Spectroscopic Investigation (IR and NMR) and HOMO-LUMO Analysis of Aromatic Imines Using Theoretical Approach

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***Abstract*—In this work, we present the experimental alongside the theoretical vibrational (IR and NMR) spectra of (E)-N-benzylidenebenzenamine (A1) and (E)-N-(2, 4'-dichlorobenzylidene) propan-1-amine (A2). In the theoretical investigations, the structure of the molecules, their vibrational frequencies and NMR spectra were determined utilizing the Density Functional Theory (DFT) method with the B3LYP 6-311++G (d, p) basis set. The infrared (IR) spectra for the imine molecules have been recorded in the region of 500–4000cm^{-1}. ^{13}C and ^{1}H nuclear magnetic resonance (NMR) chemical shifts of the molecules have been calculated based upon the gauge-independent atomic orbital (GIAO) method. The computed results were finally used for simulation of IR, ^{1}HNMR and ^{13}CNMR spectra of the molecules which showed in accordance with the available experimental data. UV–Vis spectrums of the molecules were computed in order to determine the HOMO-LUMO energies and hence to attain the insight of the electronic properties. Mulliken population analysis on atomic charges of the molecules was also calculated by HF and B3LYP method. All the calculations indicated that the B3LYP method provides the most satisfactory results and can be employed for the structural identification of organic compounds. It also demonstrates the way towards characterization of molecules and can guide in the fundamental research in chemical science.**

Keywords*— *Aromatic Imine, IR, NMR, HOMO-LUMO, DFT

I. INTRODUCTION

Nitrogen-containing compounds are prevalent in nature and they play an important role in the metabolic function of every living cells [1]. Imines are compounds containing C=N functional group which are produced through the condensation reaction of primary amines with aldehyde or ketone [2]. They are unique class of ligands and play an influencing role in the progress of chemistry science [3]. Imines are known to exhibit biological activities like antibacterial [4], anti-inflammatory [3], antitubercular [5], antimalarial [6], and anticancer [7]. Apart from biological activities, imines also serve as the backbone for heterocyclic compounds synthesis [8]. Imines play a very important role in the field of coordination chemistry as well as in the development of inorganic chemistry and optical materials [3]. Aromatic Imine derivatives promote researchers to design aryl aromatic amines for the emergence of new environmental-friendly technology [9]. The Quantum Chemical Computations in recent years have become an effective resource in the investigation of molecular structure and vibrational frequencies of organic molecules [10]. The literature survey shows several reports on the successful application of DFT calculation to Imines for the computation of structural characteristics, energies and vibrational frequencies [11]–[13]. DFT is a broadly utilized technique for electronic structure calculations because of its precision and efficiency. DFT has a great deal of potential to turn into an entirely important tool for challenging problems existing in medicinal Chemistry. Imines are biologically significant dominant ligand in chemical science and therefore, study of their energy and structural parameters are always useful for study of many complex biological processes occurring in the cells. The objective of the present work is the application and potentiality of DFT for the investigation of aromatic imines. As far as we could possibly know, DFT calculations and experimental studies have not been accounted for the molecules **A1** and **A2**. Considering all the aspects, we present here the theoretical methods for the investigation of IR and NMR spectroscopy and also HOMO-LUMO analysis along with the experimental support [14] to illustrate the structural information of the molecules **A1** and **A2**. The HF (Hartree-Fock) and DFT (Density functional theory) computations were done to support the accuracy of vibrational frequencies. The DFT method was used in computing the HOMO-LUMO energies using 6-311G (d, p) level of theory [15]. In addition, NMR and Mulliken population analysis has also been achieved to support the structural properties [10].

II. EXPERIMENTAL DETAILS

A. Synthesis of A1 and A2

(E)-N-benzylidenebenzenamine **A1** and (E)-N-(2, 4'-dichlorobenzylidene) propan-1-amine **A2** were synthesized in accordance with the literature procedure [16].

B. IR and NMR spectra

The IR spectra of **A1** and **A2** were recorded in the region 500–4000cm^{-1}. Carry 630 FT-IR spectrophotometer was used to record the Infrared (IR) spectra and expressed as ν_{max} cm^{-1}. Bruker AvIII HD- 400 MHz FTNMR spectrometer was used for the Nuclear Magnetic Resonance (NMR) spectra using Tetramethylsilane (TMS) as internal standard.

III. COMPUTATIONAL DETAILS

Hartree-Fock (HF) and Density functional theory (DFT) methods with 6-311G (d, p) basis set was used for quantum mechanical calculation with the help of Gaussian 09W software package [17]. The vibrational wavenumbers were calculated using B3LYP method and the HOMO-LUMO energies were studied at time-dependent TD-SCF based on the optimized structure of **A1** and **A2** [18]. The ^{1}HNMR and ^{13}CNMR chemical shifts were computed using GIAO