Study and Calculation of Structure of Compound Heteroaromatic Have Factor Group (NH) with the Cobalt Complex

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Abstract: (N'EN'E)-N'-((1Hpyrrole -2-yl) methylene) - N - (1-phenylethylidene) ethane-1, 2-diamine [C_12H_17N_3] were prepared by the reaction of acetophenone with ethan-1,2-diamine and 1H-pyrrole-2-carbaldehyde. The synthesized derivatives were characterized by FT-IR, ^1_H, ^13_CNMR spectrometry and elemental analysis. The molecular geometry and vibrational frequencies calculated by using the UHF methods with 3-21G basis set and frequencies [^1_H],[^13_C],[^15_N] NMR calculated by using the UB3LYP method with 3-21G E(UB+HF+LYP) basis Sets. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies show that charge transfer occurs with in the molecule. The reaction was performed by using ordinary condensation type, which enabled to easy work-up and good yield.

Key words: 1H-pyrrole-2-carbaldehyde • Synthesize • LUMO • HOMO

INTRODUCTION

Complexes of Schiff bases with paramagnetic metal ions have received the most attention as a new class of potential magnetic resonance imaging (MRI) contrast agent [1-2] and manganese Schiff base complexes have been demonstrated to be effective as imaging agents for liver and kidneys [3]. In the area of bioinorganic chemistry the interest on Schiff base complexes has centered on the role that such complexes may have in providing synthetic models for the metal-containing sites in metallo-proteins and -enzymes [4].

In normal practice, two group of agents (chemotherapeutic, analgesic and anti-inflammatory) are prescribed simultaneously. Isatin, a heterocyclic compound was identified in animals as a major component of the endogenous monoamine oxidase inhibitor. Isatin derivatives have gained unique importance due to the broad spectrum of pharmacological activities which are reflected by their use as antimicrobial [5] analgesic [6] anti-inflammatory [7] and anti-convulsant [8-10]. The various substituent at 3rd position of the isatin which were reported various substituted phenyl ring moieties, heterocyclic rings and aliphatic system.

Ligand,a metal surrounded by a cluster of ions or molecule, is used for preparation of complex compounds named as Schiff bases[11], which are condensation products of primary amines and aldehydes or ketones (RCH=NR', Where R and R' represents alkyl and/or aryl substituents).

Radical mediated alkylations are also known to occur. [12-14] Herein, we describe an unprecedented attack by amide at the imine carbon atoms of tridentate Schiff base ligands to give unusual tetradentate ligand systems.

We plan to synthesis of some novel Schiff bases by Schiff reaction.

MATERIALS AND METHODS

Instruments: The infrared spectra were determined on a NEXUS 670 FT-IR spectrometer with KBr pellets. The ^1_H NMR spectra were recorded on a Bruker300 MHz Avance spectrometer. Melting points were determined in an Electrothermal 9200. The reaction and suggested structure of NHMNPE in shown in (Scheme 1). (Scheme 1) Reaction and expected structure of

(N'EN'E)-N'-((1Hpyrrole -2-yl) methylene) - N_2- (1-phenylethylidene) ethane-1, 2-diamine
**Synthesis of the ligands**  
(N\(^{1}\)EN\(^{2}\))-N\(^{-}\)(1Hpyrrole-2-yl) methylene)-N\(^{-}\)(1-phenylethylidene) ethane-1, 2-diamine: Measured (1.85gr, 30mmol) of 1,2-ethylene diamine and (3.7gr, 30mmol) of acetophenones and solved in 20 ml absolute ethanol at 50°C. Then the second mixture added in the 1H-pyrrole-2-carbaldehyde solution and refluxed for 24 h. (Scheme 1).

After complete refluxation yellow coloured precipitate was separated after removal of the solvent at room temp. The precipitate was recrystallised at room temperature with some solvent like as petroleum ether and it was dried under vacuum. Reaction was monitored on TLC. Yield: 60%;

\[ C_{10}H_{13}N; IR \ (KBr, \ cm^{-1}) : \ 3175.15w \ (N-H), \ 2866.91w, \ 2753.11w \ (C-H), \ 1641.40m \ (C=N), \ 1012.65w \ (C-H, In plane), \ 752.82w, \ (C-H, OPP), \ 3085.58w \ (C-H, sp\(^{2}\)), \ 2969.58w, \ 2940.72w, \ (C-H, sp\(^{3}\)); \]

\[^{1}\text{H}NMR \ (300MHz, \ CDCl): \ \delta, ppm \ 9-10 \ (s, 1H, N-H), \ 8-9 \ (s, 1H, =C-H), \ 6-7.5 \ (m, 8H, Ar-H), \ 3-4 \ (s, 4H, -CH\(_{2}-CH_{2}-\)); \]

\[^{13}\text{C}NMR \ (300MHz \ CDCl): \ \delta, ppm \ 20-40 \ (-CH), \ 50-60 \ (-CH\(_{2}-CH\(_{2}-\)), \ 70-80 \ (CDCl), \ 100-140 \ (Phenyl group and hetroaromatic group), \ 140-160 \ (=C-H), \ 160-180 \ (Ph-C=\ N); \ (Figure \ 6,7), \ (Table3) \]

**Computational Method:** All calculations were performed using the Gaussian 03 package of program on a Windows-XP operating PC. The molecular structure of the title compound in the ground state is computed by performing UHF methods with 3-21G basis set and method UB3LYP with 3-21G E(UB+HF+LYP) basis Sets. Full optimization for the all molecule were carried out by the UHF method using with the 3-21G basis set.

**RESULTS AND DISCUSSION**

**IR Spectral Studies:** In the bands IR spectraum, the (Ar-NH) observed at 3175 cm\(^{-1}\) in the ligand (NHMNPE) and disapiared in metal complexes showing the participation of the N-M group in coordination. The IR spectra of ligands shows strong band in the region1590-1641cm\(^{-1}\) due to C=N which is assignable to Heteroaromatic Schiff bases. In spectra of cobalt (III) complexes, very sharp peak in region 700-800cm\(^{-1}\) suggests the presence of Heteroaromatic bond.. The band due to C=N has shifted to lower frequency in the complexes indicating the coordination through azomethine nitrogen. It is found from the IR spectra of the complexes that there are wide and strong band at 601-800 cm\(^{-1}\) for (M-N) bonding which are assigned to metal stretching vibration. (Figure 1, 2 ).

![Scheme 1](image)

(Scheme 1) Syntheses of (N\(^{1}\)EN\(^{2}\))-N\(^{-}\)((1Hpyrrole-2-yl) methylene) - N\(^{-}\)(1-phenylethylidene) ethane-1, 2-diamine
Fig. 1: FT-IR spectrum of NHMNPE in KBr disk

Fig. 2: FT-IR spectrum of Co\([\{(C_{15}H_{15}N_{3})Cl\}_2\}.2\text{H}_2\text{O}\) in KBr disk

Fig. 3: Spectrum $^1$H NMR of the synthesized ligands NHMNPE in the magnetic field 300 MHz In the solvent CDCl$_3$
Fig. 4: Spectra 1HNMR of synthesized ligands NHMNPE scale expansion ppm corresponding to three protons of (CH3)

Fig. 5: Spectrum 1HNMR of the synthesized ligands NHMNPE in the magnetic field 300 MHz In the solvent CDCl₃, 6-8 ppm
Fig. 6: Spectra $^{13}$CNMR related to the structure of the synthesized ligands NHMNPE in the solvent CDCl$_3$.

Fig. 7: Spectra $^{13}$CNMR related to the structure of the synthesized ligands NHMNPE in the solvent CDCl$_3$. 
Fig. 8: Wire frame models and System adopted in the study for complexe Co[(C_5H_5N)_2Cl_2].2H_2O at UHF/3-21G (d, p) level

Fig. 9-a: Stick models and Optimized geometry of [C_5H_5NCl_2]_2 (NHMNPE) at UHF/3-21G (d, p) level, (Solvent Accessible Surface: Dots)

Fig. 9-b: Stick models and Optimized geometry of [C_5H_5NCl_2]_2 (NHMNPE) at UHF/3-21G (d, p) level, (Solvent Accessible Surface: Translucent)

Fig. 10-a: Stick models and System adopted in the study for complexe Co[(C_5H_5N)_2Cl_2].2H_2O at UHF/3-21G (d, p) level

Fig. 10-b: Stick models and System adopted in the study for complexe Co[(C_5H_5N)_2Cl_2].2H_2O at UHF/3-21G (d, p) level

Fig. 11-a: Ball & Stick models and Optimized geometry of [C_5H_5NCl_2]_2 (NHMNPE) at UHF/3-21G (d, p) level

Fig. 11-b: Ball & Stick models and system adopted in the study for complexe Co [C_5H_5NCl_2].2H_2O at UHF/3-21G (d, p) level

Fig. 12-a: Space-filling model and Optimized geometry of [C_5H_5NCl_2]_2 (NHMNPE) at UHF/3-21G (d, p) level
Molecular Geometry: The optimized molecular structure of (N\textsuperscript{E}N\textsuperscript{E})-N\textsuperscript{N}-(1Hpyrrole -2-yl) methylene - N\textsuperscript{2}- (1-phenylethylidene) ethane-1,2-diamine molecule is obtained from Gaussian 03 package of program are shown in the (Figure 8-10).

The optimized structural parameters of (NHMNPE) calculated by ab initio- UHF levels with the standard 3-21G (d,p) basis set are listed in (Table 1), (Figure 11-a,b).
Fig. 16: Ball & Stick models and system adopted in the study for complexe Co \([C_6H_5N_2Cl_2]_2\) at UHF/3-21G (d, p) level (Solvent Accessible Surface: Translucent) (Connolly Molecular Surface: Dots)

Fig. 18-a: Calculated \(^1\)H NMR of \(\text{N}^1\)-((1Hpyrrole -2-yl) methylene) - \(\text{N}^2\)- (1-phenylethylidene)ethane -1,2-diamine, \([C_6H_5N_2Cl_2]\) (Reference: TMS H\(\text{F}/6-31G(d)\) GIAO)

Fig. 17: Calculated infrared spectra of \((\text{N}^\text{EN}^\text{N}^\text{E}) - \text{N}^1\) - ((1Hpyrrole -2-yl) methylene) - \(\text{N}^2\)- (1-phenylethylidene)ethane -1,2-diamine, \([C_6H_5N_2Cl_2]\). (top to bottom, frequencies in cm\(^{-1}\), intensities in arbitrary units).

Fig. 18-b: Calculated \(^1\)H NMR of \(\text{N}^1\)-((1Hpyrrole -2-yl) methylene) - \(\text{N}^2\)- (1-phenylethylidene)ethane -1,2-diamine, \([C_6H_5N_2Cl_2]\).

Fig. 19-a: Calculated \(^1\)C NMR of \(\text{N}^1\)-((1Hpyrrole -2-yl) methylene) - \(\text{N}^2\)- (1-phenylethylidene)ethane -1,2-diamine, \([C_6H_5N_2Cl_2]\).

Fig. 19-b: Calculated \(^1\)C NMR of \(\text{N}^1\)-((1Hpyrrole -2-yl) methylene) - \(\text{N}^2\)- (1-phenylethylidene)ethane -1,2-diamine, \([C_6H_5N_2Cl_2]\).
Fig. 19-c: Calculated $^1$CNR of (N'EN'E)-N'-((1Hpyrrole -2-yl) methylene) - N'-2(1-phenylethylidene) ethane-1,2-diamine, [C$_{11}$H$_{17}$N$_2$Cl$_2$] Reference: TMS HF/6-31G(d) GIAO)

Fig. 20-a: Calculated $^1$NMR of (N'EN'E)-N'-((1Hpyrrole -2-yl) methylene)-N'-2(1-phenylethylidene) ethane-1,2-diamine, [C$_{11}$H$_{17}$N$_2$Cl$_2$].

Fig. 20-b: Calculated $^1$NMR of (N'EN'E)-N'-((1Hpyrrole -2-yl) methylene)-N'-2(1-phenylethylidene) ethane-1,2-diamine, [C$_{11}$H$_{17}$N$_2$Cl$_2$] (Reference: NH3 HF/6-31G (d) GIAO)

Vibrational spectroscopy is extensively used in organic chemistry for the identification of functional groups of organic compounds, the study of molecular
HOMO (UHF) \( E_{\text{HOMO}} = -0.321 \text{ a.u.} \) (Ground State)

\[ E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad \text{(Energy gap)} = -0.049 \text{ a.u.} \]

**Fig. 21-b:** The atomic orbital compositions of the frontier molecular orbital for NHMNPE at the UHF/3-21G, Wavefunction: (Unrestricted (Alpha))

LUMO (UHF) \( E_{\text{LUMO}} = -0.272 \text{ a.u.} \) (Excited State)

\[ \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = -0.049 \text{ a.u.} \]

**Fig. 22:** The atomic orbital compositions of the frontier molecular orbital for NHMNPE at the UHF/3-21G, Wavefunction: (Restricted).

HOMO (UHF) \( E_{\text{HOMO}} = -14.29216 \text{ a.u.} \) (Ground State)

LUMO (UHF) \( E_{\text{LUMO}} = -2.65536 \text{ a.u.} \) (Excited State)

\[ \Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} = -16.94746 \text{ a.u.} \]
conformations, reaction kinetics, etc. The observed and calculated data of the vibrational spectrum of (NHMNPE) are given in (Table 2),(Figure 17). The comparative graph of calculated vibrational frequencies by UHF method at 3-21G basis sets for the (NHMNPE) are given in the (Figure 12-a,b), (Figure 13).

CONCLUSIONS

A new Schiff’s bases bearing N(N’E(E))-N’-((1Hpyrrole-2-yl)methylene)-N’-(1 phenylethylidene) ethane-1,2-diamine cobalt were synthesized by the steps mentioned in experimental part (Figure 14-a,b). The structure of the synthesized compounds was confirmed by IR, 'HNMR. The Schiff bases are coordinated with Co(III) ion through azomethine nitrogen and -NH (Figure 15).

The structure of (N(E(E))-N’-((1Hpyrrole-2-yl)

methylen)-N’-(1-phenylethylidene) geometry was compared with optimized parameters obtained by means of ab initio calculations with the 3-21G and 3-21G E(UB+HF+LYP) basis set. (Figure 16) (Figure 18-20) The geometries and normal modes of vibrations obtained from UHF/3-21G calculations are in good agreement with the experimentally observed data (Figure 23). The HOMO and LUMO levels of (N(E(E))-N’-((1Hpyrrole-2-yl)methylene)-N’-(1-phenylethylidene) ethane-1,2-diamine have been studied with UHF/3-21 G level (Figure 21-a,b), (Figure 22).

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