Electronic Structure of Two New Bis-Schiff Base Ligands using DFT Method

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.

ABSTRACT

Two Bis-Schiff Bases **1** and **2** are ligands that can coordinate with manganese metal to form stable complexes and have biological activity. Thermodynamic parameters, HOMO-LUMO energy levels and FTIR spectra of two ligands have been computed using B3LYP/G-6311++(d,p) functional of the DFT calculations. The two ligands are favored thermodynamically, and the ligand **1** has been shown to be more stable than ligand **2**. The Polarizability values of two ligands have been investigated. The results refer that ligand **2** interacts earlier than ligand **1** to the metal ion. The FTIR spectra of two ligands have been evaluated. All results show the good agreement between the theoretical and experimental data.

Keywords: Electronic Structure, DFT, Bis-Schiff Bases, Complexes, HOMO, LUMO, Spectroscopy.

1. INTRODUCTION

Schiff bases are organic compounds contain the substituted imine. The condensation of aldehydes or ketones with a diamine produce the bis-Schiff base compounds. All bis-Schiff bases can be coordinated as ligands with the central transition metal such as manganese ion to form complexes. The Schiff bases and bis-Schiff ligands and their complexes have been studied widely due to interesting and important applications. They are used as irregular binding model in peptides [1], and have antibacterial activity [2], are able to bind toxic and heavy metal atoms [3], and exhibit photo-chromisms [4]. These properties of the bis-Schiff ligands and their complexes can be related to the molecular structure of these compounds.

On the other hand, a density functional theory DFT is a very important computational method to investigate and calculate structures and energies in many medical systems [5]. The molecular structures of some organic compounds were studied using DFT methods such as nitroaniline [6], vanillins [7-9], diazo dyes [10-14], and Schiff bases [15-18]. Some bis-Schiff bases and their complexes [19-20] were also reported and investigated using DFT methods.

Recently, we have been synthesized, characterized and studied the antibacterial activity of new tetradentate ligands **1-2** and their complexes with manganese^{II} **3** and **4**, Fig. 1 [2]. Moreover, we have been reported the synthesis, characterize of some diazo dyes [21], investigated an intramolecular hydrogen bonds and the dipole interaction of them [22], studied their electronic structure using density functional theory DFT [23], and molecular docking with human serum albumin HSA of those compounds [24]. In this work, the electronic and the spectroscopic parameters of compounds **1-4** are computed using DFT method at B3LYP/6-311++G(d,p) level.

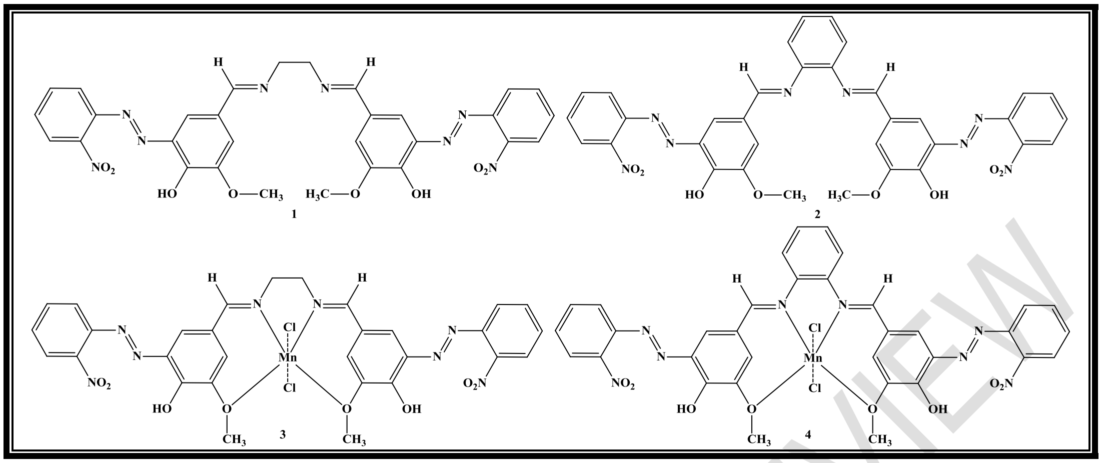

Fig. 1. The chemical structures of bis-Schiff bases 1 and 2, and their manganese^{II} complexes 3 and 4.

2. EXPERIMENTAL PARTS

2.1 General

All FTIR spectra were recorded on a JASCO FTIR 4600 spectrometer, Single beam, Path Laser, using KBr disk technique in the frequency range of 4000–400 cm^{-1}. The instrumental equipment is performed at PCB Research Laboratory, Faculty of Science, Hadhramout University, Mukalla, Hadhramout, Yemen.

2.2 Synthesis of bis-Schiff bases 1-2

Bis-Schiff bases 1-2 were synthesized as described previously [2,25-27].

2.3 Synthesis of Complexes 3-4

The complexes 3-4 were synthesized by the methods described earlier [2,28].

2.4 Computational Methods

The starting structures of the studied compounds were built using GaussView while the DFT calculations were conducted using Gaussian09 software [29]. The combination of the functional, B3LYP with the basis set 6-311++G(d,p) has shown good correlation between the cost of the calculations and the accuracy of the results. The geometry of the studied compounds was optimized to the ground state and that was confirmed by the calculations of the vibrational frequencies and in specific by the missing of imaginary frequencies. For the optimized structures, the frontiers molecular orbitals, HOMO and LUMO were elucidated using the optimized wave function and visualized using GaussView software [29].

3. RESULTS AND DISCUSSION

The newly bis-Schiff bases ligands **1** and **2** were synthesized and identified using elemental analysis, mass, UV-Vis, and IR spectroscopic techniques, previously [2]. The synthesized ligands are soluble in ethanol, and stable at room temperature in the solid state. They have melting points 397.15 ^{o}K and 472.15 ^{o}K, respectively. The electronic structure of two ligands were studied and performed on the basis set B3LYP/G-6311++(d,p) level of the DFT calculations, Fig. 2.

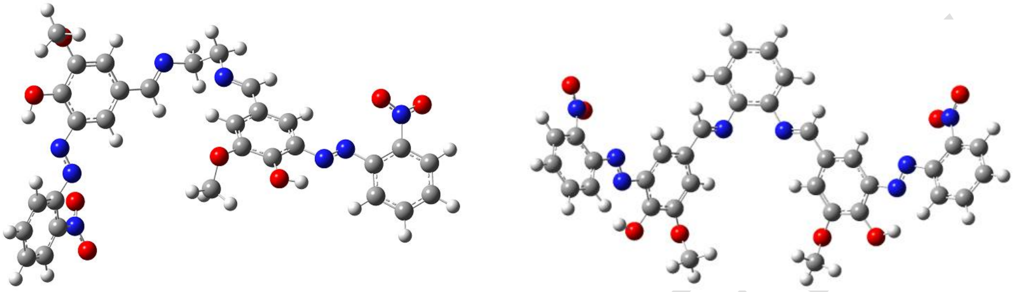

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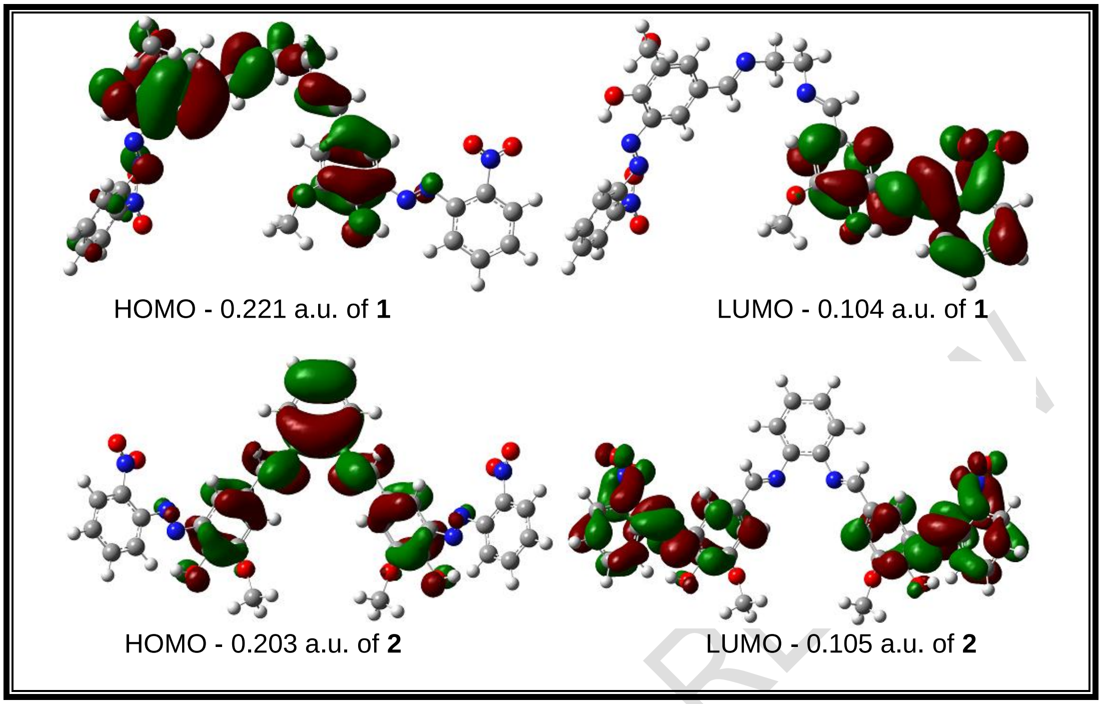
Fig. 2. The chemical structures of bis-Schiff bases 1 and 2.

The thermodynamic parameters that are electronic energy *E*, enthalpy change ΔH, entropy change ΔS, and Gibbs free energy change ΔG of the two ligands were obtained and summarized in Table 1. All values of thermodynamic data reflect the thermal stability of ligands **1** and **2**, and revealed that they are preferred thermodynamically. The entropy change value of ligand **2** is more positive, whereas its heat formation and Gibbs free energy change values are more negative than the ligand **1**.

The highest occupied molecular orbital HOMO and the lowest unoccupied molecular orbital LUMO of ligands are studied at the same level of theory and their molecular orbitals are shown in Fig. 3. The Energy gap, dipole moment, and polarizability are also listed in Table 1. The obtained energy gap values between HOMO and LUMO suggest that ligand **1** is more stable than ligand **2**. In contrast, the ligand **2** has high polarizability value that reflects its ability to interact earlier with the ion metal in the complex formation reaction as compared to the ligand **1**. Experimentally, both ligands can coordinated with the Mn^{II} to produce stable manganese complexes **3** and **4** [2].

Table 1. Energy, thermodynamic parameters, dipole moment and polarizability as determined for ligands 1 and 2 at b3lyp\6-311++g(d,p) level

Physical Properties	**Compounds**	
	1	**2**
Electronic Energy a.u.	- 2,198.302992	- 2,350.736305
Entropy ΔS cal/mol.K	267.87	275.59
Enthalpy ΔH a.u.	- 2,197.72	- 2,350.13
Free Energy ΔG a.u.	- 2,197.85	- 2,350.26
Energy gap kJ/mol	307.18	257.30



HOMO - 0.221 a.u. of **1**

LUMO - 0.104 a.u. of **1**

HOMO - 0.203 a.u. of **2**

LUMO - 0.105 a.u. of **2**

Fig. 3. The molecular orbitals (HOMO and LUMO) of compounds 1 and 2.

The FTIR spectra of the studied ligands have been computed at the B3LYP/G-6311++(d,p) level of theory and shown in Fig. 4. Both spectra show the intense O-H stretching absorptions centered around 3500 cm^{-1}. The absorptions characteristic double bonds at about 1600 cm^{-1}, the C-H stretch near 3150 and 3100 cm^{-1}. The spectra of the two ligands also reveal the presence of the imine groups at around 1650-1600 cm^{-1}. In addition to the stretching vibrations of the azo –N=N– and nitro functional groups at frequencies just near 1350 and 1450 cm^{-1}, respectively. Both spectra were in good agreement with the experimental FTIR spectra [2].

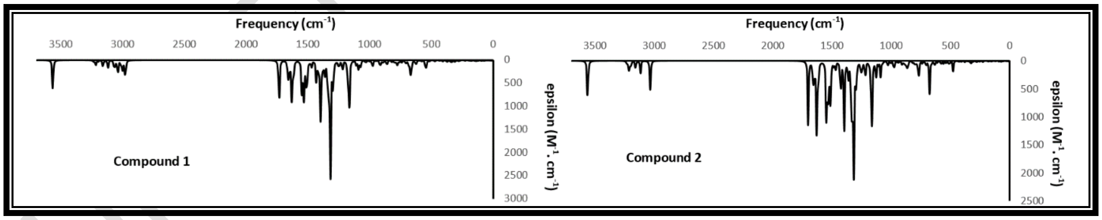


Fig. 4. The calculated IR frequencies of compounds 1 and 2.

4. CONCLUSION

Density functional theory DFT at B3LYP/G-6311++(d,p) level was used to calculate the thermodynamic parameters, HOMO-LUMO energy levels and FTIR spectra of two ligands **1** and **2**. The results suggest that two ligands prefer thermodynamically due to the positive value of entropy and negative values of both Gibbs free energy and heat of formation. The ligand **1** was found to have higher energy gap that reflects the stability of this ligand as compared to the ligand **2**. Polarizability values of two ligands indicate the ability of them to interact with the ion metal in the complex formation reaction, and ligand **2** interacts earlier than ligand **1**. The computational FTIR spectra give the characteristics absorptions of the most functional groups in the two ligands. In conclusion, it was found that these theoretical data are in the good agreement with our results available experimental data. This is worth to indicate the ability of the B3LYP/G-6311++(d,p) to evaluate the molecular structure and spectroscopic data of the ligand **1** and ligand **2**.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

REFERENCES

1. Atkins R, Brewer G, Kokot E, Mockler GM, Sinn E. Copper (II) and Nickel (II) Complexes of Unsymmetrical Tetradentate Schiff Base Ligands. Inorg Chem. 1985;24(2):127-134. DOI: 10.1021/ic00196a003
2. Selim EAB, Al–Douh MH, Al–Nohey DS, Al–Haik WM, Sonbol KS. Synthesis, Characterization, and Antimicrobial Activity Studies of New Schiff Base Tetradentate Ligands and Their Manganese (II) Complexes. Asian J Chem Sci. 2020;7(4):35-46. DOI: 10.9734/AJOCS/2020/v7i419030
3. Soliman AA, Linert W. Investigations on New Transition Metal Chelates of the 3-Methoxy-salicylidene-2-aminothiophenol Schiff Base. Thermochim Acta. 1999;338(1-2):67-75. DOI: 10.1016/S0040-6031(99)00201-4
4. Lambi E, Gegiou D, Hadjoudis E. Thermochromism and Photochromism of *N*-Salicylidenebenzylamines and *N*-Salicylidene-2-aminomethylpyridine. J Photochem Photobiol A: Chem. 1995;86(1-3):241-246. DOI: 10.1016/1010-6030(94)03943-O
5. Sholl DS, Steckel JA. Density Functional Theory: A Practical Introduction. 1st ed., John Wiley & Sons, Inc., New Jersey: Hoboken, USA, 2009. DOI: 10.1002/9780470447710
6. Chis V, Venter MM, Leopold N, Cozar O. Raman, Surface-Enhanced Raman Scattering and DFT Study of *para*-Nitro-aniline. Vib Spectro. 2008;48(2):210-214. DOI: 10.1016/j.vibspec.2008.01.001
7. Velcheva EA, Stamboliyska BA, Boyadjieva PJ. DFT and Experimental Study on the IR Spectra and Structure of 2-Hydroxy-3-methoxybenzaldehyde (*o*-Vanillin) and its Oxyanion. J Molec Struc. 2010;963:57-62. DOI: 10.1016/j.molstruc.2009.10.014
8. Hernandez-Vazquez E, Castaneda-Arriaga R, Ramirez-Espinosa JJ, Medina-Gampos ON, Hernandez-Luis F, Chaverri JP Esmuel-Soto S. 1,5-Diarylpyrazole and Vanillin Hybrids: Synthesis, Biological Activity and DFT Studies. Eur J Med Chem. 2015;100:106-118. DOI: 10.1016/j.ejmech.2015.06.010
9. Rodriguez MR, Pla JD, Piro OE, Echeverria GA, Espino G, Pis-Diez R, et al. Structure, Tautomerism, Spectroscopic and DFT Study of *o*-Vanillin derived Schiff Bases Containing Thiophene Ring. J Molec Struc. 2018;1165:381-390. DOI: 10.1016/j.molstruc.2018.03.120
10. Touafri L, Hellal A, Chafaa S, Khelifa A, Kadri A. Synthesis, Characterisation and DFT Studies of three Schiff Bases Derived from Histamine. J Molec Struc. 2007;1149:750-760. DOI: 10.1016/j.molstruc.2017.08.052
11. Sener N, Bayrakdar A, Kart HH, Sener I. A Combined Experimental and DFT Investigation of Disazo Dye having Pyrazole Skeleton. J Molec Struc. 2017;1129:222-230. DOI: 10.1016/j.molstruc.2016.09.082

12. Shinde S, Sekar N. Synthesis, Spectroscopic Characteristics, Dyeing Performance and TD-DFT Study of Quinolone Based Red Emitting Acid Azo Dyes. Dyes Pigments, 2019;168(9):12-27. DOI: 10.1016/j.dyepig.2019.04.028
13. Georgiev A, Stoilova A, Dimov D, Yordanov D, Zhivkov I, Weiter M. Synthesis and Photochromic Properties of Some *N*-Phthalimide Azo-azomethine Dyes. A DFT Quantum Mechanical Calculations on *imine-enamine* Tautomerism and *trans-cis* Photoisomerization. Spectrochim Acta Part A: Molecu Biomolecu Spectro. 2019;210:230-244. DOI: 10.1016/j.saa.2018.11.033
14. Maliyappa MR, Keshavayya J, Mahanthappa M, Shivaraj Y, Basavarajappa KV. 6-Substituted Benzothiazole Based Dispersed Azo Dyes having Pyrazole Moiety: Synthesis, Characterization, electrochemical and DFT Studies. J. Molec. Struc., 2020;1199:126959. DOI: 10.1016/j.molstruc.2019.126959
15. Al–Douh MH, Ba–Mutairef SK, Abdullah HH. *N*–Benzylidene Pyridine-4-amines: DFT and PM3 Theoretical Study. J Hadh Univ. 2008;14(7):235-246. SBN–National Library Aden 18–2004
16. Elmaci G, Duyar H, Aydiner B, Seferoglu N, Naziri MA, Sahin E, Seferoglu Z. The Syntheses, Molecular Structure Analyses and DFT Studies on New Benzil Monohydrazone Based Schiff Bases. J Molec Struc. 2018;1162:37-44. DOI: 10.1016/j.molstruc.2018.02.035
17. Alyar S, Sen T, Sen C, Alyar H, Adem S, Ozdemir UO. Synthesis, Spectroscopic Characterizations, Enzyme Inhibition, Molecular Docking Study and DFT Calculations of New Schiff Bases of Sulfa Drugs. J Molec Struc. 2019;1185:416-424. DOI: 10.1016/j.molstruc.2019.03.002
18. Sykula A, Kowalska-Baron A, Dzeikala A, Bodzioch A, Lodyga-Chruscinska E. An Experimental and DFT Study on Free Radical Scavenging Activity of Hesperetin Schiff Bases. Chem Phys. 2019;517:91-103. DOI: 10.1016/j.chemphys.2018.09.033
19. Dede B, Gorgulu G. Spectroscopic Properties and Quantum Chemical Calculations of Novel Diimine Molecules and their Mononuclear Cu(II) Complexes. Acta Phys Polo A. 2018;133(2):256-262. DOI: 10.12693/APhysPolA.133.256
20. Chand S, Tyqgi M, Tyagi P, Chandra S, Sharma D. Synthesis, Characterization, DFT of Novel, Symmetrical, N/O-donor Tetradentate Schiff's Base, Its Co(II), Ni(II), Cu(II), Zn(II) Complexes and Their *in-vitro* Human Pathogenic Antibacterial Activity. Egypt J Chem. 2019;62(2):291-310. DOI: 10.21608/EJCHEM.2018.3991.1395
21. Al–Douh MH, Selim EAB, Al–Haik WM, Mahram SMB, Al–Bakri AK, Al–Nohey DS, Sonbol KS. Synthesis and antimicrobial activity of some compounds derived from diazo dyes. Intern J Chem Stud. 2019;3(4):6-12. ISSN: 2581-348X. Available: http://www.chemistryjournal.in/archives/2019/vol3/issue4/3-3-16
22. Selim EAB, Al–Douh MH. Unusual effects of intramolecular hydrogen bonds and dipole interaction on FTIR and NMR of some imines. Asian J Appl Chem Res. 2019;3(3):1-6. DOI: 10.9734/AJACR/2019/v3i330096
23. Al–Douh MH, Selim EAB, Salim HAM, Abdullah HH. Molecular structure and spectroscopic studies of some diazo dyes compounds using DFT method. Toward Intelligent solutions for developing and empowering our societies. The first International Conference of Intelligent Computing and Engineering ICOICE-2019, Mukalla, Hadhramout, Yemen. Computing and Engineering. IEEE. 2019;49:1-4. DOI: 10.1109/ICOICE48418.2019.9035176
24. Al–Douh MH, Selim EAB, Tahir EM, Esmail SAA, Naji YA, Abdullah HH. Biophysical Study for the Interactions of Some Diazo Dyes with Human Serum Albumin. Asian J Appl Chem Res. 2019;4(3):1-10. DOI: 10.9734/AJACR/2019/v4i330113
25. Al–Douh MH, Al–Fatlawy AA, Abid OH. Synthesis and Characterization of Some 2-(*N*-Benzoyl-*N*-pyrid-4-yl aminobenzyl)-aminobarbituric Acids *via* Schiff's Bases. Hadh Stud Res. 2003;4(2):37-49. SBN–National Library Aden 18–2004
26. Al–Douh MH, Al–Fatlawy AA, Abid OH. Synthesis and Characterization of 2-(*N*-Benzoyl-*N*-pyrid-3-yl aminobenzyl)-aminobarbituric Acids *via* *N*-Benzylidene Pyridine-3-amines. Fac Sci Bull. 2003;16(3):83-94. ISSN: 1684–100X

27. Al–Douh MH, Al–Fatlawy AA, Abid OH. Synthesis and Characterization of Some 2-(*N*-Benzoyl-*N*-pyrid-2-yl aminobenzyl)-aminobarbituric Acids *via* *N*-Benzylidene Pyridine-2-amines. Univ Aden J Nat Appl Sci. 2004;8(1):181-194. ISSN: 1606-8947
28. Temel H, Cakir U, Otludil B, Ugras HI. Synthesis, spectral and biological studies of Mn(II), Ni(II), Cu(II), and Zn(II) complexes with a tetradentate Schiff base ligand. Complexation studies and the determination of stability constants (Ke). Synth React Inorg Metal-Org Chem. 2001;31(8):1323-1337.
29. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 16 Software. Revision C.01, Gaussian, Inc., Wallingford: CT, USA; 2016. Available: https://gaussian.com