, this observation agrees with that found in the NMR studies, that there is no planarity of the imine bond with the benzene ring that the effect must be a field effect (through space rather than along the bonds).

The dual substituent parameters was able to explain and differentiate the (poorer) trend that Hammett has and conclusively show that conjugation is not the controlling factor within the imines.

Percy and Thornton [34] previously conducted an infrared study of *N*-arylsalicylaldimine complexes substituted in both aryl rings. Substitution on the aryl ring was found to relate to the Hammett parameter, and to Swain's field parameter, but not to any resonance capacity of the substituent [34]. They also observed that, with exception to the 3-methoxy substituent, on substitution of the salicylaldimine a correlation with the Taft resonance polar parameter was observed for the νC-N and νC-O, and an inverse correlation was observed for νC=N and νM-N [34]. They concluded that, on coordination, stabilization of the M-N and C=N bonds occurs at the expense of the C-N and C-O bonding, and they accounted for the anomalous 3-methoxy behaviour to steric effects of the bulky group *ortho* to the enol [34]. Clearly the presence of the 2-hydroxy group and the resultant chelate effect promotes aligning the imine double bond with that of the benene ring.

The lack of correlation of νC=N for N, N'-(aryl)benzaldiimine ligands with the resonance parameters may simpily be due to the non co-planar of the imine π bond with that of the aromatic ring or may be because the system is not coordinated to a metal ion to allow for the delocalization of the electrons around the chelate of the ring. Regretably, because the copper is a strong enough Lewis acid to hydrolise the Schiff base, it was not possible to determine whether on chelation the N, N'-(aryl)benzaldiimine undergoes a similar alignment of the imine and benzene π bonds.

4.5.3 Group frequencies of the N, N'-(aryl)benzaldiamines

Secondary amines show a sharp single NH stretching absorption of variable intensity between 3450-3300 cm^{-1} [35]. The vibration is known to be sensitive the nature of the surroundings [30], and a broad second band below 3200 cm^{-1} may also be observed if hydrogen bonded (with both free and hydrogen bonded forms often being simultaneously observed [35]). A weak bend (δN-H) is expected between1550-1650 cm^{-1} [35] (easily masked by the bend for water), with the second bend of medium to weak intensity between 700-850 cm^{-1} [35]. The former can be mistaken for the in-plane aromatic ring stretches (Wilson modes 8a and 8b); the latter can be either masked by or mistaken for the planar ring vibrations (modes 1,6a), and the out-of plane bends (modes 10a, 11, 17b) [31], or the CH_2 rock of the methylene bridge (ρCH_2) [32, 33]. The C-N stretch is a weak to medium band found between 970-960 cm^{-1} [32-35], and is considered of no practical significance [35] due to the abundance of the spectrum, while the weak C-C stretch between 860-850 cm^{-1} [32, 33] is an even poorer characteristic group.

Within the present study only the νN-H could contidently be identified for all the substituents and a correlation analysis performed.

Table 4.12 Correlation of νN-H for N, N'-(aryl)benzaldiamine ligands with various substituent parameters

Parameters	νN-H	$\nu H\text{-}N_{(CuCl)}$	$\nu H\text{-}N_{(CuBr)}$
Hammett (ζ_ρ)	0.3164	0.7471	0.5400
Swain (ζ_I)	0.6720	0.4583	0.8508
Swain (ζ_R)	0.0563	0.6076	0.2232
Williams & Norrington (ζ_I)	0.5955	0.6243	0.7897
Williams & Norrington (ζ_R)	0.0259	0.6411	0.2100

The relative poor correlation between the substituent parameters and the νN-H of N, N'-(aryl)benzaldiamine ligands suggest that a moderate inductive effect is observed among the νN-H. The Swain parameters for the inductive effect provide a better correlation for free ligand and bromide complexes (In contract, the chloride complexes appear more susceptible to the resonance effect). This is expected because as the ζ value of the withdrawing substituent increase, then the more negative charge is being pulled away from the N into the ring, the sp^2 hybrid state will be more stable and νN-H will increase [31]. The proton NMR colleration studies show similar observations.

The lack of correlation of νN-H for the coordinated N, N'-(aryl)benzaldiamines with the ζ_R, resonance parameter for bromide complexes suggest that on coordination for N, N'-(aryl)benzyaldiamine ligand system, unlike the salicylaldimes there is no delocalization around the coordinated ring. While the correlation for chloride complexes suggest there may be some alignment of the π system of the beznene ring on complex similar to the salicylaldimes. This suggests that the chloro and bromo complexes may not be isostructural in the solid state.

4.5.4 Group frequencies of the N, N'-(aryl)benzaldiamine salts

For the secondary amine salts, the NH_2^+ stretching absorption is expected to be broad and of medium intensity, with highly structured major maxima found between 2700-2250 cm^{-1} [35] due to strong combination bands. The higher δNH_2^+ is found over a wider range (1600-1460 cm^{-1}) [35] than that of the uncharged primary amine, and the degeneracy may be removed to give two bands, with the aliphatic secondary amine salt being less intense [34] than the δNH_2 for ethylenediamine [32, 33]. The behaviour of the lower δNH_2^+, the C-N stretch and the C-C stretch is not known, although for primary amines two medium to weak δNH_2 bands are expected between 850-700cm^{-1} [35].

Within the present study only the νNH_2^+ and the first δNH_2^+ could be identified for all the substituents and a correlation analysis performed. The low frequency, strong hydrogen bonding of the amine salt is clearly observed (figure 4.5.1).

Table 4.13 Correlation of νNH_2^+ and δNH_2^+ for N, N'-(aryl)benzaldiamine dihydrochloride salts with various substituent parameters

Parameters	νNH_2^+	δNH_2^+
Hammett (ζ_ρ)	0.3046	0.0861
Swain (ζ_I)	0.3134	0.1275
Swain (ζ_R)	-0.6797	-0.1859
Williams & Norrington (ζ_I)	0.1799	0.1054
Williams & Norrington (ζ_R)	-0.7342	0.2650

The correlations (irrespectively of the parameters employed) are poorer for the δNH_2^+. This is not unexpected as with the lower symmetry and the expected wavelength range (1600 – 1460 cm^{-1}) this fundamental vibration is expected to couple with the C−N−H bend and the H−C−N bend (the extent of which coupling would be very influenced by the nature of the molecule), hence substituent effects could be diluted out because of the variable coupling. The correlation of $\nu N{-}H^+$ is unusual because, unlike the imine and amine, the stretch is inversely affected by the resonance parameters, whether employing the Swain or the Williams & Norrington parameter. This is agreement with the behaviour observed for the proton NMR.

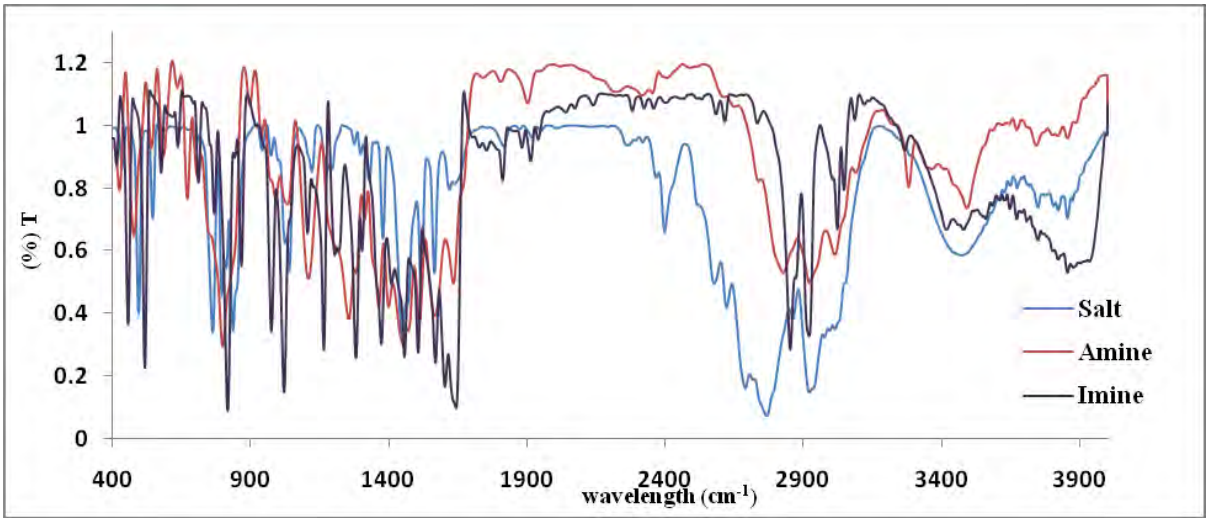

Figure 4.5.1 Mid-infrared spectra of 4-CH_3 analogues

4.5.5 Group frequencies of the N, N'-*bis*(cinnamaldehyde)1, 2-diiminoethanes and their Cu(I) and Cu(II) complexes:

The very prominent νC=N of an imine, occurring at about 1645 cm^{-1} where there are few alternate assignments, is an ideal characteristic group frequency to monitor metal binding. As mentioned above, the in-plane bend δ_{ip}C-C=N (about 635 cm^{-1} [31]) and out-of-plane δ_{op}C-C=N (about 720 cm^{-1} [31] are not as suitable due to the additional benzene modes, possible substituent internal vibrations [31], and also the CH_2 rock of the methylene bridge (ρCH_2) [31, 32].

Table 4.14 Comparison between the νC=N stretches of the BEN and CA_2EN ligands

R	BEN	CA_2EN	
	νC=N	νC=N	ΔνC=N
H	1614	1615	1
$N(CH_3)_2$	1636	1620	16
ΔνC=N	22	5	

In the current study only two N, N'-*bis*(cinnamaldehyde)1, 2-diimineoethanes were investigated. The difference in the shift of νC=N between the substituted Schiff bases {($N(CH_3)_2$-CA_2EN and $N(CH_3)_2BEN$)} suggests that the two Schiff bases are not the same, there may be a presence of an extensive conjugation of the ethene and imine π bonds with that of the aromatic ring, and that on coordination, like the complexes of the salicylaldimes, there is possible delocalisation around the chelate ring.

The shifts of the νC=N of the coordinated complexes indicate that the νC=N of the free ligand, CA_2EN is metal sensitive. Since the presence of Cu(I) caused different shifts to the νC=N, this suggests the presence of an extensive conjugation of the ethene and imine π bonds with that of the aromatic ring. The opposite is observed for Cu(II). These observations are in agreement with the UV/vis studies of the the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane ligands and their copper(I)-halide and copper(II) halide complexes.

Table 4.15 Comparison between the νC=N stretches of the CA_2EN ligand and their copper Complexes

compound	CA_2EN	$[Cu(I)(CA_2EN)Cl]_2$	$[Cu(I)(CA_2EN)Br]_2$	$[Cu(I)(CA_2EN)I]_2$	$Cu(II)(CA_2EN)Cl_2$
νC=N	1614	1624	1627	1627	1612
ΔνC=N		10	13	13	-2

4.6 Conclusion

The NMR studies of the free N, N'-(aryl)benzaldiimine ligands have confirmed that the presence of the electron withdrawing groups and the electron donating group at the *para*–position of the free N, N'-(aryl)benzaldiimine ligands reduces the co-planarity of the imine group and the benzene ring but that through flexibility of the molecule, a through space field effect is induced on the protons of the bridge, an effect which is not observed in the carbon NMR studies of the free N, N'-(aryl)benzaldiimine ligands. This is in agreement with the infrared studies of the free N, N'-(aryl)benzaldiimine ligands, whereby the inductive effect is highly dominating in the νC=N of the free imine ligands.

Both in the N, N'-(aryl)benzyaldiamine ligands and their dihydrochloride salts the benzene ring and the nitrogen atom are non-parallel to each other, the disappearance of the through space inductive effect in both ligands may be due to the reduction of the imine bond to an amine bond and because of the solvent effect.

The studies further show that the presence of the double bond within the N, N'-(aryl)benzyaldiimine ligand, N, N'- *bis*(benzyl)-1, 2-diiminoethane does not necessarily affect the chemical shifts of the aromatic protons, but stabilizing N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane with a donor group at the *para*- position brings a change in the chemical shifts of the protons at the side chain of the N, N'- *bis*(benzyl)-1, 2-diiminoethane. This is supported by the infrared studies of the νC=N of the N, N'-*bis*(cinnamaldehyde)-1, 2-diiminoethane.

The amine salt studies suggested that the electron withdrawing substituents were unable to withdrawn the negative charge away from the positively charged N into the ring, this is supported by the correlation analysis of the three substituent parameters. This is expected, given the position in which the nitrogen atom is, relative to the *para*-position of the benzene ring.

The UV/vis studies of the N, N'-(aryl)benzaldiimine ligands in ethanol solution indicated that the electronic effect produced by the substituents {electron donor or electron acceptor except for 4-N(CH_3)$_2$} onto the system affect is similar throughout the absorption bands of the imines. The effect of the solvent, ethanol enhances the bathochromic shift.

It can be concluded that, on the reduction of the iminic bond in N, N'-(aryl)benzaldiimine ligands, the $\pi \rightarrow \pi^*$ transitions of the benzene ring (amine ligands) both in ethanol and chloroform behave similarly (red shift). For both chloro and bromo complexes a slight mixing between the $\pi -$ orbitals of the benzene ring of the free ligand and the $\pi -$ orbitals of the benzene ring of the metal complex is observed. The mixing of these orbitals depends on the nature of the solvent. In chloroform a non-linear relationship in enhanced within the data of the complexes (both bromo and chloro), while in ethanol the opposite is favoured.

The streochemistry of the Cu(R-BENH)Br_2 complexes was found to be predominately distorted tetrahedral, while for the chloro complexes tetragonal coordination involving the solvent was observed.

4.7 References

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