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TD-DFT and DFT studies on geometry, spectral, thermal and NMR of N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide

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Abstract
N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide was prepared and characterized in good yield by reflux of equivalent amounts of salicylic hydrazide with 2-dipyridylketone. The structure of the desired hydrazide was analyzed based on: elemental analysis, EI-MS, TG/DTG, UV-Visible, FT-IR, ^{1}H-NMR and ^{13}C-NMR spectral analysis.The condensation reaction was monitored by FT-IR and UV Visible spectroscopy.The geometries, studied based on DFT was investigated using the B3LYP levels. The TDSCF-DFT (B3LYP and HF) calculations were compared to the experimental UV–Vis. spectrum.

Keywords: 2-dipyridylketone, hydrazide, NMR, TD-DFT.

1. Introduction
Hydrazides with >C=N–N< functional group are considered to be a special type of Schiff base with consequence triatomic linkage, takes their position as mono or polydentate ligands in developing or building new coordination metal ions complexes [1-6].The metal complexes of Schiff bases have been found to exhibit physicochemical, biological, electrochemical, stereo-chemical, and structural properties [7].
Recently, hydrazides have gained sufficient importance due to their wide biological properties such as antifungal, antibacterial, anticonvulsant, anti-inflammatory, anti-tuberculosis and antimalarial activities [7-10].
Despite the huge number of organic compounds, there is always urgent need to develop novel chelate hydrazide ligands and enhance their properties as well as their applications.
In connection with previous research in our group on the synthesis, characterization, complexation and biological application of several types of Schiff bases [11-16], here in this work, N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide was synthesized and characterized by various spectral techniques. The reaction was monitored by UV and IR spectroscopy. DFT optimization as well as TD-DFT UV-Vis theoreticalcomputation were performed under B3LYP and HF level of calculations.

2. Experimental section

2.1 Instrumental

The UV-visible spectrum was measured on TU-1901 double-beam UV–Visible spectrophotometer. The IR spectra for samples were recorded by PerkinElmer Spectrum 1000 FT-IR Spectrometer. High-resolution ^{1}H, and $^{13}C\{^{1}H\}$ were recorded on Bruker DRX 250 spectrometer (Bruker, Mainz, Germany) (^{1}H, 500 MHz and ^{13}C, 62.5 MHz frequency) at 298 K. EI-MS data was obtained on a Finnigan 711A (8 kV) (PerkinElmer Inc., Waltham, MA, USA). TG spectrum was measured by using a TGA-7 PerkinElmer thermogravimetric analyzer (PerkinElmer Inc., Waltham, MA, USA).

2.2 Synthetic procedure

A solution of 2-dipyridylketone 2.2 mmol in absolute ethanol (20.0 mL) was mixed with 2.0 of mmol salicoyl hydrazide, 3 drops of conc. HCl was added, and the mixture was refluxed for 4h. The resulting mixture was concentrated under reduced pressure and the title compound was precipitated by the addition of 40 mL of *n*-hexane. The precipitates were filtered off, washed three times with 80 mL of distilled water.

Yield 88%, Colorless, m.p: 147.0 ^{o}C; Molecular formula; ^{1}H NMR (250 MHz, d^{6}, DMSO): (ppm) 6.8–9.0 (2s, 4d. 4t, CH and CH_2 function groups) see Fig. 1. IR: 3480 $cm^{-1}{}_{O-H}$, 3180 $cm^{-1}{}_{N-H}$, 3020 $cm^{-1}{}_{C-H\ Ph}$, 1755 $cm^{-1}{}_{C=N}$.

3. Results and Discussion:

3.1. Synthesis, elemental analysis and mass spectroscopy

Condensation of 2-dipyridylketone with salicoyl hydrazide in acidic ethanoic solution revealed the formation of N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide in a very good yields, as shown in Scheme 1.

Scheme 1. Synthesis of N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide.

The product is a white powder with 147.0 ^{o}C melting point, completely soluble in chlorinated solvent, DMSO and DMF and partially soluble in ROH. The product is insoluble in non-polar like *n*-hexane and polar solvent like. To accelerate the reaction and enhance the yield, a slight excess of 2-dipyridylketone was inserted to the mixture, the unreacted residue was washed out at the end of the reaction by excess of *n*-hexane solvent.

The elemental analysis and mass spectroscopy of the compound is consistent with the proposed molecular formula (Calcd. for $C_{18}H_{14}N_4O_2$:C, 67.91; H, 4.43; N, 17.60. Found: C, 67.75; H, 4.21; N, 17.35). Molecular ion $[M^{+}]$ *m/z* = 318.1 (M. Wt = 318.3 theoretical).

3.2. The geometrical structure of the desired hydrazide.

The molecular structure geometry of the desired compound on ground-state was first optimized in gaseous state without symmetry constraints at B3LYP level. The optimized geometries is illustrated in Fig. 1.

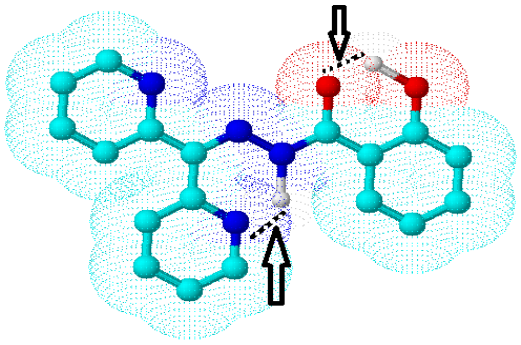

Fig. 1. Optimized geometrical structure of N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide.

The optimized structure revealed two important point: two intramolecular hydrogen-bondsper molecule were detected in the structure O-H….O with bond length = 2.2 A and N-H….Npy with bond length = 2.4 A, as labeled in Fig. 1, such H-bonds stabilized the compound in two semi-hexacyclicheteroatomic rings and effected the physical properties, phenyl occupied semi-perpendicular plane to the two pyridine ring plane and this to minimized the internal repulsion.

3.3. IR investigation

In order to monitor the reaction using FT-IR, the starting materials before and after its condensation to produce the desired compound, was subjected to IR measurement, as seen in Fig. 2.

The formation of the product was easily monitored by shifting of C=O group belongs to 2-dipyridylketoneat 1675 cm^{-1} down to 1655 cm^{-1} due to formation of C=N function group belongs to N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide, as seen in Fig. 2a-c.

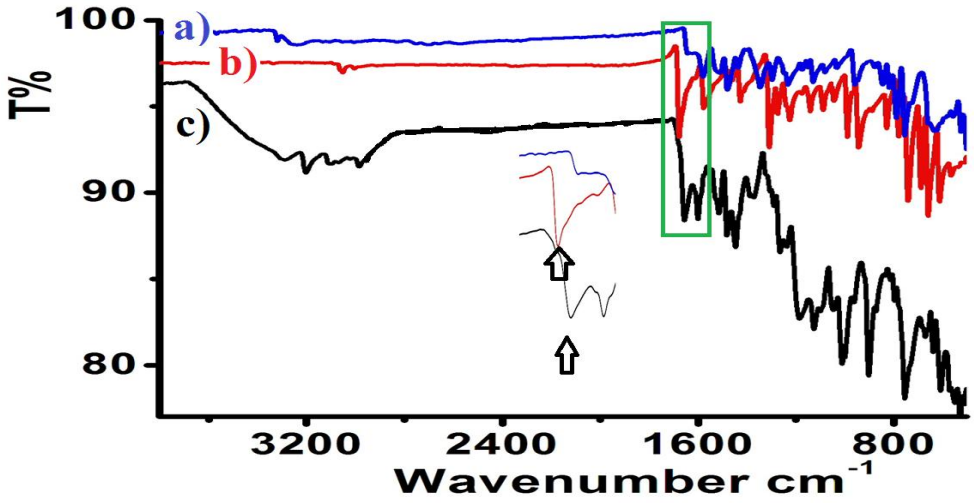

Fig.2. IR spectra of: a) salicoyl hydrazide(starting material), b) 2-dipyridylketone (starting material) and c) N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide (product).

3.4. Electronic structures and charges

Thefrontier molecular orbital's HOMO–LUMO energies and their corresponding density of state of the desired product are shown in Fig. 3. The HOMO–LUMO gap in vacuumis 0.390 au. DFT 6-31++g(d,p).

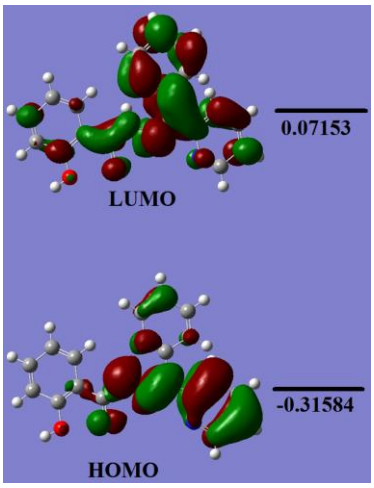

Fig. 3. HOMO and LUMO plots of the prepared hydrazide.

3.5. The UV-visible electronic absorption spectroscopy

The electronic absorption spectra of the starting materials and prepared compound in EtOH was monitored before and after refluxing by UV-visible, as seen in Fig. 4.Before reflux, a) salicoylic hydrazide which revealed two electron transition maxims at λ_{max} = 265 and 300 nm, b) 2-dipyridylketone with four electron transition maxims at λ_{max} = 208, 223, 243 and 273 nm, after refluxed, c) only two new electron transfer maxims at λ_{max} = 273 and 330 nm were observed due to formation ofN'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide. All electron absorbance in both starting and product material were resonated n - π* or π-π* electron transition.

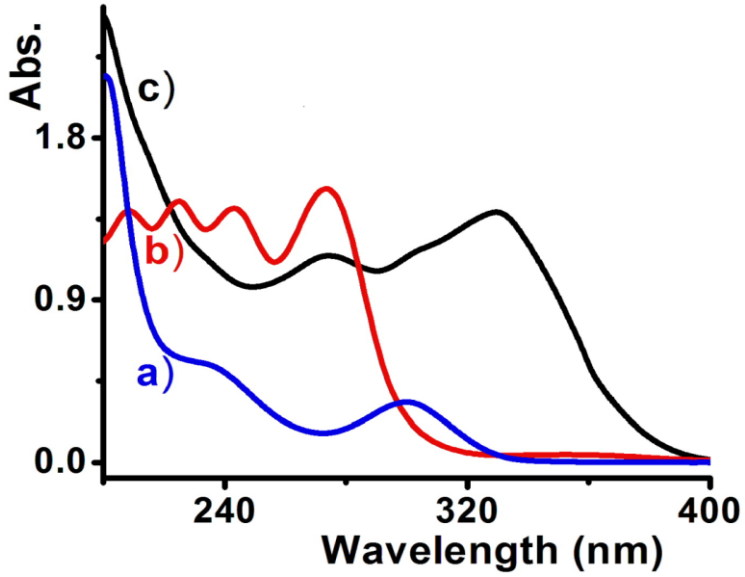

Fig. 4 UV–Vis spectra of a) salicoyl hydrazide b) 2-dipyridylketone and c) N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazidein EtOH at RT.

3.6. TDSCF-DFT electronic absorption spectra

The time dependence electronic absorption spectra of the desired hydrazide in gaseous state were performed using TDSCF-DFT (B3LYP and HF)/at different level of calculations. The results are reported in Fig. 5. It is observed for the molecule at each level that the absorption in the visible region is much weaker than that in the

UV region. The maximum value of the oscillator strength is reached for0.035at a wavelength of around 398 nm using B3LYP 3-31 level (as in Fig. 5a) and 0.045 at the same wavelength using B3LYP 6-31++g(d,p) level (as in Fig. 5b). The maximum value of the oscillator strength is reached for 0.007at a wavelength of around 280 nm using HF 3-31 level (as in Fig. 5c) and 0.45 at wavelength round 250 nm using HF 6-31++g(d,p) level (as in Fig. 5d). Experimental measurements of electronic absorption is performed in water and revealed two maxims at λ_{max} = 273 and 330 nm. The TD-DFT B3LYPcalculations have an appreciable red-shift, while TD-DFT HF calculation revealed blue-shift compared by experimental result in water. The discrepancy between experimental and TD-DFT theoretical may result due to two reasons: solvent effects, polar solvent, could affect the electronic structure and the geometry through the expected interaction between solute and solvent molecules. The smaller HOMO-LUMO gap of compound induced smaller excited energies.

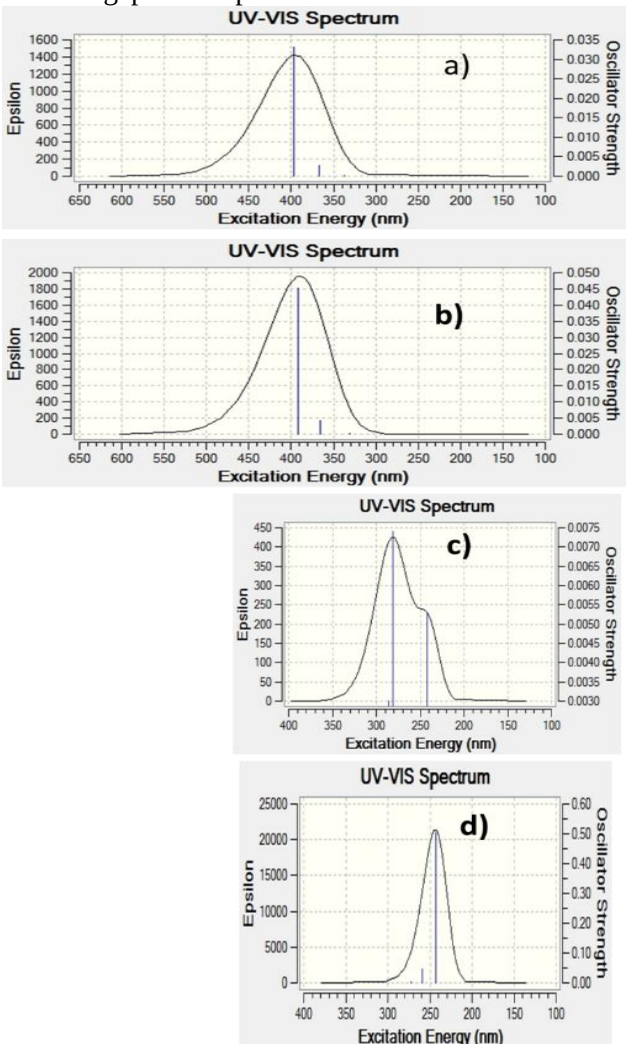

Fig. 5.TD-DFT UV/Vis electronic absorption spectra ofthe desired product at different levels of calculations a)B3LYP 3-31, b) B3LYP 6-31++g(d,p), c)HF 3-31 and d) HF 6-31++g(d,p) .

3.7. TG/DTG thermal analysis

The thermal properties TG/DTG of the N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide was investigated under an open atmosphere in the range of 0–700 °C and heating rate of 10 °C/min. Fig. 6 showed simple decomposition process with one broad step typical decomposition, started from 160 °C and ended at 280 °C with weight loss ~99%.

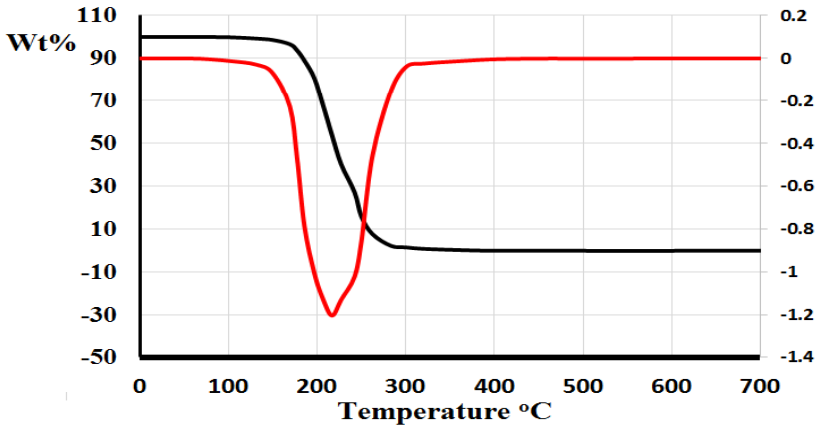

Fig. 6. TG/DTG thermal curve of the desired compound at heating rate of 10 °C/min.

3.8. NMR investigations

The ^{1}H-NMR spectrum (in DMSO) of the desired compound revealed several types of protons in high chemical shifts 7.0-10.5 ppm as seen in Fig. 7. The ^{1}H-NMR chemical shifts, integration and their splitting supported the combination of salicoyl hydrazide and 2-dipyridylketone parts to form N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazideproduct without impurities. The high chemical shift of N-H at ~ 8.7 ppm may be resonated to the H-bond formation with N of Py aromatic ring. The ^{1}H-NMR chemical shifts and their splitting of each protons were labeled directly to their position as seen in Fig. 7**.** The ^{13}C-NMR spectral data agree with the assigned structure, signals belongs to the carbons are cited to their positions.

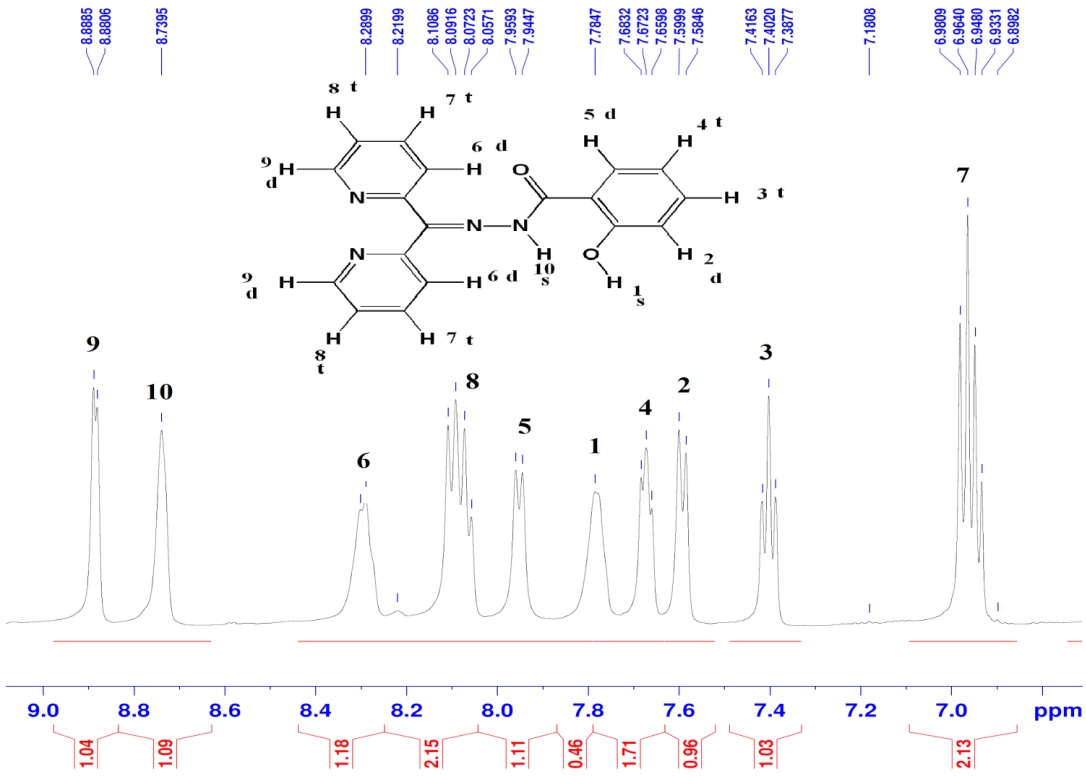

Fig.7. ^{1}H NMR (ppm) spectrum of desired compound in d^{6} DMSO at RT.

Conclusion

N'-(di(pyridin-2-yl)methylene)-2-hydroxybenzohydrazide was made available in good yield by condensationsalicoyl hydrazide with 2-dipyridylketone under reflux condition. The condensation reaction was monitored by FT-IR and UV visible spectroscopy.The structure of the compound was spectrally analyzed.The compound revealed high degree of thermal stability and one step mechanism decomposition. Structural optimization and TDSCF-DFT (B3LYP and HF) calculations were compared to experimental result, the difference in UV–Vis. spectra were resonated to solvent effect and low HOMO-LOMOU gap electron transfer.

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