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A new approach of Quantum chemical study on 2, 4-Dintrophenylhydrazine derived Schiff base ligand (H_2L) using DFT/B3LYP level computation method-Theoretical & Experimental results comparison

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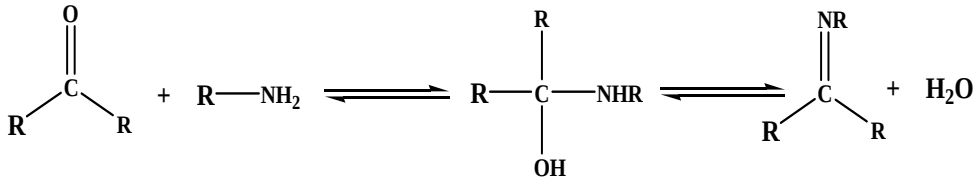
Abstract
We have synthesized a new novel Schiff's base ligand 2-[(2,4-Dinitro-phenyl)-hydrazono]-1,2-diphenyl-ethanol (H_2L) by 1:1 condensation of 2,4-Dinitrophenyl hydrazine (2,4-DNP) and 2-hydroxy-1,2 biphenyl-ethanone (benzoin).The ligand has been characterized by IR, mass and UV-Vis spectroscopic study as well as common elemental analyses(carbon, hydrogen & nitrogen). In this paper we have reported detailed the optimized structure (fig.1) of Schiff base ligand H_2L with the aid of DFT/B3LYP level computation method and proper basis set used 6-31G (d-p). Theoretical IR, UV-Vis spectra are more lucidly interpreted with experimental ones using the optimized structure of reference Schiff base. Schiff base H_2L important experimental parameter like bond distances & angles are thorough compared with DFT computation results and they are matched very well.

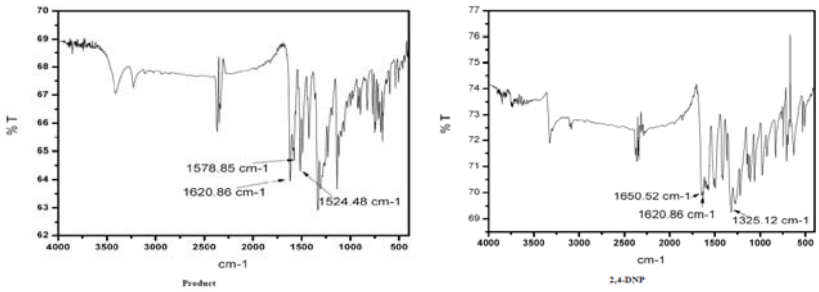
Keywords: Schiff base ligand, IR & UV-Vis spectra, DFT/B3LYP method, basis set 6-31G (d-p) & structure optimization

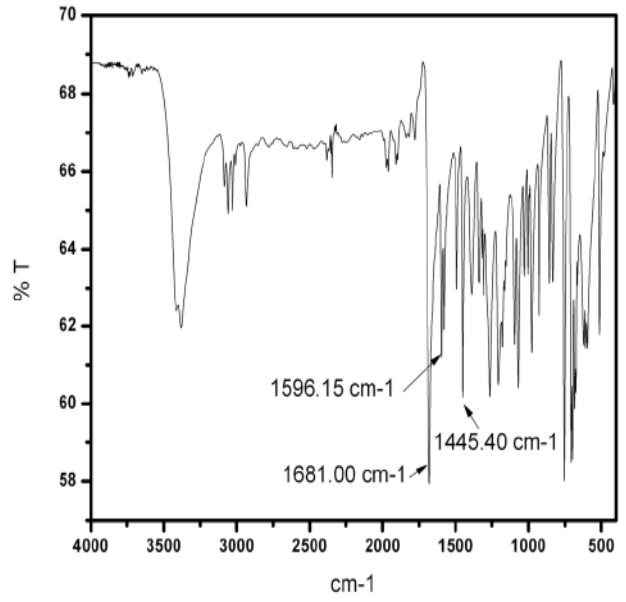
1. Introduction
Schiff bases also popularly known as imine or azomethine, named after novel scientist Prof. Hugo Schiff, was reported in the 19th century (1870's) [1]. Since that time a variety of methods for synthesis of imines have been described. It is most commonly synthesized by the condensation reaction between an aldehyde or a ketone and a primary amine and is well characterized by the presence of azomethine functional group (C=N) with the nitrogen atom attached to the alkyl, aryl, hetero aryl and hydrogen. The classical synthetic path [2] of Schiff base ligand is according to the following reaction.



Carbinolamine

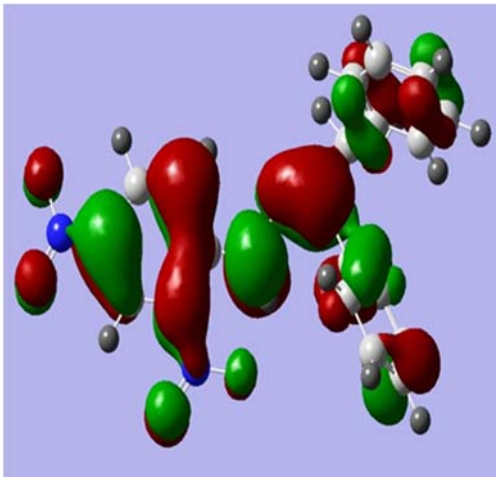
Scheme 1: Common synthetic procedure of Schiff bases





Benzoin

The formation of a Schiff base from an aldehydes or ketone is completely a reversible reaction and generally takes place under acid or base catalysis, or upon heating. The formation is generally driven to the completion by separation of the product or removal of water, or both. Many Schiff bases can be hydrolyzed back to their aldehydes or ketones and amines by aqueous acid or base. A Schiff base ligands are ubiquitous particularly in the field of coordination chemistry being used in the synthesis of a large variety of transition metal complexes due to their potential chelating donor center N, O or even S [3] which remains an important area of research due to their simple synthesis, good yield, high purity of product and wide range of applications [4-10]. The sole applications of Schiff base transition metal complexes have received great attention for their biological, medicinal [11], industrial and catalytic Activities [12-20]. Schiff bases are popularly used as catalysts for industrial purpose, as anticancer, antibacterial, antifungal and antivirus agents in the field of core medicinal chemistry [21]. The present research work highlighted the novel synthesis of reference Schiff base ligand (H_2L), its characterization, geometry optimized by DFT/B3LYP level computation method, theoretical IR,UV-Vis spectra comparison with experimental ones and finally optimized structure important parameter like bond distances, angles are lucidly compared with experimental results.



Graphical Abstract

2. Experimental

2.1 Materials

2, 4-Dinitrophenyl hydrazine and 2-hydroxy-1, 2 biphenyl-ethanone were purchased from Sigma Aldrich Chemical Company(U.S.A).Other commercially available chemicals and solvents like CH3OH, C2H5OH, & CH3CN purified by standard procedures.

2.2.1 Synthesis of Schiff base ligand (H_2L)

2, 4-Dinitrophenyl hydrazine (1.98 g, 10 mmol) was dissolved in a mixture of 100 ml dry methanol and 5 ml dil. HCl. A methanolic solution (100 ml) of 2-Hydroxy-1, 2-diphenyl-ethanone (2.12 g, 10 mmol) was added to it in a vigorous stirring condition and the resulting mixture was refluxed on a steam bath for 7 hrs. The resulting solution was concentrated to 30 ml and kept for overnight. A yellowish orange coloured compound precipitated out. The ppt. was filtered, washed with ether and dried over $CaCl_2$ in vacuum dessicator. (Yield: 75%). M.Wt. (392). m/e 392.1, Anal. Calc. for $C_{20}H_{16}N_4O_5$: C, 61.22; H, 4.11; N, 14.28. Found: C, 61.23; H, 4.12; N, 14.26 %. IR (KBr, ν_{max}/cm^{-1}): ν (O-H) 3474; ν (C=N) 1620, UV-Vis spectrum, λ_{max} (CH_3OH+CH_3CN): 425.2 nm, 375 nm, 330 nm & 309 nm.

2.2. Physical measurement

Elemental analyses (carbon, hydrogen and nitrogen) of title Schiff base ligand were determined with a Perkin–Elmer CHN analyzer 2400. Mass spectra (e/m) were done with a JEOLJMS-AX 500 mass spectrometer. IR spectra (KBr pellet, 400–4000 cm^{-1}) were recorded on a Perkin–Elmer model 883 infrared Spectrophotometer. UV-Vis spectra of Schiff base ligand in 1:1 CH_3OH+CH_3CN mixture were taken in a Perkin-Elmer 950 spectrophotometer.

2.3. DFT computation method

All computations were performed using the Gaussian 09 (G09) [22] software package by using the Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr non-local correlation functional (B3LYP) [23]. In the calculation the 6-31G (d-p) basis set was assigned to all elements. The geometric structures of the Schiff base ligand in the ground state (singlet) was fully optimized at the B3LYP level computation method. The vibration frequency calculation was performed to ensure that the optimized geometry represent local minima associated with positive Eigen values only. Vertical electronic excitations based on B3LYP were obtained with the time-dependent density functional theory (TD-DFT) formalism in gas phase. Gauss Sum [24] was used to calculate the fractional contributions of various groups to each molecular orbital.

2.4 Energy and other physical properties of H_2L and model compound

Charge	0
Spin	Singlet
Energy (eV)	-37156.81
Dipole moment (D)	9.6408
Point group	C1

3. Results and discussion

3.1 Synthesis

Title Schiff base ligand synthesis has been successfully fulfilled in our laboratory as orange yellow crystal form. Ligand was characterized by different physicochemical

techniques like elemental analyses, IR, UV-Vis & mass (m/e) spectroscopic studies.

3.2 IR & Mass spectra Characterization of Schiff base H_2L

The infrared spectra of Schiff base ligand are consistent with the structural data given in this paper. An intense strong IR band in the region 1620 cm^{-1} for Schiff base are strongly indicates the formation of (C=N) functional group. Additional significant peak in the IR region of 3200-3500 cm^{-1} clearly reflects that there will be free –OH group present in the Schiff base ligand. Mass spectrum confirmed the chemical formula of Schiff base must be $C_{20}H_{16}N_4O_5$.

3.3 DFT calculations and electronic structure

The geometry of Schiff base ligand were optimized without any symmetry restrictions by means of density functional theory (DFT) calculations using the hybrid DFT /B3LYP level method with the basis set used 6-31G(d-p) and the GAUSSIAN 09 software package. After geometry optimization for Schiff base ligand local energy and dipole moment values obtained are -37156.81ev, 9.6408 where DFT/B3LYP method and proper 6-31G (d-p) basis set used. But for reference Schiff base ligand H_2L, in all cases theoretical values are slightly higher than experimental results. The different experimental parameter of H_2L like IR & UV-Vis spectral data, bond distances & angles were compared with the theoretical values in Table1a-Table2a. According to Table1a-Table2a, the agreement between the most important experimental parameters calculated at the different DFT/B3LYP levels with 6-31G (d-p) basis set used and the experimental data's are matched maximum satisfactory. Hence DFT/B3LYP computation method producing a maximum reliable geometry of Schiff base H_2L.The slight discrepancy of calculated frequencies represent vibrational signatures of Schiff base ligand in its gas phase. Hence, experimentally observed spectra of solid Schiff base samples may differ to some extent from the calculated spectrum. Beside calculated frequencies are usually higher than that of experimental quantities due to combination of electron correlation [25]. This is the reason to use scalling factor for theoretical calculations. The scalling factors depends both on computation method choice and basis set used. The composition of selected MOs of Schiff base H_2L are summarized in Fig.2. & Fig.3 clearly depicted the details contour or surface plots of Schiff base H_2L.

Table 1a: Selected bond distances (Å) data for H_2L

Selected Bonds	Value(Å)	Selected Bonds	DFT Value(Å)
O1- N1	1.238(3)	O1-N1	1.239
O2 -N1	1.229(3)	O2- N1	1.230
O3- N2	1.230(3)	O3- N2	1.24
O4- N2	1.233(3)	O4-N2	1.245
O5- C14	1.225(3)	O5-C14	1.227
N1-C1	1.450(3)	N1-C1	1.46
N2-C3	1.453(3)	N2-C3	1.47
N3 -N4	1.356(3)	N3-N4	1.363
N4- C7	1.298(3)	N4-C7	1.30
N3- C6	1.370(3)	N3-C6	1.373

Table-1b: Selected bond angles (º) data for **H_2L**

Selected Angles	Value (º)	DFT
O1- N1- C1	119.0(2)	120.0
O2- N1- O1	122.3(2)	124.1
O2- N1- C1	118.6(2)	120.0
O3- N2- O4	123.4(2)	124.1
O3- N2- C3	118.5(2)	119.0
O4- N2- C3	118.1(2)	118.3
N4- N3- C6	119.1(2)	120.0
C7- N4- N3	119.3(2)	119.4
C2- C1- N1	116.1(2)	116.3
C2- C1-C6	121.6(2)	122.0

Table2a: Experimental and theoretical data's comparison of Schiff base ligand H_2L

Experimental	Values	DFT
IR (cm^{-1})	1620	1598
UV-Vis (nm)	425.2 nm, 375 nm, 330 nm & 309 nm.	426.38nm, 388.20nm, 340.37nm, 317.87nm due to HOMO→LUMO $\pi \rightarrow \pi^*$ transitions.

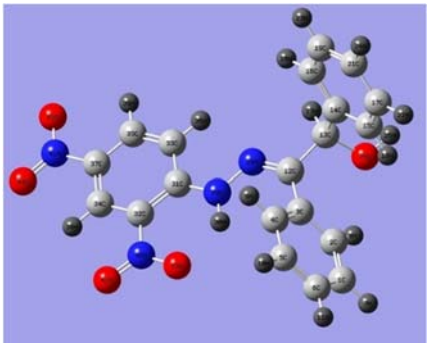
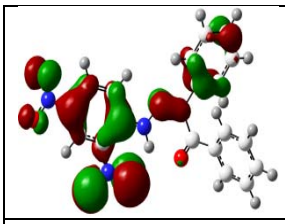
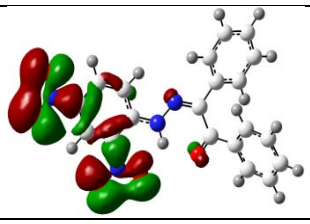
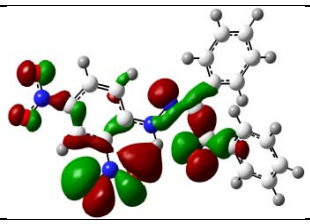
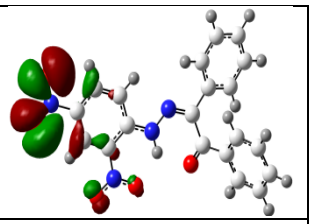


Fig 1: Optimized structure of H_2L

			
HOMO-5, 96, E = -7.65 eV, composition: carbonyl 4 (%) Aromatic ring92 (%) Nitro gr.1 (%) Imine3 (%)	HOMO-4, 97, E= -7.47 eV composition: carbonyl 9 (%) Aromatic ring76 (%) Nitro gr.2 (%) Imine12 (%)	HOMO-3, 98, E = -7.42 eV composition: carbonyl 2 (%) Aromatic ring94 (%) Nitro gr.1 (%) Imine3 (%)	HOMO-2, 99, E = -7.28 eV composition: carbonyl 16 (%) Aromatic ring77 (%) Nitro gr.1 (%) Imine7 (%)

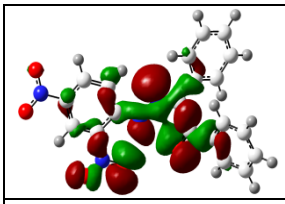
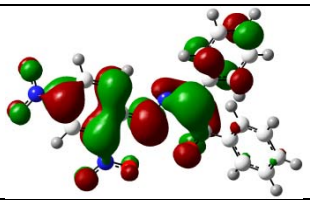
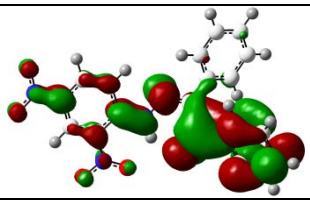
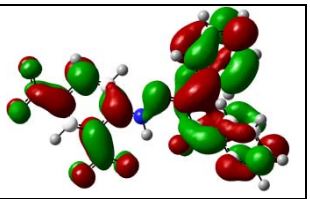
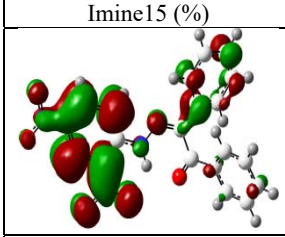
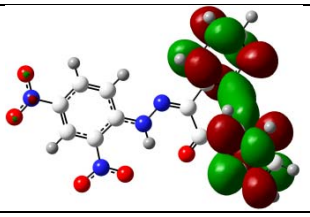
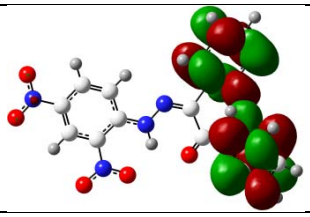
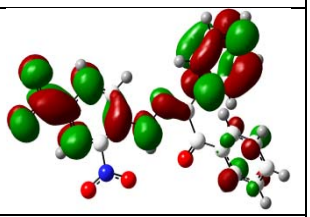
			
HOMO-1, 100, E= -7.19 eV composition: carbonyl 31 (%) Aromatic ring53 (%) Nitro gr.1 (%) Imine15 (%)	HOMO, 101, E = -6.3 eV composition: carbonyl 2 (%) Aromatic ring54 (%) Nitro gr.6 (%) Imine39 (%)	LUMO, 102, E = -2.96 eV composition: carbonyl19 (%) Aromatic ring34 (%) Nitro gr. 28(%) Imine19 (%)	LUMO+1, 103, E = -2.62 eV composition: carbonyl 5(%) Aromatic ring32 (%) Nitro gr. 60(%) Imine4 (%)
			
LUMO+2, 104, E = -2.25 eV composition: carbonyl20 (%) Aromatic ring 33(%) Nitro gr.37 (%) Imine11 (%)	LUMO+3,105 E = -1.38 eV composition: carbonyl5 (%) Aromatic ring65 (%) Nitro gr.7 (%) Imine22 (%)	LUMO+4, 106, E = -0.71 eV composition: carbonyl 0 (%) Aromatic ring99 (%) Nitro gr. 0 (%) Imine0 (%)	LUMO+5, 107, E = -0.49 eV composition: carbonyl 0 (%) Aromatic ring80 (%) Nitro gr.18 (%) Imine2 (%)

Fig 2

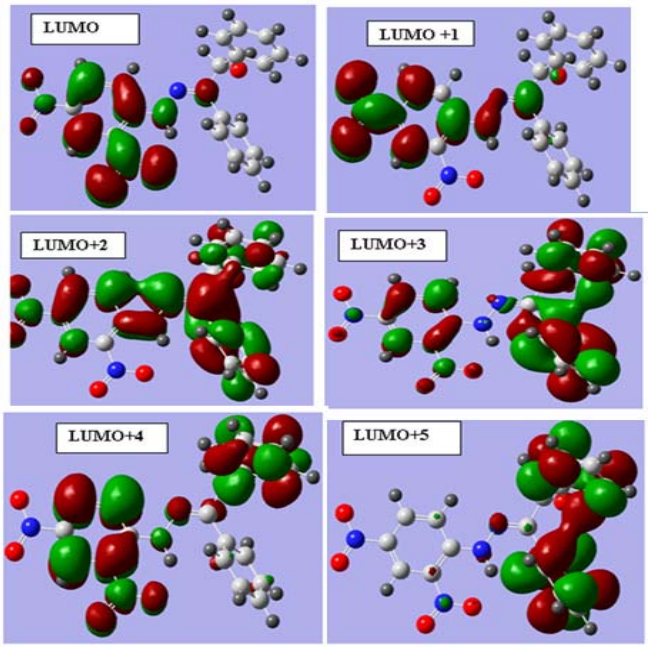
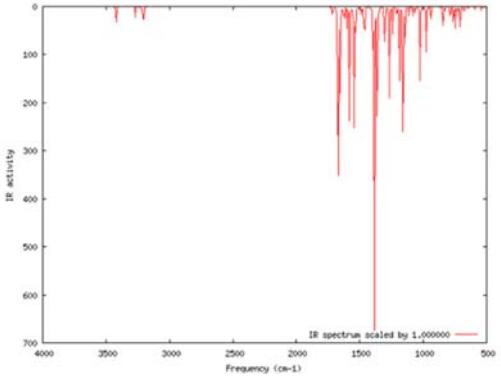
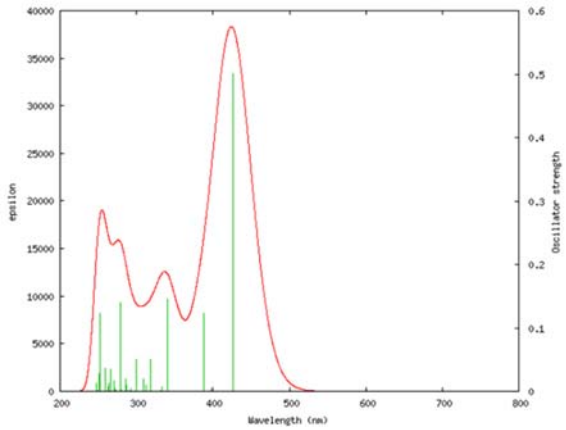


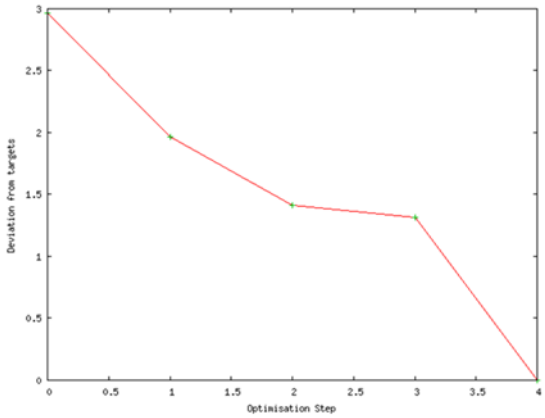
Fig 3: Contour plots of some selected MOs of Schiff base H_2L



Theoretical IR spectra of Schiff base H_2L.



Theoretical UV-Vis spectra of Schiff base H_2L.



Optimisation step vs deviation from targets plot.

4. Conclusion

We have successfully synthesized Schiff base H_2L and characterized by elemental analyses, FT-IR, UV-Vis and mass spectroscopic study. The geometry of Schiff base has been

optimized with the DFT-B3LYP level computation method using LanL.2DZ basis sets. The best agreement between theoretical and experimental results of Schiff base H_2L were obtained by using B3LYP level with 6-31G (d-p) basis set.

5. Acknowledgements
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