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Research Article

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Study of Sum Physical and Biological Parameters of 5, 5¯-((Pentane-2,4-Diylidene bis (-1-yl-1Yalideneazan)) bis (1,3,4-Thiadazole-2-thiol) by Density Functional Theory

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ABSTRACT

Geometry optimization calculations for 5, 5¯-((Pentane-2,4-Diylidene bis (-1-yl-1Yalideneazan)) bis (1,3,4-Thiadazole-2-thiol), 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 Athraa and co-workers. The investigation of HOMO and LUMO approved that this molecule is very suitable to be a semiconductor material because it has a very low energy band gap equal to 0.13628 eV.

Keyword: 1, 3, 4-Thiadiazole Derivatives, heterocyclic compounds, HOMO-LUMO energies, DFT Studies, B3LYP functional

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INTRODUCTION

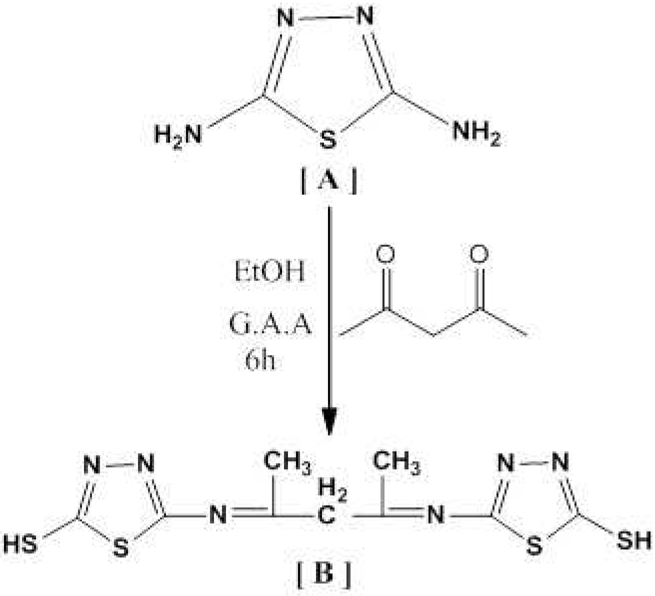
Heterocyclic compounds are acquiring more importance in recent years as these can be found in a large number of compounds which display biological activities [1]. Heterocyclic compounds particularly five and six member heterocyclic have attracted the attention of pharmaceutical community over the years due to their therapeutic values [2]. The biological activity of the compounds is mainly dependent on their molecular structures [3]. Thiadiazole contains the five-membered diunsaturated ring structure having molecular structure formula C2H3N3S containing a two carbon atom, three hydrogen, three nitrogen and one sulphur [4].

Also thiadiazoles carrying mercapto, hydroxyl and amino substituent's can exist in many tautomeric forms and this property is being intensively studied using many modern methods [5]. The nitrogen atom in these compounds and their derivative's my has a different positions such as 1, 2, 3-thiadiazole [6], 1, 2, 4-thiadiazole [7], 1, 3, 4-thiadiazole [8] and 1, 2, 5-thiadiazole [9] and etc. 1, 3, 4-thiadiazoles and its derivatives are very interesting compounds due to their important applications in many pharmaceutical, biological and analytical field [10-11].

Recently, density functional theory (DFT) [12] has been accepted by the quantum chemistry community as a cost effective approach for the computation of molecular structure, vibration frequencies, and energies of chemical reactions, many theoretical studies performed on thiadazole derivatives because of their importance [13-15]. Here, we are study geometry optimization for 5,5¯-((Pentane-2,4-Diylidene bis (-1-yl-1Yalideneazan)) bis (1, 3, 4-Thiadazole-2-thiol), B, derivative which was studied previously by Athraa and coworker[16] by using DFT theory [17-22] with B3LYP hybrid functional [23-25], 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.

EXPERIMENTAL SECTION

Athraa and co-workers [16]employed ^{1}H-NMR and IR techniques to explored the production of 5,5^{-}-((Pentane-2,4-Diylidene bis (-1-yl-1Yalideneazan)) bis (1,3,4-Thiadazole-2-thiol), B, and follow up the reaction by Thin Layer Chromatography (TLC). An addition of a mixture of acetyl acetone, absolute ethanol and glacial acetic acid to 2-amino-5-mercapto-1-3-4-thiadazole [A] at 65C° after that reflex to 8h. a new compound, B, was formed (Scheme 1).



Scheme 1: Structure [B] proposed by Athraa and co-workers [16] formed from 2-amino-5-mercapto- 1-3-4-thiadiazol, [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 (1604 cm^{-1}) refers to isomethene group (C=N), also two stretching band at (3012, 2960 cm^{-1}) refers to aliphatic (C-H) group, finally stretching band for (C=N) group at (1521 cm^{-1}) and for (C-S) group at (1053 cm^{-1}) of thiadazole ring.

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

Group	Imine (C=N)	Thiadiazole (C=N)	Aliphatic (C-H)	Thiadiazole (C-S)
Freq. (cm^{-1})	1604	1521	2960	1053

The hydride chemical shift investigation which utilized appear at δ = 2.5 ppm, were assigned to (CH_2) group which bonded the isomethene groups. While δ = 2.678 ppm indicates a terminal CH_3 position which associated with isomethene group. A single bends appears at δ = 3.423 ppm, δ = 7.687 ppm refers to (S-H) and (N-H) groups spontaneously, (Table 2).

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

Group	(CH_2)	(CH_3)	(S-H)	(N-H)
δ (ppm)	2.50	2.678	3.423	7.687

RESULTS AND DISCUSSION

Geometry Optimization Methodology

The optimize structure was performed by using density functional theory (DFT) with the basis set level of B3LYP/6-31G[26]. IR and ^{1}H-NMR[27] 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, there are two same and optimum parts, any side have a thiadazole ring bonded with the core system by amine group and from the other side it's have a terminal SH group. IR and the single point energy calculations are clearly identify compound, B, (Tables 3, 4).

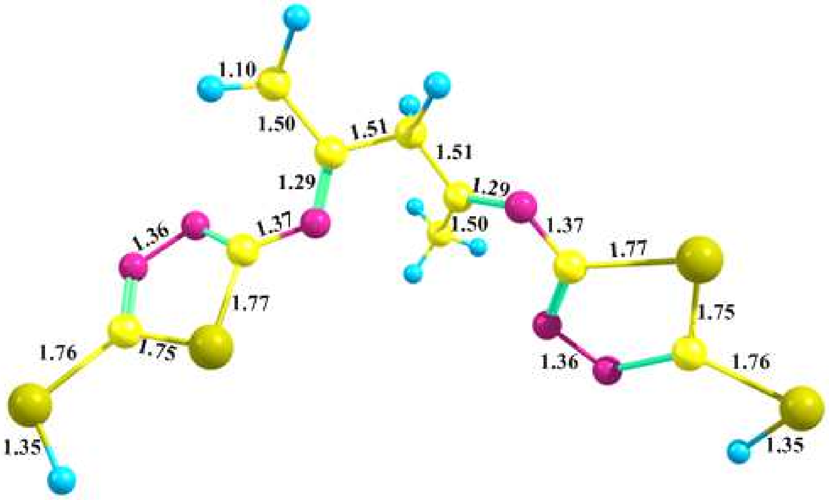


Figure 1: The optimize structure of compound B

Table 3: IR calculations of compound B compared to experimental IR spectra [16]

Group	Imine (C=N)	Thiadiazole (C=N)	Aliphatic (C-H)	Thiadiazole (C-S)
Freq. $(cm^{-1})_{Exp.}$	1604	1521	2960	1053
Freq. $(cm^{-1})_{Theo.}$	1691	1514	3048	1043
Error%	5%	0.4%	2%	0.9%

Table 4: ^{1}H-NMR calculation of compound B compared to experimental NMR spectra [16]

Group	(CH_2)	(CH_3)	(S-H)
δ $(ppm)_{Exp.}$	2.50	2.678	3.423
δ $(ppm)_{Theo.}$	2.75	2.8	3.23
Error%	10%	7%	6%

IR Methodology

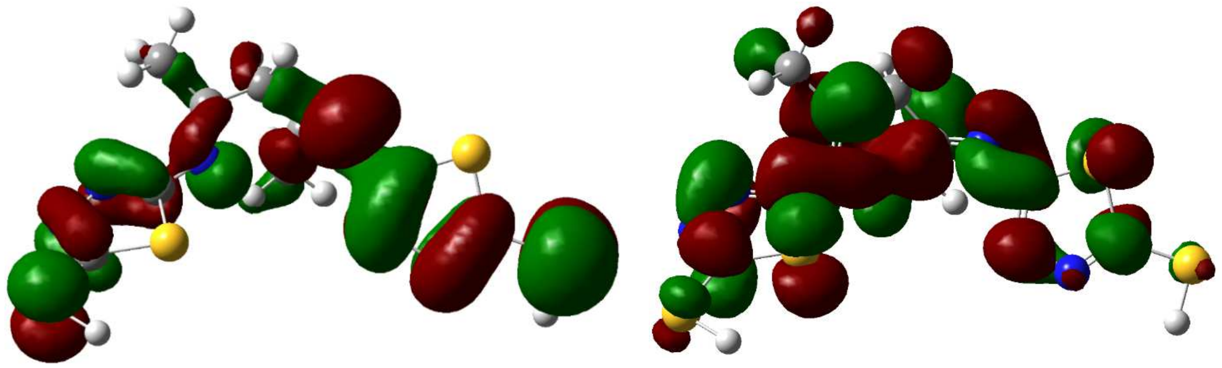
The theoretical IR data give a good agreement with the experimental data by the percent of error under the theoretical value (20%). (C=N) thiadazole giving a satisfactory (1514 cm^{-1}) agreement rather than (C=N) imine (1619 cm^{-1}) with error percent (0.4%, 5%) respectively. While (C-H) aliphatic 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 argues 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. No tautomerism is showing so no chemical shift for NH appears.

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 [28]. 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 [29]. In (Figure 2), the computed chemical data was given, including EHOMO = -0.2455 eV, ELUMO = -0.0784 eV and the energy band gap (ΔE = 0.1671 eV). The HOMO located on the thiadazole ring except sulfur atoms while the LUMO comes from thiadazole ring including the sulfur atoms. 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[30]. In addition, the dipole moment which consider an important factor on the corrosion inhibition process. The dipole moment of, B, molecule (7.7424 Debye (15.17X10^{-30} Cm)) is higher than that of H_2O molecule (μ= 6.23X10^{-30} Cm), which is probably in favor of the adsorption between organic molecule and mild steel surface via physical interaction [29-32].



HOMO **LUMO**

Figure 2: The frontier molecular orbitals of compound B

On the basis of EHOMO and ELUMO, the electronegativity (x), chemical potential (μ), global hardness (η), global softness (S) and global electrophilicity index (ω), which describe the electrophilic behavior [33] , can be calculating .Eqs. (1) – (5):

$$(x) = -{}^{1}/_{2}\,(\text{EHOMO} + \text{ELUMO}) = 0.1620\ \text{eV} \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

$$(\mu) = -(x) = -0.1620\ \text{eV} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (2)$$

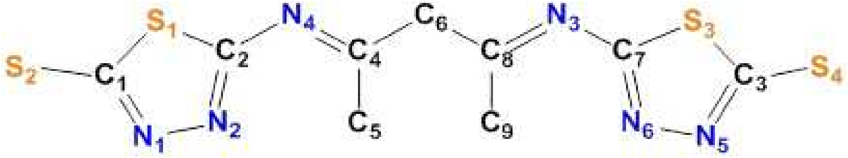
$$(\eta) = {}^{1}/_{2}\,(\Delta E) = 0.084\ \text{eV} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3)$$

$$(S) = {}^{1}/_{2\eta} = 5.95\ \text{eV}^{-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

$$(\omega) = {}^{\mu^2}/_{2\eta} = 0.155\ \text{eV} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (5)$$

The Relation between Mullikan Charge and Biological Activity

Mullikan charges of atoms gives explain for how the receptor interacts with the molecule. If we taking DFT/B3LYP/6-31G for example again, (Table 5), three atoms C4, C5, C8, S1 and S2 or S1 and S2 are the most positively charged ones, which can interact with the negative charged part of the receptor easily. The negative charges are mainly located on atoms N1, N2 and N3 or N4, N5 and N6, so they can interact easily with the positive part of the receptor (Scheme 2).



Scheme 2: Structure of compound B with hidden hydrogen atoms

Table 5: Mulliken charges with hydrogens summed into heavy atoms

Atom	Charge
C1	-0.376918
C2	-0.033363
C3	-0.385289
C4	0.267832
C5	0.103134
C6	0.022257
C7	-0.029906
C8	0.282899
C9	0.097533
N1	-0.231236
N2	-0.230368
N3	-0.382821
N4	-0.377667
N5	-0.225741
N6	-0.230189
S1	0.543675
S2	0.322505
S3	0.536333
S4	0.327328

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 [16]. 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. No tautomerism is showing so no chemical shift for NH appears. 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. With Mulliken charges, our study illustrated how the receptors can combination with this compound. This work illustrates the important and complementary role that the computation of spectroscopic fingerprints can play in the process.

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