
SYNTHESIS AND QUANTUM CHEMICAL STUDIES OF [2,6-DIACETILPYRIDINE BIS- (BENZOIC HYDRAZONE)].

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ABSTRACT

2,6-diacetylpyridine was condensed with a freshly prepared benzoic acid hydrazide in a 1:2 mole ratio. The white compound obtained was characterized using infrared spectra studies and the quantum chemical investigations of the physical and chemical properties were determined theoretically using density functional theory (DFT) level of calculation at the hybrid B3LYP exchange-functional combination with the Poples group split valence basis set. The infrared spectrum of the compound showed the C=O stretching frequency at 1730 cm^{-1} while the ν (C=N) and the ν (N-H) were observed respectively at 1653 cm^{-1} and 3386 cm^{-1} . The theoretically calculated values of 1732 cm^{-1} and 1764 cm^{-1} for the C=O stretching frequency and 1664 cm^{-1} , 1660 cm^{-1} and 1661 cm^{-1} for the ν (C=N) and 3388 cm^{-1} for ν (N-H) were in good agreement with experimental result. In the theoretically calculated electronic spectrum, the electronic properties observed are -6.02eV for HOMO, -1.90eV for LUMO, while energy band gap is 4.12eV . The ground state was found to be a singlet while the excited states consist of six transitions, all of which are also singlet. The $^1\text{HNMR}$ studies of this compound showed all the aromatic protons between 7.03ppm and 8.51ppm while the amide protons appeared at 13.42ppm and 7.74ppm . The methylene protons observed as singlet at 2.2 ppm and 2.3 ppm . $^{13}\text{C NMR}$ showed that all the aromatic carbon of this compound at 7.07ppm and 8.51ppm except the two carbons adjacent to the nitrogen atom on the pyridine ring. These two carbon atoms were deshielded due to the nitrogen environment and appear at of 155.8ppm and 157.9ppm respectively. The carbonyl carbons are also deshielded and appeared at 169.80ppm due to inductive effect.

Keyword: Infrared, DFT, deshielded, electronic, HOMO

INTRODUCTION

Hydrazides are an important class of biologically active organic compounds with their therapeutic uses well investigated Kumar et al., 2012. These hydrazides and their condensation products are reported to possess a wide range of biological activities which include antibacterial activity, tuberculostatic properties, HIV inhibitors, pesticidal, antifungal properties and so on, Kumar et al., 2012; Katritzky et al.: 2001, Gohil et al., 2010.

Some of these hydrazides and corresponding hydrazones are known to be psychopharmacological agent, e.g monoamine oxidase (MAO) inhibitor and serotonin antagonists, Kumar et al., 2012.

Hydrazides have also been known to be used as important intermediates in synthesis of various heterocyclic compounds such as 1,2,4-triazoles, 1,3,4-thiadiazole, 1,3,4-oxadiazoles, 1,2,4,5-tetrazines which are known to possess diverse pharmacological properties Kumar et al., 2012.

A variety of methods have been employed in the preparation of hydrazides, by reaction of acids or their derivatives with hydrazine hydrates, acid chlorides and acyl anhydride have been used to prepare hydrazides, Kumar et al., 2012; Katritzky et al. The reaction of acid chlorides and acyl anhydride with hydrazines often leads to the formation of diacyl derivatives due to their high reactivity, Kumar et al., 2012. Hydrazides are generally prepared by the hydrazinolysis of esters with hydrazine hydrate Kumar et al., 2012; Katritzky et al.

2,6-diacetylpyridine has been found to be a versatile tridentate chelating agent having two reactive carbonyl groups that are capable of undergoing Schiff base condensation with various di- and polyamines, Sharma and Srivastava 2007. The isothiosemicarbazones of 2,6-diacetylpyridine (which are potentially very active pentadentate ligands) involving N₅ donor set of atoms have been investigated, Sharma and Srivastava 2007.

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Quantum chemical investigations of the physical and chemical properties of novel compounds are important in order to examine the relationship between structures, properties and performance, and to assist in the design and synthesis of new derivatives with improved properties. Generally, the DFT results can be credited with a higher confidence in the quantitative respects due to their treatment of correlation effects, Reed et al. 1988: Fuentealla et al. 2010: Xiao Jun Li and Geng Sheng Jiao, 2009: Maroulis and Xenides, 2003.

Quantum molecular orbital calculations performed in the framework of DFT approach by using the hybrid B3LYP exchange-functional, Chis et al.2008”a”: Becke 1993: Lee et al. 1988,in combination with the Poples group split valence basis set, Hehre et al. 1986,have been shown to provide excellent compromise between accuracy and computational efficiency of molecular structures, as well as the vibrational and NMR spectra of molecules, Chis et al. 2005 “b”:Brycki et al.2006: Dega- Szafran 2006.

Herein we report the synthesis of 2,6-diacetylpyridine bis-(benzoic acid hydrazone), the infrared spectra and the Quantum chemical investigations of the physical and chemical properties.

EXPERIMENTAL

Materials

High purity 2,6-diacetylpyridine, benzoic acid, ethanol, hydrazine hydrate, acetone, methanol, acetonitrile, chloroform, dichloromethane, diethylether, nitromethane and distilled water.

Preparation of 2,6-diacetylpyridine bis-(benzoic acid hydrazone) (DPBH), Sharma and Srivastava 2007

2,6-diacetylpyridine 1g (6.1 mmoles) dissolved in 10ml ethanol in a round- bottom flask. To this, 1.67g (12.30 mmoles) freshly prepared benzoic acid hydrazide was added. The reaction mixture was left to reflux for 5hrs. 5mins into refluxing, gave a clear yellowish solution and the refluxing continued. After the 5hrs refluxing, a creamish white precipitate appeared on cooling on crushed ice for 1-2hrs. The compound which separated out by filtration, washed with cold methanol and dried in desiccator over fused calcium chloride. Yield: 1.79g (67%).

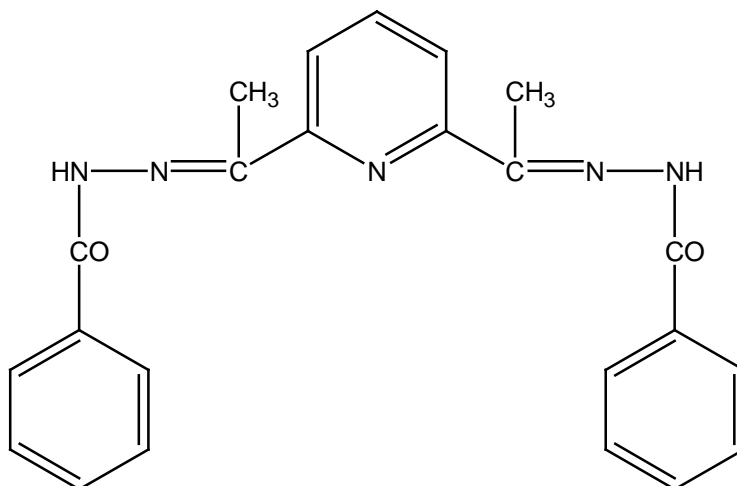


Fig 1: 2,6-diacetylpyridine bis-(benzoic acid hydrazone)

Computational methodology:

The structure was initially optimized using Molecular Mechanics Force Field (MMFF) to obtain a stable conformer. The stable conformer was re-optimized using DFT. All the calculations were performed using Spartan 10 program package using B3LYP methods which uses the exchange functional proposed by Becke,1993 and the correlation functional given by Lee, et al.1988. The 6-31(D) basis set by Hehre,et al.1986, has been used in conjunction with DFT method. This basis set has the advantage of being flexible enough to guarantee reliable theoretical results and being small enough for rapid calculations. It represents an excellent compromise between completeness and economy. The molecular geometry was fully optimized without any constraint using analytical gradient procedure implemented within the programme. In order to obtain the Ultraviolet visible absorption for this compound, we employed the excited state computation with Time-dependent density functional theory (TDDFT) with B3LYP and basis set of 6-31(D). We computed the properties of five excited states with keyword "INCLUDE TRIPLETS". The molecular geometry was fully optimized without any constraint using analytical gradient procedure implemented within the Spartan '10 software programme. The structure of 2,6-diacetylpyridine bis-(benzoic acid hydrazone) is shown in Fig. 1, while the optimized structure is presented in Fig. 2.

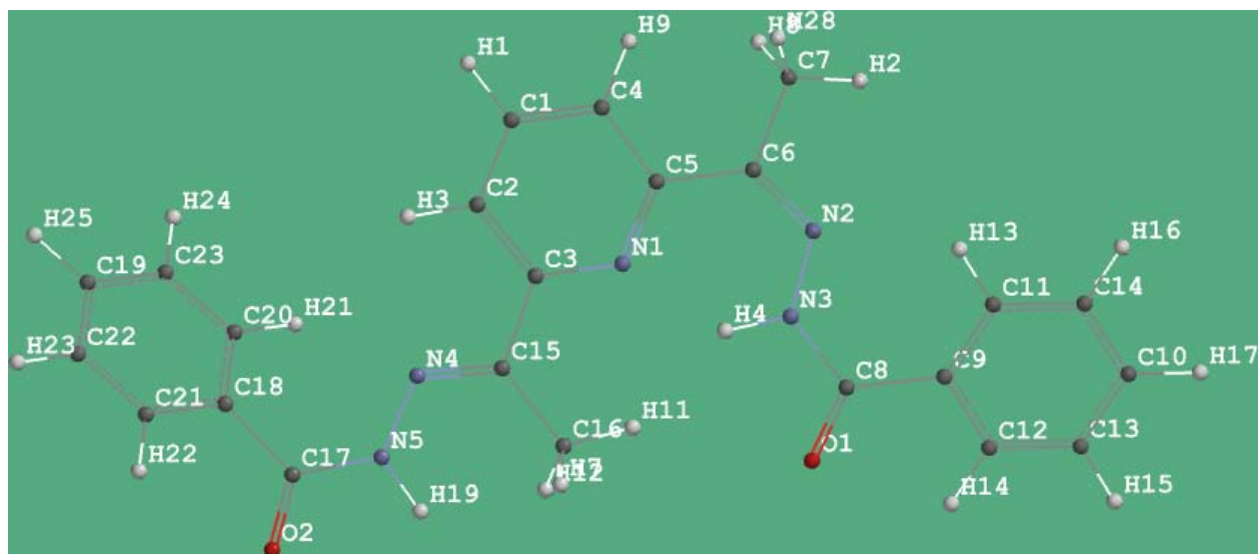


Fig. 2: Optimized geometry of 2,6-diacetylpyridine bis-(benzoic acid hydrazone).

RESULTS AND DISCUSSION

The compound was obtained by reacting 2,6-diacetylpyridine with a freshly prepared benzoic acid hydrazide in a 1:2 mole ratio. The white compound obtained in an appreciable yield was found to be soluble in acetone, acetonitrile, chloroform and diethylether but not soluble in distilled water and methanol. In both ethanol and nitromethane it was observed to be sparingly soluble.

Vibrational Spectra: Vibrational spectrum consists of 54 atoms; its vibrational spectra therefore contain 147 normal modes of vibration. To aid in mode assignments, we based on the direct comparison between experimental and calculated spectra by considering both the frequency sequence and the intensity pattern. The IR signature contains the bands which are due to the stretching vibrations of the carbonyl, C-H and N-H bonds. The calculated infra-red values for the C=O are 1732cm^{-1} and 1764cm^{-1} while the N-H stretch occurred at 3388cm^{-1} and 3501cm^{-1} . The C=N appeared at 1664cm^{-1} , 1660cm^{-1} and 1611cm^{-1} . Experimentally, in the infrared spectrum of the compound the C=O stretching frequency appeared at 1730cm^{-1} while the C=N was observed at 1653cm^{-1} . The band at 3386cm^{-1} was assignable to the N-H stretching frequency of the amide group. From the data above, it was observed that both the theoretically calculated infrared values are consistent with the experimentally determined values.

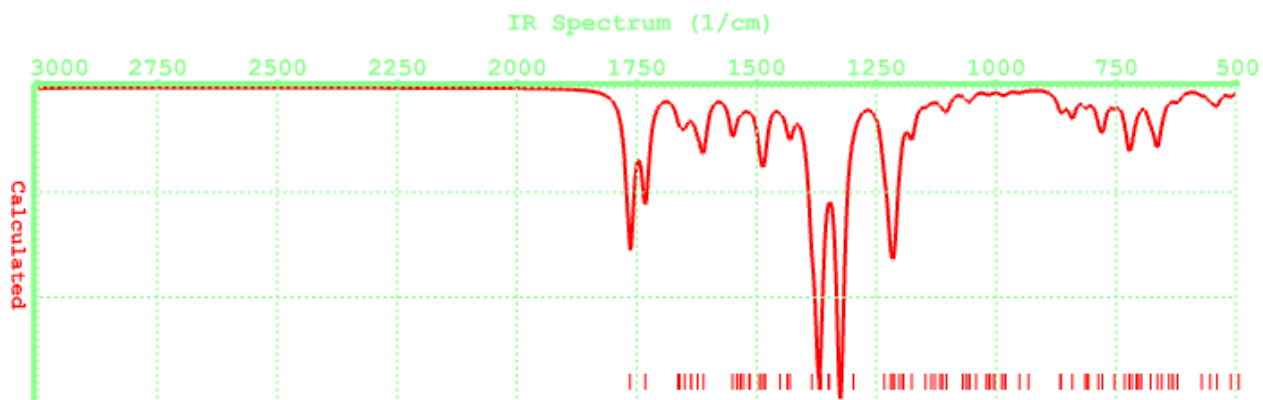


Figure 2: Infra-red spectrum of 2,6-diacetylpyridine bis-(benzoic acid hydrazone)

NMR Spectrum: The ^1H NMR studies of this compound showed that, all the aromatic protons showed within the range 7.03ppm and 8.51ppm while 13.42ppm and 7.74ppm was obtained for the amide protons. The methylene protons each appeared as singlet at about 2.2ppm and 2.3ppm because they are in the same chemical environment.

^{13}C NMR showed that all the aromatic carbon of this compound appeared at 7.07ppm and 8.51ppm except the two carbons adjacent to the nitrogen atom on the pyridine ring. These two carbon atoms were deshielded due to the electronegativity of nitrogen. Consequently, they appear at higher values of 155.8ppm and 157.9ppm respectively. The carbonyl carbons also deshielded and appeared at 169.80ppm due to inductive effect (Oxygen and nitrogen attracting electron from carbonyl carbon).

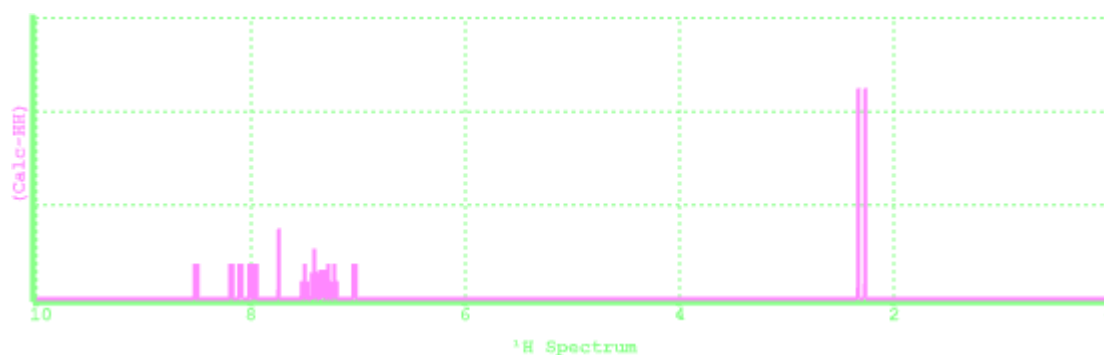


Figure 3: ^1H NMR spectrum of 2,6-diacetylpyridine bis-(benzoic acid hydrazone).

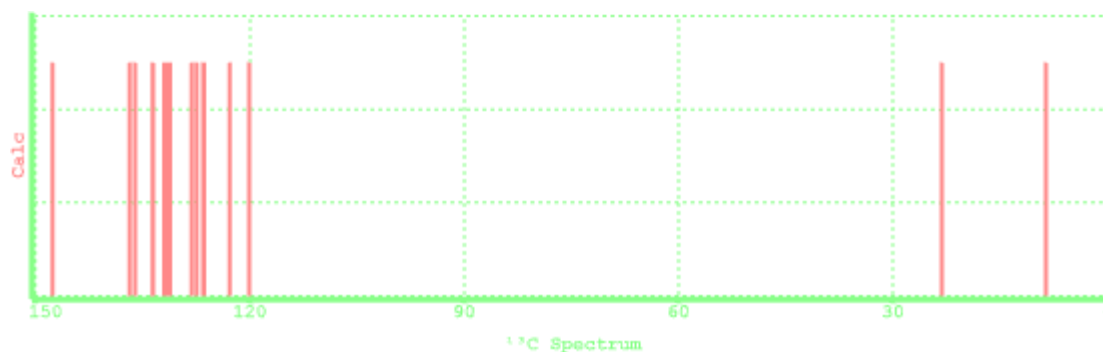


Figure 4: ^{13}C NMR spectrum of 2,6-diacetylpyridine bis(benzoic acid hydrazone).

Electronic Spectrum: The electronic spectrum of 2,6-diacetylpyridine bis-(benzoic acid hydrazone) gave absorption band at 312nm, this is assigned to an overlap of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$.

The HOMO possesses a π -bonding character within sub-units and π -antibonding character excited state properties between the consecutive sub units. On the other hand, the LUMO possesses a π -antibonding character within the subunit and a π -bonding character between the subunits. Theoretically, the HOMO and LUMO energies are calculated using DFT B3LYP at the basis set 6-31G*, while the electronic excited state were studied using Time - dependent density functional theory. The calculated electronic properties are -6.02eV for HOMO, -1.90eV for LUMO, while energy band gap is 4.12eV. Although, the ground state is a singlet, the excited state consists of six transitions, all of which are singlet. This is shown Table 1, while the ultraviolet spectrum, HOMO and LUMO energy diagrams are displayed in Figures 5 and 6 respectively.

Table 1: Calculated transition energies (eV), wavelengths (nm) and oscillator strengths for 2,6-diacetylpyridine bis-(benzoic acid hydrazone).

Excited State no	Total energy/ a.u	Excitation energy/eV	Strength	Wavelength/nm	Multiplicity
5	-1313.14	3.6832	0.1393	336.62	S
8	-1313.13	3.9736	0.4426	312.02	S
9	-1313.13	4.0345	0.0104	307.20	S
10	-1313.13	4.1781	0.2329	296.75	S
11	-1313.12	4.2253	0.2977	293.44	S
12	-1313.12	4.2733	0.0144	290.14	S

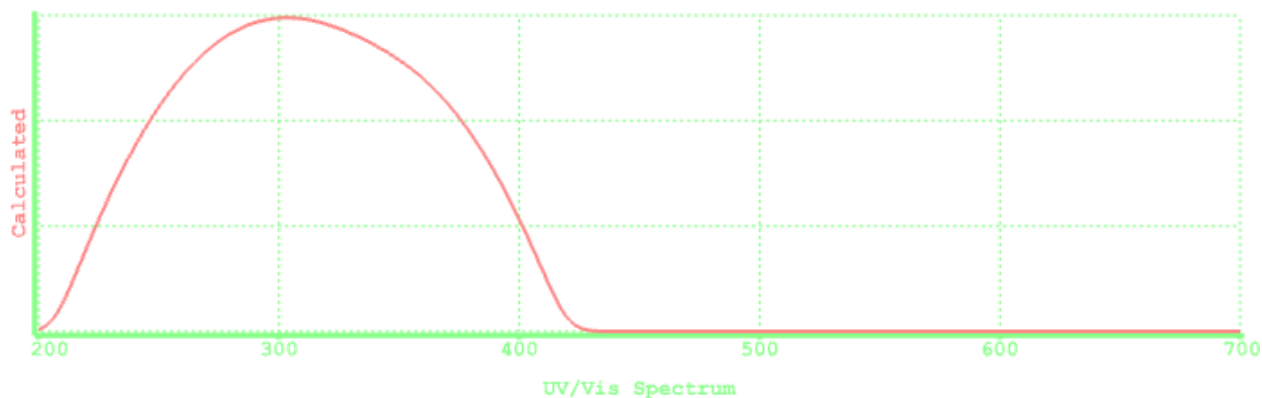


Figure 5: Ultra-violet spectrum of 2,6-diacetylpyridine bis-(benzoic acid hydrazone)

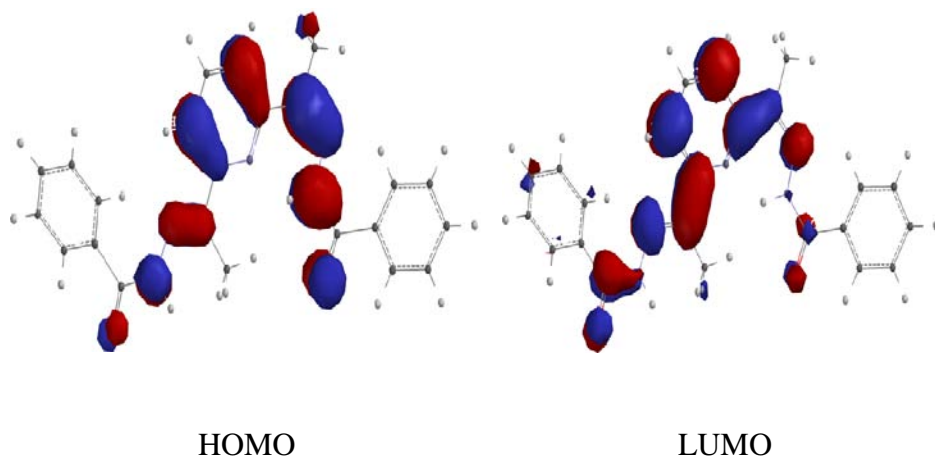


Figure 6: HOMO and LUMO of energy diagram 2,6-diacetylpyridine bis-(benzoic acid hydrazone)

In conclusion, it was observed that the compound 2,6-diacetylpyridine bis-(benzoic acid hydrazone) was successfully prepared and characterized using infrared spectrum. The Quantum mechanical studies were also carried out. From the results obtained, it was found that the calculated values were in good agreement with the experimental infrared values.

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