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Synthesis and Theoretical Analyses of Novel 5-mercapto-2-(5-methyl-furan-2-yl-methylidenamino)-1,3,4-thiadiazole Molecule

Gül KOTAN[1]*, Hilal MEDETALİBEYOĞLU[2], Murat BEYTUR[2], Onur AKYILDIRIM[3], Haydar YÜKSEK[2]

ABSTRACT : In this study, the novel 5-Mercapto-2-(5-methyl-furan-2-yl-methylidenamino)-1,3,4-thiadiazole molecule was synthesized from the reaction of 2-amino-5-mercapto-1,3,4-thiadiazole with 5-methyl-furan-2-carbaldehyde. The 5-Mercapto-2-(5-methyl-furan-2-yl-methylidenamino)-1,3,4-thiadiazole was optimized by using DFT(B3LYP)-HF methods. The mulliken charges, HOMO-LUMO energy, E_{LUMO}-E_{HOMO} energy gap (ΔEg), dipole moments, electron affinity (A), ionization potential (I), chemical softness (σ), chemical hardness (η), electronegativity (χ), bond angles, total energy and bond lengths of the molecule were calculated by using 6-31G(d,p) basis set with DFT (B3LYP) and HF methods. Otherwise, the ^{1}H-NMR and ^{13}C-NMR isotropic shift values were calculated by using GIAO methods with GaussianG09W package program. The experimental/theoretical values were compared and the regression analysis were found. Defining IR values were used the veda4f program. The theoretical infrared spectrums are visualised.

Keywords: 1,3,4-Thiadiazole, HOMO-LUMO, DFT, HF, GIAO.

Yeni 5-Merkapto-2-(5-metil-furan-2-il-metilidenamino)-1,3,4-tiyadiazol Molekülün Sentezi ve Teorik Analizi

ÖZET: Bu çalışmada, yeni 5-Merkapto-2-(5-metil-furan-2-il-metilidenamino)-1,3,4-tiyadiazol molekülü 5-metil-furan-2-karbaldehid ile 2-amino-5-merkapto-1,3,4- tiyadiazolün reaksiyonundan sentezlenmiştir. 5-Merkapto-2-(5-metil-furan-2-il-metilidenamino)-1,3,4-tiyadiazol DFT(B3LYP)-HF metodları kullanılarak optimize edilmiştir. Molekülün mulliken yükleri, HOMO-LUMO enerjisi, E_{LUMO}-E_{HOMO} enerji farkı(ΔEg), dipol moment, elektron ilgisi (A), iyonizasyon potansiyeli (I), kimyasal yumuşaklık (σ), kimyasal sertlik (η), elektronegativite (χ), bağ açıları, toplam enerjisi ve bağ uzunlukları DFT(B3LYP)-HF metodları ile 6-31G(d,p) temel seti kullanılarak hesaplanmıştır. Ayrıca, ^{1}H-NMR ve ^{13}C-NMR isotropik kayma değerleri GaussianG09W programı ile GIAO metodları kullanılarak hesaplanmıştır. Deneysel ve hesaplanan teorik değerler karşılaştırılmış ve regrasyon analizi yapılmıştır. IR değerlerini belirlemek için veda4f programı kullanılmıştır. DFT-HF metodlarına göre elde edilen IR verileri uygun skala faktörleri ile çarpılmış ve teorik infrared spektrumları çizilmiştir.

Anahtar Kelimeler: 1,3,4-Tiyadiazol, HOMO-LUMO, DFT, HF, GIAO.

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[1] Gül KOTAN (Orcid ID: 0000-0002-4507-9029) , Kafkas University, Kars Vocational School, Kars, Turkey
[2] Hilal MEDETALİBEYOĞLU (Orcid ID: 0000-0002-1310-6811), Murat BEYTUR (Orcid ID: 0000-0002-7098-5592), Haydar YÜKSEK (Orcid ID: 0000-0003-1289-1800), Kafkas University, Department of Chemistry, Kars, Turkey
[3] Onur AKYILDIRIM (Orcid ID: 0000-0003-1090-695X), Kafkas University,Department of Chemical Engineering, Faculty of Engineering and Architecture, Kars, Turkey

* Sorumlu Yazar/Corresponding Author: Gül KOTAN, e-mail: gulkemer@hotmail.com

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INTRODUCTION

Heterocyclic molecules are very common in nature and are used in many fields. Among these molecules, thiadiazoles, which have an important place among the 5-membered heterocyclic containing nitrogen and sulfur, are widely used in pharmaceutical chemistry, materials science and organic synthesis (Shahcheragh et al., 2017). 1,3,4-Thiadiazole and its derivatives have a broad spectrum of biological activity such as antimicrobial (El-Gohary et al., 2013), antibacterial (Li et al., 2015), antioxidant (Gür et al., 2017), anticonvulsant (Luszczki et al., 2015), analgesic (Ragab et al., 2016), and anticancer (Polkam et al., 2017). In addition, 1,3,4-thiadiazole derivatives are widely used in bactericides, insecticides, pesticides, fungicides and herbicides in many areas of agriculture and technology (Zarei, 2017; Zou et al., 2002). In the literature, experimental and theoretical studies on the structural and vibrational properties of 1,3,4-thiadiazole have been reported in order to understand the basic issues of this class of materials (Dani et al., 2013; Romano et al., 2013). The theoretical calculations on heterocyclic molecules have been reported so far (Kotan et al., 2018).

In this study, the novel 5-Mercapto-2-(5-methyl-furan-2-yl-methylidenamino)-1,3,4-thiadiazole was synthesized from the reaction of 2-amino-5-mercapto-1,3,4-thiadiazole with 5-methyl-furan-2-carbaldehyde. The structure of synthesized new compound was established from IR, ^{1}H NMR and ^{13}C NMR spectral data. Then, we examined theoretical features of titled new compound 5-mercapto-2-(5-methyl-furan-2-yl-methylidenamino)-1,3,4-thiadiazole. All theoretical computer calculations of the target compound were performed with the Gaussian09W (Frisch et al., 2009). Firstly, titled molecule were optimized by using the restricted DFT(B3LYP)-HF/6-31G(d,p) level of theory (Frisch et al., 2009; Wolinski et al., 1990). Optimized structure is the most stable structure of the molecule. Then, the dipole moments, HOMO-LUMO energies, bond lengths, mulliken atomic charges, bond angles and electronic properties; E_{LUMO}-E_{HOMO} energy gap (ΔEg), ionization potential (I), softness (σ), electron affinity (A), global hardness (η), electronegativity (χ), thermodynamics data; (entropy (S), thermal energies (E) and capacity (CV), total energy of titled molecule from optimized structure were calculated by using both methods. Furthermore, The theoretical calculations ^{1}H-NMR and ^{13}C-NMR were performed by using DFT/HF 6-31G(d,p) level. ^{1}H-/^{13}C-NMR isotropic shift data were performed by using the GIAO method with the GaussianG09W (Wolinski et al., 1990). The visualization of all results has been carried out using GaussView 5 (Dennington et al., 2009). Theoretical and experimental results were carried out the graphic by equation of δ exp$_{=}$a+b. δ calc. The standard error data were calculated.

Finally, the veda4f program was used in defining IR data (Jamróz, 2004). The theoretical vibrational spectra were calculated at the DFT(B3LYP)-HF 6-31G(d,p) basis sets in the gas phase and these data are scaled with 0.9613 and 0,8929 factors for DFT(B3LYP)-HF 6-31G(d,p) basis set (Merrick et al., 2007). The IR spectrum values obtained according to DFT(B3LYP)-HF methods are performed using theoretical and experimental data. The experimental and theoretical IR spectra are given in Fig. 5.

MATERIALS AND METHODS

Experimental

5-mercapto-2-(5-methyl-furan-2-yl-methylidenamino)-1,3,4-thiadiazole,

2.05 g (91%); mp: 185 ^{0}C; IR (υ, cm^{-1}): 2879, 2977 (CH_3), 2715 (SH), 1666 (N=CH), 1614 (C=N), 1556, 1495 (C=C), 1181 (C-O, furan), 1101 (N-N), 673 (C-S); ^{1}H-NMR (400 MHz, DMSO-d_6): δ: 2.43 (s, 3H, CH_3), 6.49 (d, 1H, ArH; J=2.80 Hz), 7.38 (d, 1H, ArH; J=3.20 Hz), 8.36 (s, 1H, N=CH), 13.28 (s, 1H, SH); ^{13}C-NMR (100 MHz, DMSO-d$_6$) δ: 13.80 (CH_3), 110.73, 125.46, 149.06, 159.90 (Ar-C), 153.57 (N=CH), 169.32 (Thiazole C2), 177.11 (Thiazole C5).

RESULT AND DISCUSSION

Computational Details

NMR spectral analysis

Experimental ^{1}H and ^{13}C-NMR spectra of the target molecule were measured in DMSO-d$_6$. ^{1}H and ^{13}C chemical shift values with GIAO were calculated using the DFT(B3LYP)/HF methods with the 6-31G(d,p) basis set for DMSO solvent. The calculated chemical shift values and experimental are given in Table 1.

In the ^{13}C-NMR spectra for the methyl group carbon (C8) was assigned at 13.80 ppm whereas calculated at 22.75/11.77 ppm for B3LYP/HF 6-31G(d,p). The aromatic furan ring carbons (C4, C5, C6, C7) have been assigned at 149.06, 125.46, 110.73, 159.90 ppm in the experimental respectively. Their calculated values were 155.87/138.97; 124.85/118.75; 117.07/101.38; 166.84/155.43 ppm, respectively.

The characteristic -N=CH peak was observed at 153.57 ppm in the experimental and same peak was calculated at 150.79/155.74 ppm according to 6-31G(d,p) basis sets of B3LYP and HF methods. The thiazole C2 and thiazole C5 peaks were observed experimentally at 169.32 and 177.11 ppm, these peaks were calculated theoretically at 171.41/163.17 ppm, respectively. In the ^{1}H-NMR spectra for the methyl group protons (H12, H13, H14), the singlets were observed at 2.43 ppm. Their theoretical values were 3.19, 3.29, 3.29 ppm for the DFT/B3LYP/6-31G(d,p) and 2.65, 2.67, 2.67 ppm for the HF/6-31G(d,p), respectively. The aromatic furan ring protons (H10, H11) were seen at 7.38 and 6.49 ppm in the experimental. The calculated values of these protons were 8.46/8.22 and 7.42/6.77 ppm for B3LYP/HF 631G(d,p), respectively. Although the singlet peaks for characteristic -N=CH proton (H9) and -S-H proton (H15) were assigned at 8.36 and 13.28 ppm in the experimental, their were calculated at 9.95/9.62 and 6.25/5.72 ppm, respectively.

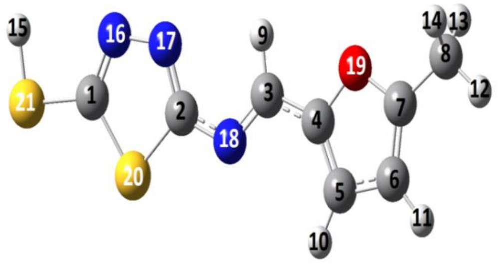

Figure 1. The Gausview structure of the molecule

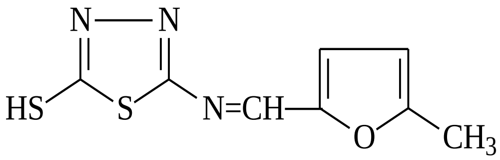

Figure 2. The chemical formula of the molecule

The R^2 values of the compound

B3LYP(DFT)-631G(d,p) in DMSO solvent: ^{13}C: 0.9815, ^{1}H: 0.9807; HF-631G(d,p) in DMSO solvent: ^{13}C: 0.9915, ^{1}H: 0.9807.

There is such a relationship between R^2-values of the compound. Found a, b constants regression values and standard error rate were performed. These values for titled compound were given in Table **2**. Theoretical/experimental proton (^{1}H-)-carbon (^{13}C-)-NMR chemical shifts values between according to a, b data and R^2 were performed and observed a lineer correlation.

Table 1. ^{13}C- /^{1}H-NMR isotropic chemical shifts in DMSO (δ/ppm) (6-31G(d,p))

no	Experimental	DFT	Differ.DFT	HF	Differ.HF
C1	169.32	171.41	-2.09	163.17	6.15
C2	177.11	184.63	-7.52	171.14	5.97
C3	153.57	150.79	2.78	155.74	-2.17
C4	149.06	155.87	-6.81	138.97	10.09
C5	125.46	124.85	0.61	118.75	6.71
C6	110.73	117.07	-6.34	101.38	9.35
C7	159.90	166.84	-6.94	155.43	4.47
C8	13.80	22.75	-8.95	11.77	2.03
H9	8.36	9.95	-1.59	9.62	-1.26
H10	7.38	8.46	-1.08	8.22	-0.84
H11	6.49	7.42	-0.93	6.77	-0.28
H12	2.43	3.19	-0.76	2.65	-0.22
H13	2.43	3.29	-0.86	2.67	-0.24
H14	2.43	3.29	-0.86	2.67	-0.24
H15	13.28	6.25	7.03	5.72	7.56

Table 2. The correlations data of the molecule (^{1}H and ^{13}C-NMR)

	^{13}C				^{1}H			
6-31G (d,p)	**R**	**S. error**	**a**	**b**	**R**	**S. error**	**a**	**b**
DFT	0.9815	6.4084	1.0546	-12.191	0.9807	0.3357	0.9234	0.5884
HF	0.9915	4.3428	0.9823	5.5069	0.9807	0.3357	0.9234	0.5884

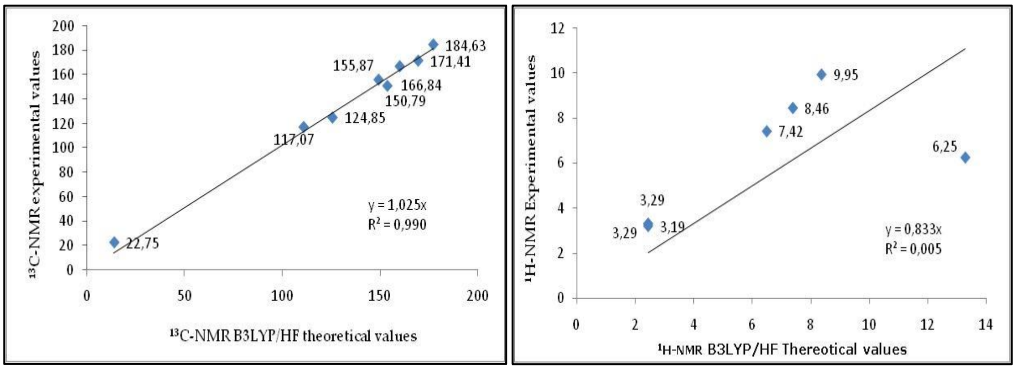

Figure 3. The correlation graphs for B3LYP/HF 631G(d,p) chemical shifts of molecule

The vibration frequency analysis

The calculated IR data were carried out according to veda4f program and the scaled DFT/HF values were obtained. The calculated IR data are multiplied with 0.9613 (for DFT), 0.8929 (for HF) adjustment factors according to 6-31G(d,p) basis sets. All frequencies of the compound were found possitive. All theoretical spectrums were drawn according to obtained results from B3LYP and HF methods. Theoretically infrared data were compared with experimental data. These results were found corresponding with each values.

C=C stretching vibrations have been assigned to two weak band in the regions 1556, 1495 cm^{-1} in the experimental whereas their calculated value for B3LYP/HF 631G(d,p) were in the region 1515/1551 cm^{-1}. The C=N stretching vibration in the experimental IR spectrum was observed at 1614 cm^{-1} though the calculated values appeared at 1573/1625 cm^{-1} according to 6-31G(d,p) basis sets of B3LYP and HF methods. The band HC=N is 1666 cm^{-1} in the experimental IR spectrum and the calculated values are in the region 1583/1665 cm^{-1}. The C-O stretching vibration was observed at 1181 cm^{-1} for experimental value which was calculated at 1188/1193 cm^{-1} for the HF and DFT methods with the 6-31G(d,p) basis set, respectively. The strong S-H stretching vibration band were assigned at 2715 cm^{-1} in FT-IR spectrum. The same vibration band was calculated theoretically 2584/2621 cm^{-1}. The C-H stretching vibration of aromatic furan ring was observed experimentally at 3078 cm^{-1}. Its calculated value were 3141/3181 cm^{-1} and 3160/3198 cm^{-1}. The C-H shear and angle banding stretching vibration bands of the methyl group have been assigned at 2879, 2977 cm^{-1} in the experimental whereas The computed values for these C-H vibration bands have been calculated at 2983, 2930 cm^{-1} for the B3LYP/6-31G(d,p) and 2928, 2873 cm^{-1} for the HF/6-31G(d,p). The C-S stretching vibration has been assigned to a weak band in the region 673 cm^{-1} and calculated value for B3LYP/HF 631G(d,p) were in the region 598/612 cm^{-1} (Table 3,4).

Table 3. Significant vibrational frequencies (cm^{-1})

Significant vibrational frequencies	Experimental IR (cm^{-1})	B3LYP/DFT/HF 6-31G(d,p) IR (cm^{-1})	
		Scaled DFT	Scaled HF
ν C=C	1556, 1495	1515	1551
ν C=N	1614	1573	1625
ν CH=N	1666	1583	1665
ν C-O	1181	1188	1193
ν S-H	2715	2584	2621
ν C-H	2879, 2977	2983, 2930	2928, 2873
ν C-S	673	598	612

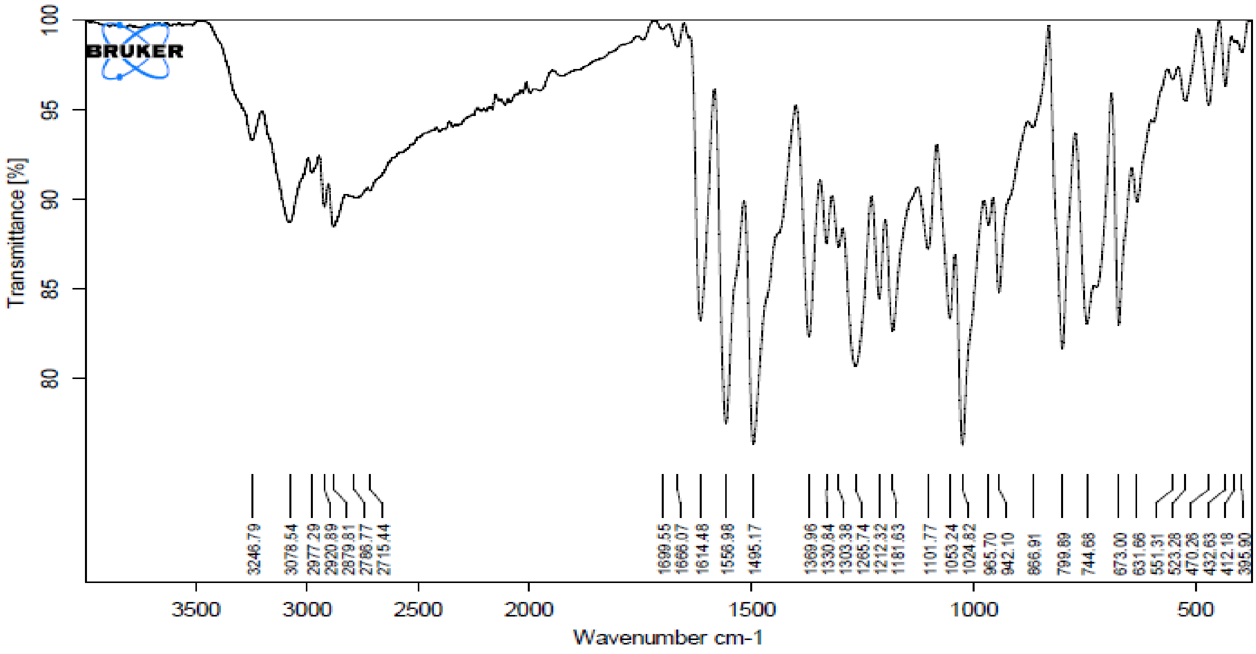

Figure 4. Experimental IR spectrum of the molecule

Table 4. The calculated IR frequencies (cm^{-1}) of compound (6-31G(d,p))

Vibrational frequencies	Scaled DFT	Scaled HF	Vibrational frequencies	Scaled DFT	Scaled HF
τ CNNC(66)	4	21	δ HCH(14), ν CC(16), ν OC(13)	942	960
τ NCCC(22), τ NNCN(20),τ CCOC(10)	44	47	ν OC(26), ν CC(11), δ COC(17)	958	968
δ CNNC(34), δ CCO(20)	54	54	τ HCNC(45)	976	993
τ CNNC(24), τ CCOC(30)	95	96	δ COC(23), ν CC(13)	990	1017
δ SCN(30),δ CNN(16), δ CCO(28)	106	128	δ HCC(13), ν CC(40), δ COC(14)	1011	1032
τ CNCN(20), τ CCCC(14)	161	154	δ HCH(18), τ HCCC(30)	1025	1048
ν CC(14), δ NCC(10), δ CNC(20)	185	180	ν NN(15), ν SC(38), δ NSC(12), δNNC(15)	1045	1074
τ CNCN(15), τ CCNC(15)	202	187	ν NN(51), δ NNC(19)	1104	1142
τ CCOC(35), τ CNCN(30),τ CCON(11)	215	204	ν NN(12), ν NC(28), δ NNC(15)	1152	1183
δ CCC(11), τ CCCC(15), τ NNCN(11)	244	240	ν OC(15), δ HCC(43)	1188	1193
τ CCOC(27), τ COCC(12), τ NNNC(14)	257	259	ν OC(11), ν CC(16), δ HCC(14), δ CN(12)	1206	1225
τ HCCN(21)	290	302	ν OC(30), δ HCC(14), δ HCN(12)	1231	1234
δ NNC(10), δ CCO(43), δ SCN(13)	347	350	ν NC(16), δ HCN(36)	1345	1356
τ SSNC(33), τ CNCC(16), τ NCN(10)	375	398	ν NC(59)	1360	1391
ν SC(31), δ SCN(30)	409	421	ν NC(10), δ CCO(21), δ CN(10), δCOC(18)	1365	1398
δ CNN(14), δ CCO(21)	484	488	δ HCH(91)	1372	1439
τ NNCN(10), τ SCNN(10), τ SCN(10)	551	577	ν NC(30)	1414	1454
τ CNNC(47), τ COCC(17),τ SCNN(13)	589	607	τ HCCC(10), δ HCH(80)	1428	1514
ν SC(47), δ SCN(12)	598	612	δ HCH(67), τ HCCC(10)	1444	1527
τ CCOC(52)	613	632	ν CC(40)	1515	1551
ν CC(28), δ CCO(17)	635	637	ν CC(47), ν NC(13)	1573	1625
δ SCN(11), δ CNN(22), δ CCO(25)	646	662	ν NC(22)	1583	1665
δ HCC(27), δ CCC(13), τ CNNC(13)	681	697	ν SH(100)	2584	2621
ν NC(10), ν SC(20), δ CNN(20)	730	742	ν CH(92)	2930	2873
τ CHNC(46)	785	820	ν CH(50)	2983	2928
δ CNC(20), δ COC(10)	828	846	ν CH(56)	2993	2959
τ HCNC(78)	858	910	ν CH(46)	3029	2977
δ HSC(74)	881	914	ν CH(75)	3141	3081

υ *– stretching;* ***δ*** *- In plane bending;****τ*** *– Twisting*

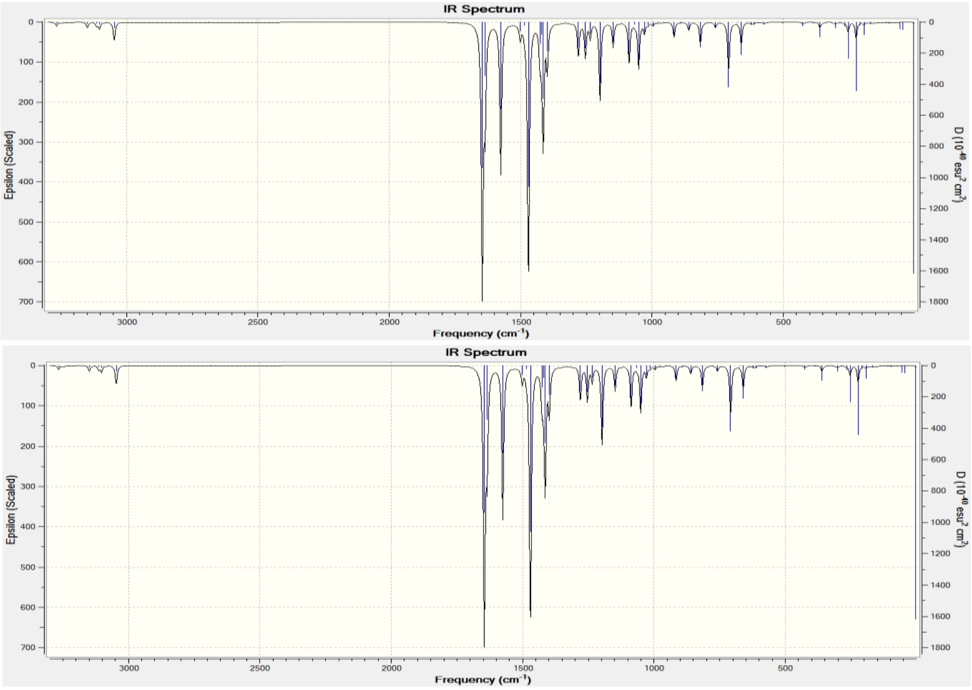

Figure 5. Theoretical IR spectrums

Molecular geometry

The molecular geometric and electronic data such as bond lengths, mulliken atomic charges and bond angles of optimized molecule were calculated by using the DFT/(B3LYP)-HF 6-31G (d,p) basis set and obtained data were shown in Table 4-6. According to these data, the longest bond length is between C2-S20 atoms that this values are 1.773/1.742 Å. The electronegative oxygen (O), sulfur (S), nitrogen (N) atoms have negative atomic charge values. The carbon atoms surrounded by electronegative atoms have positive atomic charge values. The C1 atom surrounded by three electronegative atoms bond lengths in the thiadiazol ring N16-N17, N16-C1, C2-N17, C2-S20, S20-C1 are calculated 1.362/1.363, 1.308/1.271, 1.309/1.273, 1.773/1.742, 1.748/1.735 6-31G(d,p) basis sets (Table 5). In the literature, the C=N and N-N bond lengths are measured as 1.280, 1.404, 1.212 Å (Ocak et.al., 2003; Ustabaş et.al., 2007). The biggest bond angle is between C(2)-N(59)-O(60) atoms, which is 134.17/133.6^0 (Table 6).

The mulliken atomic charges (Mulliken, 1955) were calculated by DFT/(B3LYP)-HF methods. The N16, S20, S21 and C2 atom is surrounded by three electronegative atoms N17, N18, S20. All hydrojen and sulfur atoms of the compound have positive atomic charge values. Also, all nitrogen and oxygen atoms have negative atomic charge values (Table 7).

Table 5. The calculated bond lengths of the molecule (B3LYP/HF 6-31G(d,p))

Bond lengths	DFT	HF	Bond lengths	DFT	HF
C(1)-N(16)	1.308	1.271	C(4)-C(5)	1.377	1.347
S(20)-C(1)	1.748	1.735	C(4)-O(19)	1.378	1.356
C(1)-S(21)	1.765	1.761	C(5)-H(10)	1.079	1.069
S(21)-H(15)	1.348	1.325	O(19)-C(7)	1.337	1.336
N(17)-N(16)	1.362	1.363	C(5)-C(6)	1.417	1.427
N(17)- C(2)	1.309	1.273	C(6)-H(11)	1.080	1.070
C(2)-N(18)	1.372	1.381	C(6)-C(7)	1.374	1.349
C(2)-S(20)	1.773	1.742	C(7)-C(8)	1.486	1.488
N(18)-C(3)	1.297	1.266	C(8)-H(12)	1.095	1.085
H(9)-C(3)	1.094	1.081	C(8)-H(13)	1.095	1.085
C(4) -C(3)	1.429	1.444	C(8)-H(14)	1.091	1.082

Table 6. The calculated bond angles of the molecule (B3LYP/HF 6-31G(d,p))

Bond Angles	B3LYP	HF	Bond Angles	B3LYP	HF
N(16)-C(1)-S(20)	114.53	114.15	C(4)-O(19)-C(7)	107.55	107.77
C(2)-N(17)-N(16)	113.78	113.31	C(4)-C(5)-H(10)	125.17	125.72
C(1)-S(20)-C(2)	85.78	85.72	C(4)-C(5)-C(6)	106.54	106.01
N(17)-C(2)-S(20)	113.06	113.69	C(5)-C(6)-H(11)	127.41	127.51
S(20)-C(2)-N(18)	118.29	118.68	C(5)-C(6)-C(7)	106.78	106.15
N(17)-C(2)-N(18)	128.63	127.60	O(19)-C(7)-C(6)	109.86	110.24
N(16)-S(21)-C(1)	123.54	123.90	H(11)-C(6)-C(7)	125.80	126.33
S(21)-C(1)-S(20)	121.92	121.93	O(19)-C(7)-C(8)	109.86	116.86
C(1)-S(21)-H(15)	93.13	94.65	C(7)-C(8)-H(12)	110.01	110.09
C(2)-N(18)-C(3)	118.34	117.73	C(7)-C(8)-H(13)	111.18	110.62
N(18)-C(3)-H(9)	122.49	122.54	C(7)-C(8)-H(14)	111.16	110.60
H(9)-C(3)-C(4)	116.60	116.31	H(12)-C(8)-H(13)	108.46	108.77
C(3)-C(4)-C(5)	134.17	133.66	H(12)-C(8)-H(14)	108.47	108.77
C(3)-C(4)-O(19)	116.57	116.52	H(13)-C(8)-H(14)	107.43	107.91

Table 7. The mulliken atomic charges of title molecule (B3LYP/HF 6-31G(d,p))

	DFT	HF		DFT	HF
C1	-0.077	-0.106	**H12**	0.143	0.152
C2	0.268	0.325	**H13**	0.143	0.152
C3	0.097	0.183	**H14**	0.131	0.140
C4	0.303	0.272	**H15**	0.103	0.097
C5	-0.111	-0.143	**N16**	-0.243	-0.270
C6	-0.157	-0.256	**N17**	-0.292	-0.343
C7	0.340	0.363	**N18**	-0.476	-0.584
C8	-0.387	-0.363	**O19**	-0.473	-0.604
H9	0.139	0.206	**S20**	0.256	0.312
H10	0.126	0.197	**S21**	0.062	0.098
H11	0.104	0.169			

Frontier molecular orbital analysis

The FMO (frontier molecular orbitals) were used to determine the electric and electronic transitions, optical properties and kinetic stability (Fukui, et.al., 1955). The HOMO-LUMO energies of titled compound was performed using B3LYP-HF 6-31G (d,p) levels of theory. The energy gap between the HOMO and LUMO refers to the chemical stability of the molecule. If this energy gap (ΔE*g*) is small, the interaction of the reactants and the reaction is easy. The HOMO-LUMO energies gap is 3.58 eV for B3LYP 6-31G (d,p) basis set and 9.87 eV for HF 6-31G (d,p) basis set (Figure 6).

All parameters such as the global electrophilicity index (ω), ionization potential (I), chemical potential (μ), electrophilic index (ω), electronegativity (χ), global hardness (η), chemical potential (Pi), nucleophilic index (IP) for the target compound have been performed by using both methods (Table 8). The electron affinity and ionization potential are used to evaluate the energy level of the electrons. The value of the energy level of molecule is 3.58 eV. The energy gap between the frontier orbitals is hardnes. This value is 3.58 eV.

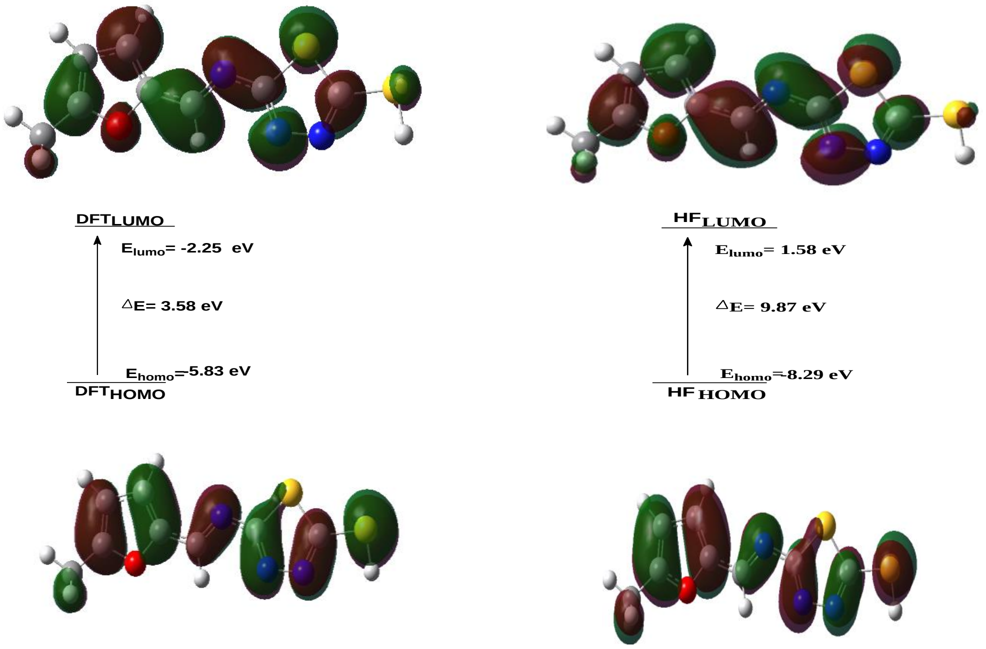

Figure 6. HOMO-LUMO and ΔE energies of the molecule

Table 8. The electronic structure parameters of the molecule

		Hartree	eV	Kcal/mol	Kj/mol
	LUMO	0,05832	1,58693	36,596	153,119
	HOMO	-0,30506	-8,3009	-191,426	-800,935
A	**Electron affinity**	-0,05832	-1,58693	-36,596	-153,119
I	**Ionization potential**	0,30506	8,3009	191,426	800,935
ΔE	**Energy gap**	0,36338	9,88782	228,022	954,054
χ	**Electronegativity**	0,12337	3,35698	77,415	323,908
Pi	**Chemical potential**	-0,12337	-3,35698	-77,415	-323,91
ω	**Electrophilic index**	0,001383	0,03762	0,86763	3,63021
IP	**Nucleophilic index**	-0,02242	-0,60993	-14,066	-58,851
S	**Molecular softness**	5,5039	149,764	3453,7	14450,4
η	**Molecular hardness**	0,18169	4,94391	114,011	477,027

Table 9. The thermodynamics parameters of the molecule

	DFT	HF
Rotational temperatures (Kelvin)		
A	0.13247	0.13433
B	0.00838	0.00850
C	0.00789	0.00804
Rotational constants (GHZ)		
A	2.76013	2.79893
B	0.17459	0.17715
C	0.16445	0.16751
Thermal Energies E(Kcal/mol)		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	95.665	102.626
Total	97.442	104.403
Thermal Capacity CV(cal/mol-K)		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	41.757	38.505
Total	47.719	44.467
Entropy S(cal/mol-K)		
Translational	42.135	42.135
Rotational	32.673	32.626
Vibrational	47.659	40.923
Total	122.467	115.684
Zero-point correction (Hartree/Particle)	0.141928	0.153824
Thermal correction to Gibbs Free Energy	0.098040	0.112356
Thermal correction to Energy	0.155284	0.166377
Sum of electronic and zero-point Energies	-1344.731901	-1340.037485
Thermal correction to Enthalpy	0.156228	0.167321
Sum of electronic and thermal Energies	-1344.718545	-1340.024933
Sum of electronic and thermal Enthalpies	-1344.717601	-1340.023988
Sum of electronic and thermal Free Energies	-1344.775789	-1340.078954
Zero-point vibrational energy (Kcal/mol)	89.06110	96.52624

Investigation of thermodynamics properties of this compound

The thermodynamics parameters of the molecule were represented with B3LYP-HF 6-31G (d,p) basis sets. Thermodynamic parameters (thermal energy, entropy, vibrational energies (ZPVE), heat capacity, rotational temperatures, zero-point correction and rotational constants) were given in Table 9. Also, the standard thermodynamic functions of enthalpy H^0, heat capacity CV^0, and entropy S^0 were obtained. The dipole moment and total energy values of titled compound were performed by using B3LYP(DFT)-HF 6-31G(d,p) method and summarized in Table 10,11.

Molecular electrostatic potential (MEP), electron spin potantial and total density

The total density, MEP of the molecule, the electron density and the electrostatic potential of titled compound have been performed by the DFT(B3LYP)-HF 6-31G(d,p) basis sets.The electron density in the molecule shows a uniform distribution. The colour scheme for the MEP surface of the molcule is as follows: while the electron rich region is red, the electron poor region is seen as blue color. The negative charges are delocalized in around N16, N17 and O19 atoms. The positive charges were observed in arround H12, H13, H14 atoms connected with C atoms and shown in Figure 7.

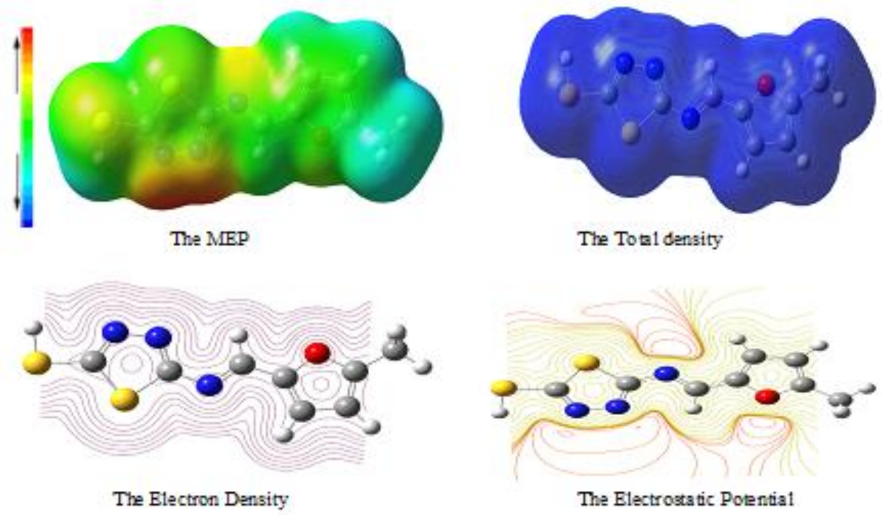
The MEP
The Total density
The Electron Density
The Electrostatic Potential

Figure 7. The calculated molecular surfaces of the molecule

Table 10. The dipole moment of the molecule

	μ_x	μ_y	μ_z	μ_{Total}
Dft	1.4434	-2.0798	0.2087	2.5402
Hf	1.4453	-2.2790	0.2998	2.7152

Table 11. The total energy of the molecule

Energy (a.u.)	**DFT**	**HF**
	-1344.873829	-1340.191309

CONCLUSION

The spectroscopic parameters such as ^{13}C-NMR, ^{1}H-NMR, IR and geometrical parameters are calculated by using DFT/HF methods with the 6-31G (d,p) basis sets the GaussianG09W program. The spectroscopic values (^{13}C- and ^{1}H-NMR, IR) are compared with experimental ones. The ^{13}C-, ^{1}H-NMR chemical shifts and IR values are found that these data to be compatible with the experimental values. Experimental and theoretical ^{13}C and ^{1}H-NMR chemical shifts values according to R^2 and a, b values were observed a lineer correlation. Also, thereotical IR vibration frequencies were determined with veda4f program and significant results given in Tablo 3. Furthermore, HOMO and LUMO, mulliken atomic charges, E_{HOMO}-E_{LUMO} energy gap (ΔEg), softness (σ), ionization potential (I), dipole moment, global hardness (η), electron affinity (A), electronegativity (χ) and total energies of the molecule were calculated with DFT (B3LYP)-HF 6-31G (d,p) basis sets.

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