RESEARCH ARTICLE Am. J. PharmTech Res. 2016; 6(3) ISSN: 2249-3387

AMERICAN JOURNAL OF PHARMTECH RESEARCH

**Journal home page:** http://www.ajptr.com/

# Theoretical Study of (5z ,5¯z) - 2,2- - methylene bis (3-(5-mercapto-1,3,4 Thiadazole-2-yal)-2-(methyl-2,3-dihydro-1,3-oxazepine-4,7-dione) by IR and 1H-NMR Parameters

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## ABSTRACT

Geometry optimization calculations for (5z,5¯z)-2,2¯- methylene bis (3-(5-mercapto-1,3,4-Thiadazole-2-yal)-2-(methyl -2,3-dihydro-1,3-oxazepine-4,7-dione), B, is carried out to establish a direct correspondence between experimental and theoretical by using density functional theory (DFT) with B3LYP/6-31G. The theoretical IR and $^{1}$H-NMR for the same molecule are performed at the same level of theory. These data suggest that the spectra of the thiadazole are consistent with the thiadazole architecture proposed by Abbas and co-workers. The investigation of HOMO and LUMO approved that this molecule is very suitable to be a semiconductor material because it's have a very low energy band gap equal to 0.13628 ev.

**Keyword:** Density Functional Theory Calculations, Thiadazole-derivative, computational chemistry, Theoretical IR, $^{1}$H-NMR spectrum , B3LYP functional

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Received 26 April 2016, Accepted 01 May 2016

Please cite this article as: Hassan., Theoretical Study of (5z ,5¯z) - 2,2- - methylene bis (3-(5-mercapto-1,3,4 Thiadazole-2-yal)-2-(methyl-2,3-dihydro-1,3-oxazepine-4,7-dione) by IR and 1H-NMR Parameters . American Journal of PharmTech Research 2016.

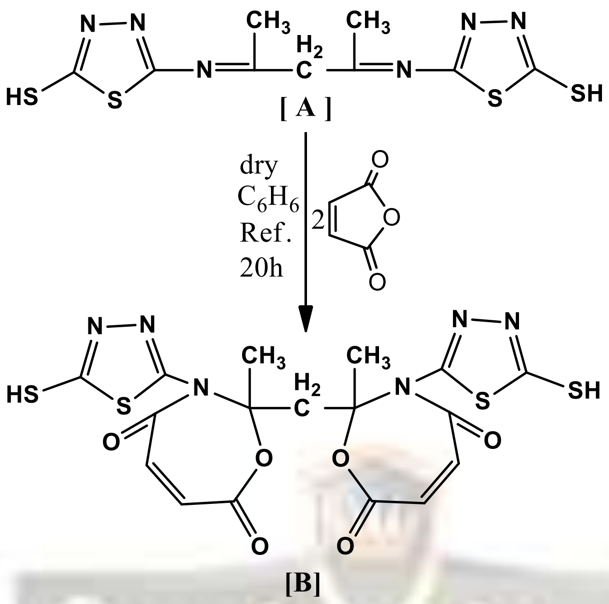
## INTRODUCTION

Thiadiazoles are heterocyclic compounds containing two nitrogen atoms and one sulfur atom as a part of the aromatic five-membered ring[1]. The nitrogen atom in these compounds and their derivative's my has a different positions such as 1,2,3-thiadiazole[2], 1,2,4-thiadiazole[3], 1,3,4-thiadiazole[4] and 1,2,5-thiadiazole[5] and their benzo derivatives[1,6] etc. Thiadiazole and its derivatives have been studied because of their biological activities such as antibacterial and antifungal, anticancer, anti-inflammatory, anti-helicobacter pylori, antimicrobial, antitubercular, analgesic, antiviral, antiepileptic and antineoplastic activity[7-9]. Recently, many theoretical studies performed on thiadazole derivatives because of their importance, F. Bentiss and coworkers[10] used Density Functional Theory (DFT)[11] to study the influence of some new 2,5-disubstituted and 1,3,4-thiadiazoles on the corrosion behavior of mild steel, they show this molecules do an excellent inhibitors of mild steel. Other theoretical study performed by Mahesh and coworker's[1] trying to find the best hybrid functional (B3lyp)[11] to optimize the structure of 2-amino-5-(m-nitrophenyl)-1,3,4-thiadiazole which used as antimicrobials, anti-inflammatory and anti-fungal. Here, we are study geometry optimization for (5z,5$^{-}$z)-2,2$^{-}$- methylene bis (3-(5-mercapto-1,3,4-Thiadazole-2-yal)-2-(methyl -2,3-dihydro-1,3-oxazepine-4,7-dione), B, derivative which was studied previously by Athraa and coworkers[12]-[13] by using DFT theory[14-20] with B3LYP hybrid functional[21-23], to find the vibrational spectra (FTIR) then compute $^{1}$H-NMR chemical shifts to obtain a deeper insight into the nature of the chemical bonding.

## RESULTS AND DISCUSSION

### The Experimental Details

Athraa and co-workers[12]-[13] employed $^{1}$H-NMR and IR techniques to explored the production of (5z,5$^{-}$z)-2,2$^{-}$- methylene bis (3-(5-mercapto-1,3,4-Thiadazole-2-yal)-2-(methyl -2,3-dihydro-1,3-oxazepine-4,7-dione), B, and follow up the reaction by Thin Layer Chromatography (TLC). A reflex of a mixture of malic anhydride with 5,5$^{-}$-((Pentane-2,4- Diylidene bis (-1-yl-1Yalideneazan)) bis (1,3,4-Thiadazole-2-thiol), [A], at 65C° to 12h. A new compound, B, was formed (Scheme 1).



**Scheme 1: Structure [B] proposed by Abbas and co-workers[12] formed from 5,5$^{-}$-((Pentane-2,4- Diylidene bis (-1-yl-1Yalideneazan)) bis (1,3,4-Thiadazole-2-thiol), [A], based on IR and NMR spectroscopies data.**

The products were fully characterized by IR and $^{1}$H-NMR spectroscopy. FT-IR spectroscopy used to identify compound, B, and the results appear (Table 1) stretching band at (1720 cm$^{-1}$) refers to ketone ester

Group (C=O), also stretching band at (1693 cm$^{-1}$) refers to ketone amine (C=O) group, finally stretching band for alkene (C-H) group at (3014 cm$^{-1}$) and for (C-H) aliphatic group at (2914 cm$^{-1}$).

**Table 1: The experimental IR absorbance bends of B compound.**

| Group | Ketone ester (C=O) | Ketone amine (C=O) | Alkene (C-H) | Aliphatic (C-H) |
|---|---|---|---|---|
| Freq. (cm$^{-1}$) | 1720 | 1693 | 3014 | 2914 |

The hydride chemical shift investigation which utilized appear at δ = 2.47 ppm, were assigned to ($CH_2$) group which bonded the isomethene groups. While δ = 1.22 ppm indicates a terminal $CH_3$ position which associated with isomethene group. A single bands appears at δ = 3.3 ppm, δ = (6.07-7.687) ppm refers to (S-H) and alkene proton spontaneously, (Table 2).

**Table 2: The experimental $^{1}$H-NMR data of B compound.**

| Group | ($CH_2$) | ($CH_3$) | (S-H) | Alkene proton |
|---|---|---|---|---|
| δ (ppm) | 2.47 | 1.22 | 3.3 | 6.07-7.687 |

## Geometry Optimization Methodology

The optimize structure was performed by using density functional theory (DFT) with the basis set level of B3LYP/6-31G[24]. IR and $^1$H-NMR[25] calculations for, B, compound were also calculated by the same method and basis set.

### The optimized structure of compound B

Compound B was optimized and labeled in (Figure 1). In this compound, the thiadazole ring, and all the groups are proved by IR and the single point energy calculations and concluded in (Tables 3, 4).

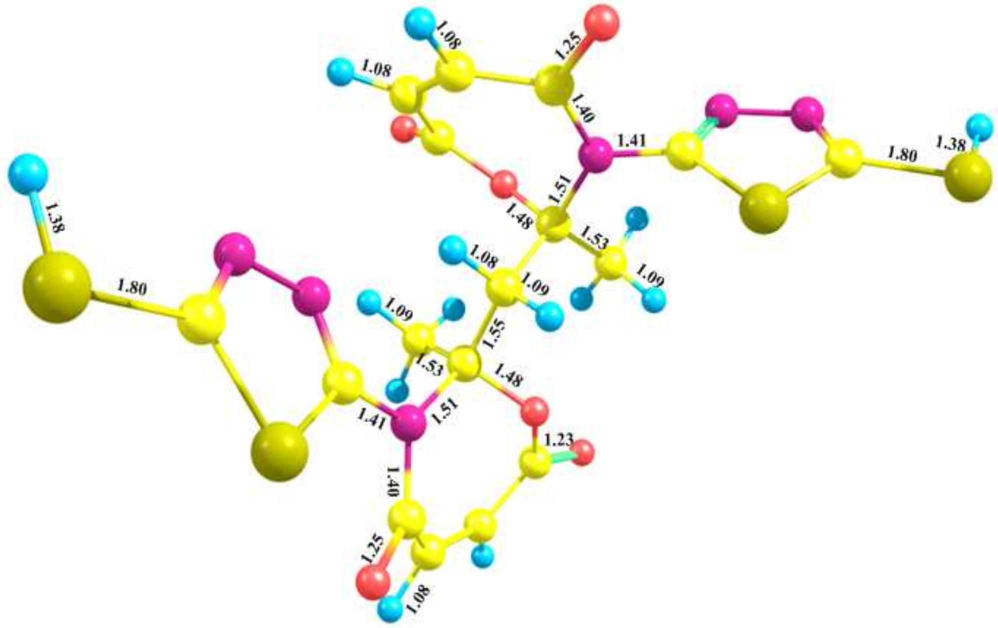


**Figure 1: The optimize structure of compound B.**

**Table 3: IR calculations of compound B compared to experimental IR spectra[12].**

| Group | Imine(C=N) | Thiadiazole (C=N) | Aliphatic (C-H) | Thiadiazole (C-S) |
|---|---|---|---|---|
| Freq. (cm-1)$_{Exp.}$ | 1720 | 1693 | 3014 | 2914 |
| Freq. (cm-1)$_{Theo.}$ | 1718.8 | 1717.9 | 3105.2 | 3094.9 |
| Error% | 0.07% | 1.47% | 3.02% | 6.20% |

**Table 4: $^1$H-NMR calculation of compound B compared to experimental NMR spectra[12].**

| Group | ($CH_2$) | ($CH_3$) | (S-H) | Alkene proton |
|---|---|---|---|---|
| δ (ppm)$_{Exp.}$ | 2.47 | 1.22 | 3.3 | 6.07-7.687 |
| δ (ppm)$_{Theo.}$ | 2.15 | 1.18 | 4.7 | 6.25 |
| Error$_{\%}$ | 12.9% | 3.2% | 42.4% | 18.6% |

### IR Methodology

The theoretical IR data give a good agreement with the experimental data by the percent of error **under** the theoretical value (20%). (C=N) thiadazole giving a satisfactory (1514 cm$^{-1}$) agreement rather than (C=N) imine (1619 cm$^{-1}$) with error percent (0.4%, 5%) respectively. While (C-H) aliphatic give a suitable result with (2%) error percent, finally (C-S) thiadazole has a value (1043

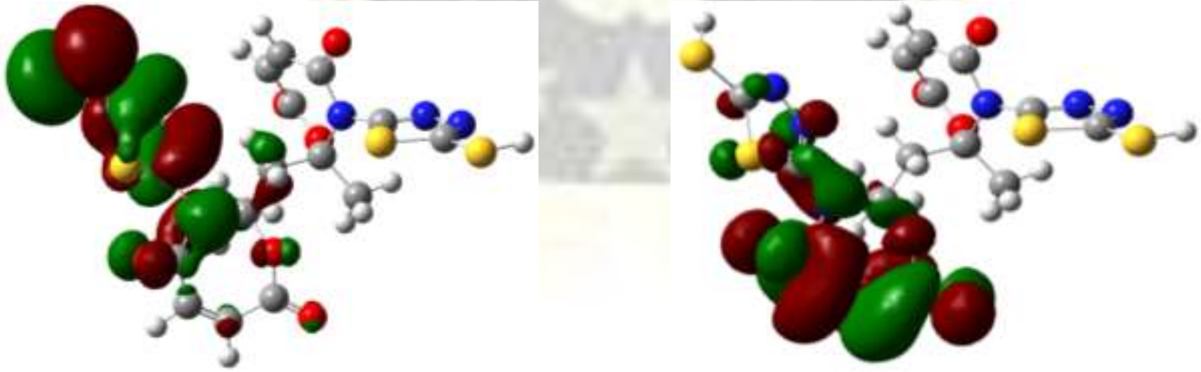
$cm^{-1}$) with error percent (0.9%) that made a suitable agreement between the experimental and theoretical data.

## $^{1}$H-NMR Methodology

The chemical shifts for all hydrides attached to the thiadazole atoms have been computed by $^{1}$H-NMR values are giving in (Table 4). These results are consistent with NMR calculations for B compound and support argue that the structure should be based on a thiadazole motif. The calculated $^{1}$H-NMR chemical shift for (CH2= 2.75), (CH3= 2.8) and (SH= 3.23) are given a satisfactory agreement with the experimental data by error% equal to (10%, 7%, 6%) respectively.

## HOMO-LUMO Calculation

The frontier orbital theory is useful to explore the interaction of the surface metal atoms and the adsorption centers of the inhibitor molecule[26]. The value of HOMO energy is often associated with the electron donating ability of a molecule, in contrast the energy of LUMO reflects its ability to accept electrons[27]. In (Figure 2), the computed chemical data was given, including EHOMO = -0.25369 ev, LUMO = -0.11741 ev and the energy band gap ($\Delta$E=0.13628 ev). The EHOMO comes from thiadazole ring motif while the LUMO comes from seven member ring moiety. According to these results, B, molecule has low energy gap candidates this molecule to be a good semiconductor and that lead to have a favorite to bond with metal surface[28]. Also, the dipole moment which consider an important factor on the corrosion inhibition process[29]. The dipole moment of, B, molecule (7.7424 Debye (25.82X10-30 Cm)) is higher than that of H2O molecule ($\mu$= 6.23X10-30 Cm), which is probably in favor of the adsorption between organic molecule and mild steel surface via physical interaction[30].



**HOMO** **LUMO**

**Figure 2: The frontier molecular orbitals of compound**

## CONCLUSION

First, we have computed two distinct criteria, IR spectroscopy and the $^{1}$H-NMR chemical shifts using density functional theory (DFT) with B3LYP/6-31G. We established a direct correspondence between experimental and theoretical. We argue that the structure is based on a thiadazole motif, where the computed IR and chemical shifts are near more consistent with experiment. The computed data suggest that the spectra of the thiadazole are consistent with the thiadazole architecture proposed by Athraa and co-workers[12-13]. The maximum deviation of the computed IR spectrum equal to 5% above those observed experimentally. Moreover, the magnitude of the computed shifts for all terminal hydrides are some ~0.07 ppm above those observed experimentally. Second, the investigation of HOMO and LUMO approved that this molecule is very suitable to be a semiconductor material because it's have a very low energy band gap equal to 0.13628 ev. This work illustrates the important and complementary role that the computation of spectroscopic fingerprints can play in the process.

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