Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 1932–1940

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectroscopic (FT-IR, ^{1}H, ^{13}C NMR, UV), DOS and orbital overlap population analysis of copper complex of (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine by density functional theory

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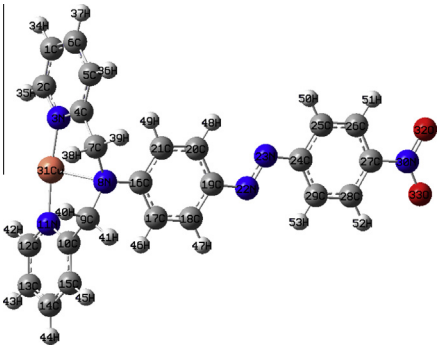
HIGHLIGHTS

- Molecular structure for title compound is reported using DFT approach.
- DOS (density of states) is studied and plotted.
- Orbital overlap population between different interacting groups is analyzed.
- Computed IR spectra confirms the formation of copper complex.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form 14 October 2014
Accepted 23 October 2014
Available online 4 November 2014

Keywords:
DFT
B3LYP
GIAO
DOS
SDD

ABSTRACT

The geometric parameters, chemical shifts, FTIR, NMR and orbital overlap population along with DOS (density of states) to know different kinds of interactions for binding of copper atom with (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine to form its copper complex has been reported by DFT methods. The theoretically predicted values for structural parameters are in agreement with the experimentally reported values. NMR chemical shifts calculated using B3LYP/DFT/GIAO level of theory gives information about binding of copper atom with three nitrogen atoms namely N (3, 8 and 11). Orbital overlap population analysis using DFT/B3LYP/SDD level of theory is used to study the kind of interactions involved in binding of copper with the three nitrogen atoms. DOS studies are done to know about the contribution of alpha, beta electrons to the valence and conduction band. IR spectroscopy investigations gave the absorption bands for the formation of title compound. Electronic spectrum along with HOMO–LUMO energies of the title compound has been investigated using Time-dependent (TD-DFT) approach.

Introduction

Copper being an important nutrient in all living systems plays a vital and key role in governing many functions of the body [1,2] hence determination of traces of copper in environmental and industrial samples has been an important topic in different type of analysis. Conventional method for the determination of traces of various metal ions like copper require sophisticated instruments and are very time consuming [3,4]. To overcome these difficulties many chemo sensors techniques have been developed and reported in the literature [5–7]. Out of these techniques, calorimetric

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http://dx.doi.org/10.1016/j.saa.2014.10.110
1386-1425/

Table 1
Optimized geometrical parameters of the (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine[$] its copper complex using B3LYP/SDD level of theory for selected Bond lengths in Angstrom.

Bond length (Å)/ copper complex	Experimental [Ref. 9]	Calculated [($)] DFT/B3LYP/ SDD	Calculated (copper complex) DFT/B3LYP/ SDD
N11-Cu31	NA	NA	1.87
N3-Cu31	NA	NA	1.87
N8-Cu31	NA	NA	1.90
N11-C10	1.35	1.36	1.38
N3-C4	1.35	1.37	1.38
C4-C7	1.50	1.52	1.53
N8-C7	1.44	1.48	1.48
N8-C9	1.45	1.48	1.48
C9-C10	1.50	1.52	1.53
N8-C16	1.36	1.39	1.43
C19-N22	1.41	1.40	1.41
N22-N23	1.27	1.29	1.31
N23-C24	1.43	1.42	1.41
C27-N30	1.47	1.47	1.45
N30-O32	1.25	1.28	1.29
N30-O33	1.27	1.29	1.29

techniques have many advantages like they are convenient to examine with naked eyes [8]. The title compound shows experimentally well proven sensing properties for selective detection of $Cu2^{+}$ ions based on azobenzene as signaling unit [9]. In interest of such applications we have reported the theoretical structure of copper complex of E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine and its quantum chemical calculations such as DOS, chemical shifts, UV–Vis, NMR, IR spectra along with orbital overlap population are the few properties which are investigated theoretically.

Computational methods

DFT [10–13] has proven to be a very useful tool in investigating the electronic structure of the molecules. The calculation on the new copper complex of (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine has been done to examine its optimized ground state geometry using B3LYP level of theory and SDD basis set as implemented in Gaussian 09 package [14] using Berny Method [15]. The main reason for choosing SDD basis set coupled with B3LYP functional is due to fact that it is small basis set in comparison to Pople 6-31+g(d) and yields excellent molecular geometries which is proved in conformational analysis done by Branca and co-workers as reported in their findings [16]. The same argument was further supported in their findings on a certain atoms/molecules that RMS error in vacuum using commonly used Pople basis set is around 0.006 eV while using SDD basis set it is 0.002 eV. Branca and co-workers also performed computational studies on the bond length and dipole moment of formaldehyde molecule and found that the values for (C—O) bond length and dipole moments for formaldehyde are very close to the experimentally calculated values using SDD basis set over Pople basis set. Another reason for choosing the SDD basis set is that they are free from Pople constraint of equal exponents of s and p primitives. Also our theoretically simulated parameters for various properties of the title compound are in close agreement with their experimental counterparts using SDD/B3LYP basis set rather than commonly used Pople basis sets. In addition to the analysis of bindings of the copper atom with three nitrogen atoms the optimized parameters of the title compound are compared with the experimentally calculated values by other authors [9] and are given in Table 1 for selected bond lengths. Optimized structural parameters are used in the isotropic chemical shifts, DOS and OP (orbital overlap), NMR, UV–Vis calculations. The nuclear magnetic resonance (NMR) chemical shift calculations are performed using Gauge-Invariant Atomic Orbital (GIAO) [17,18] method at B3LYP level of theory. Solvent effect on theoretical NMR parameters is included using Conductor Polarizable Continuum Model (CPCM) [19–22] provided by Gaussian 09 program. DMSO is used as a solvent. Density of states (DOS) [23] which provides the molecular orbital contribution of different constituting elements to the total system is also calculated by using GaussSum program [24]. Electronic spectrum along with HOMO–LUMO energies [25–30] of the title compound has been investigated using Time-dependent (TD-DFT) approach.

Results and discussion

Structural parameters

The ground state geometry of new copper complex of (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine using B3LYP [31] level of theory along with SDD basis set [32] as implemented in Gaussian 09 package has been investigated. The ground state optimized geometry of the title compound is investigated using tight convergence criteria and the obtained structure is local minima on the PES. Fig. 1 represents the ground state geometry of the (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine along with its copper complex (title compound). Both structures have been optimized using DFT methods to find the optimized ground state geometry. The

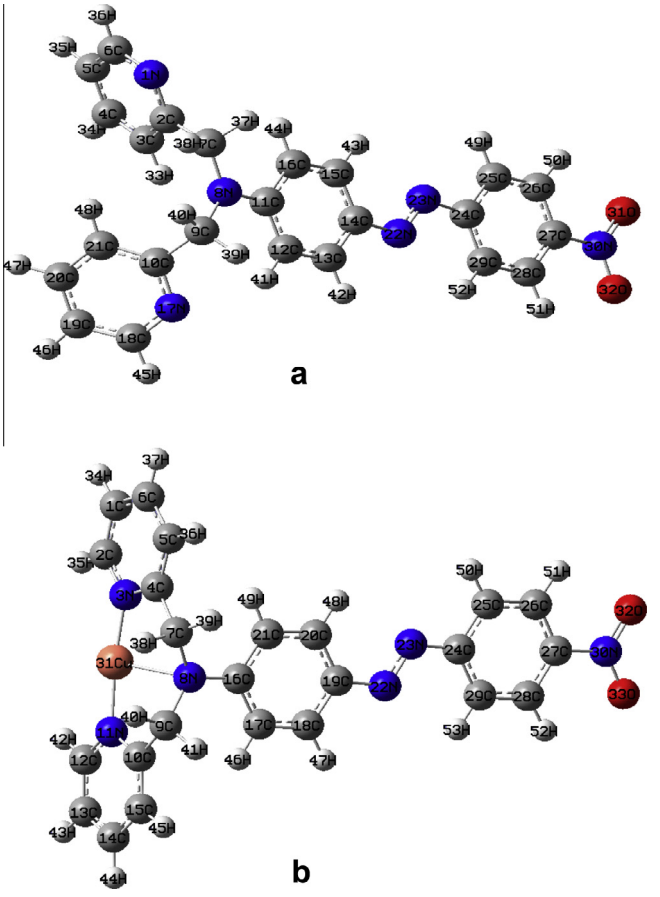

Fig. 1. Optimized ground state geometry of (a) (E)-4-(2-(4-nitrophenyl) diazenyl)-N, N bis ((pyridin-2-yl) methyl) benzamine (b) its copper complex (Title compound) using B3LYP/SDD/DFT level of theory.