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# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy



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# Molecular structure and vibrational bands and chemical shift assignments of 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione by DFT and *ab initio* HF calculations

# Tuncay Karakurt<sup>a,\*</sup>, Muharrem Dinçer<sup>a</sup>, Ahmet Çetin<sup>b</sup>, Memet Şekerci<sup>c</sup>

<sup>a</sup> Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Kurupelit, Samsun, Turkey

<sup>b</sup> Department of Chemistry, Faculty of Arts and Sciences Bingöl University, 12000, Bingöl, Turkey

<sup>c</sup> Department of Chemistry, Faculty of Arts and Sciences Fırat University, 23119, Elazığ, Turkey

# ARTICLE INFO

Article history: Received 23 December 2009 Received in revised form 3 May 2010 Accepted 13 May 2010

Keywords: X-ray structure determination DFT HF NMR IR spectra Molecular electrostatic potential

# ABSTRACT

The title molecule, 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>OS), was synthesized and characterized by IR-NMR spectroscopy and single-crystal X-ray diffraction. The compound crystallizes in the monoclinic space group is  $P_{21}/c$ , a = 9.0907(5)Å, b = 9.1288(7)Å, c = 13.6222(7)Å,  $\alpha = 90^{\circ}$ ,  $\beta = 98.442(4)$ ,  $\gamma = 90^{\circ}$  and V = 2683.7(6)Å<sup>3</sup>, F(000) = 488,  $D_x = 1.386$  g/cm<sup>3</sup>. In addition to the molecular geometry from X-ray experiment, the molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO) <sup>1</sup>H and <sup>13</sup>C chemical shift values of the title compound in the ground state have been calculated using the Hartree-Fock (HF) and density functional method (DFT/BLYP and DFT/B3LYP) with 6-31G(d) basis set. To determine conformational flexibility, molecular energy profile of the title compound was obtained by HF/6-31G(d) calculations with respect to selected degree of torsional freedom, which was varied from  $-180^{\circ}$  to  $+180^{\circ}$  in steps of 10°. Besides, molecular electrostatic potential (MEP), frontier molecular orbitals (FMO), and several thermodynamic properties were performed by the HF and DFT methods.

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# 1. Introduction

1,2,4-Triazoles are very useful ligands in coordination chemistry. Besides, derivatives of 1,2,4-triazole have been reported to exhibit diverse biological activities [1–7]. Derivatives of 4,5disubstituted 1,2,4-triazole were synthesized by intramolecular cyclization of 1,4-disubstituted thiosemicarbazides [8,9]. Furthermore, the electronic structures and thiol-thione tautomeric equilibrium of heterocyclic thione derivatives have been studied previously [10–13].

The aim of the present work was to describe and characterize the molecular structure, vibrational properties and chemical shifts on 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3thione crystalline-structure. A number of papers have recently appeared in the literature concerning the calculation of NMR chemical shift (c.s.) by quantum-chemistry methods [14–19]. These papers indicate that geometry optimization is a crucial factor in an accurate determination of computed NMR chemical shifts. Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially important in systems containing extensive electron conjugation and/or electron lone pairs. However, considering that as molecular size increases, computing-time limitations are introduced for obtaining optimized geometries at the DFT level, it was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometryoptimization procedure at the molecular mechanics level [19].

The gauge-including atomic orbital (GIAO) [20,21] method is one of the most common approaches for calculating nuclear magnetic shielding tensors. It has been shown to provide results that are often more accurate than those calculated with other approaches, at the same basis set size [22]. In most cases, in order to take into account correlation effects, post-Hartree-Fock calculations of organic molecules have been performed using (i) Møller-Plesset perturbation methods, which are very time consuming and hence applicable only to small molecular systems, and (ii) density functional theory (DFT) methods, which usually provide significant results at a relatively low computational cost [23]. In this regard, DFT methods have been preferred in the study of large organic molecules [24], metal complexes [25] and organometallic compounds [26] and for GIAO <sup>13</sup>C c.s. calculations [22] in all those cases in which the electron correlation contributions were not negligible.

In this study, the title compound is a novel compound synthesized firstly in our laboratories by us. We have calculated

<sup>\*</sup> Corresponding author. Tel.: +90 03623121919/5260; fax: +90 03624576081. *E-mail address*: tuncaykarakurt@gmail.com (T. Karakurt).

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T. Karakurt et al. /	Spectrochimica Acta	Part A 77 (20	10) 189–198
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Crystallographic data for title compound.

Formula	$C_{11}H_{11}N_3OS$
Formula Weight	219.28
Temperature(K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell	
a (Å)	9.0907(5)
b (Å)	9.1288(7)
c (Å)	13.6222(7)
$\alpha$ (°)	90
β(°)	98.442(4)
$\gamma$ (°)	90
V (Å <sup>3</sup> )	1118.22(12)
Z	4
$D_{calc}$ (g/cm <sup>3</sup> )	1.386
F(000)	488
h, k, l Range	-11≤h≤11
	-11≤k≤11
	-17≤l≤17
Reflections collected	8094
Independent reflections	2565
R <sub>int</sub>	0.0435
Reflections observed $[I \ge 2\sigma(I)]$	2288
Data/restraints/parameters	2565/0/152
$R[I>2\sigma(I)]$	0.0388
Rw $[I>2\sigma(I)]$	0.1045
Goodness-of-fit on Indicator	1.049
Structure determination	Shelxs-97
Refinement	Full matrix
$(\Delta\sigma)_{\rm max}, (\Delta\sigma_{\rm min})  ({\rm e}/{\rm Å3})$	0.333, -0.328

#### Table 3

Selected optimized and experimental geometric parameters of 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione ( $C_{11}H_{11}N_3OS$ ) in the ground state.

		Calculated	1	
Parameters	Experimental	HF	BLYP 6-31G(d)	B3LYP
Bond lengths (Å)				
C(8)-S(1)	1.679(14)	1.683	1.683	1.720
O(1)-C(1)	1.355(18)	1.345	1.376	1.385
N(1)-C(7)	1.372(17)	1.380	1.407	1.401
N(1)-C(8)	1.367(17)	1.357	1.406	1.392
N(1)-C(9)	1.466(18)	1.462	1.485	1.473
N(2)-C(7)	1.300(18)	1.273	1.327	1.324
N(2)-N(3)	1.375(16)	1.356	1.382	1.395
N(3)-C(8)	1.329(19)	1.328	1.375	1.365
C(6)-C(7)	1.472(18)	1.481	1.482	1.469
RMSE <sup>a</sup> Bond angles (° )		0.011	0.012	0.015
C(7)-N(1)-C(9)	127.23(12)	127.73	128.48	128.22
O(1)-C(1)-C(6)	117.35(12)	117.39	124.42	116.19
C(5)-C(6)-C(7)	119.73(12)	120.51	118.00	121.34
N(2)-C(7)-C(6)	125.06(12)	124.63	122.46	123.09
N(1)-C(7)-C(6)	124.23(12)	124.28	126.56	126.08
N(3)-C(8)-S(1)	128.74(11)	127.64	128.76	128.31
N(1)-C(8)-S(1)	127.30(11)	129.11	129.41	128.87
RMSE <sup>a</sup> Dihedral angles (° )		0.01	3.19	1.66
C(5)-C(6)-C(7)-N(2)	-75.76(13)	-81.85	-53.61	-55.42
C(8)-N(1)-C(9)-C(10)	-77.20(19)	-88.29	-78.94	-79.67
N(1)-C(7)-C(6)-C(5)	100.32(18)	96.47	121.15	120.64

geometrical parameters, fundamental frequencies and GIAO <sup>1</sup>H and <sup>13</sup>C NMR c.s. values of the title compound in the ground state to distinguish the fundamental from the experimental <sup>1</sup>H c.s. values, vibrational frequencies and geometric parameters, by using the HF and DFT (BLYP and B3LYP) methods with 6-31G(d) basis set. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic c.s.-molecular structure relationship. And so, these calculations are valuable for providing insight into molecular analysis. The properties of the structural geometry, electronic charge distribution, molecular electrostatic potential (MEP) and the thermodynamic properties for the title compound at the HF and DFT methods with 6-31G(d) basis set were studied. We also make comparisons between experiments and calculations.

# 2. Experimental

# 2.1. Synthesis and physical properties

Melting points were determined in open capillary tubes on a digital Gallenkamp melting point apparatus and are uncorrected. The IR spectra were recorded for KBr disks with a Mattson 1000 FT-IR spectrometer. <sup>1</sup>H-NMR spectra were recorded on a Varian-Mercury-Plus 400 MHz <sup>1</sup>H-NMR, spectrometer in DMSO-d<sub>6</sub> with TMS as an internal standard. Starting materials was obtained from Fluka or Aldrich.

**Synthesis of N-allyl-2-(2-hydroxybenzoyl)hydrazinecarbothioamide(II):** A mixture of 2-hydroxybenzohydrazide (I) (0.01

## Table 2

Hydrogen bonding geometry (Å,  $^\circ)$  for the title compound.

D—H···A	D—H	H···A	$D{\cdots}A$	$D{-}H{\cdots}A$
$\begin{array}{c} N3 - H3 \cdots S1^{i} \\ O1 - H1 \cdots N2^{ii} \end{array}$	0.840	2.45	3.28	170
	0.847	2.03	2.87	173.5

Symmetry codes: (i)-x+1, -y, -z+2; (ii) - x, y+1/2, - z+3/2

<sup>a</sup> Between the bond lengths and the bond angles computed by the theoretical method and those obtained from X-ray diffraction.

mole, 1.52 g.) and the appropriate allyl isothiocyanate (0.01 mole, 0.98 ml.) in absolute ethanole (100 ml.) was refluxed for 5 hours. The solid material obtained on cooling was filtered, washed with diethy ether, dried and crystallized from a mixture of ethanole-hexane (2;1). Yield 70%; m. p. 210-211 °C; IR  $\upsilon$  (cm-1): 3281-3131 (OH), 1668(C = O), 1641(NH), 1250(C = S), 975-910(-CH = CH<sub>2</sub>). <sup>1</sup>H-NMR (400 MHz, DMSO-d6, ppm):  $\delta$  4.08 (t, J = 5.50, 2H, NH-CH<sub>2</sub>-CH), 5.04 (dd, 1H, Jcis =7.80, 1.47, NH-CH<sub>2</sub>-CH = <u>CH<sub>2</sub></u>), 5.12(dd, 1H, Jtrans = 15.40, 1.83, NH-CH<sub>2</sub>-CH = <u>CH<sub>2</sub></u>), 5.80 (dq, J = 11.13, 5.13, 1H, NH-CH<sub>2</sub>-<u>CH</u> = CH<sub>2</sub>), 6.90 (q, J = 7.82, 2H, H<sub>1</sub>, H<sub>3</sub>), 7.42 (t, J = 8.05, 1H, H<sub>2</sub>,), 7.83 (d, J = 7.80, 1H, H<sub>4</sub>), 8.32 (br, 1H, S = C-NH-C), 9.48 (br, 1H, NH-CO), 10.55 (br, 1H, NH-CS), 11.90 (br, 1H, OH). <sup>13</sup>C-NMR (100 MHz, DMSO-d6, ppm):  $\delta$  182.33, 168.10, 160.13, 135.51, 134.77, 129.29, 119.47, 117.88, 116.01, 115.47, 46.64.

Synthesis of 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione(III): A stirring mixture of compound (II) (10 mmole, 2.51 g.) and sodium hydroxide (40 mg, 1 mmole, as a 2N solution) was refluxed for 6 hours. After cooling, the solution was acidified with hydrochloric acid and the precipitate was filtered. The precipitate was then crystallized from A mixture of ethanole-dioxane (4:1). Yield: 80%; m.p.: 298-300 °C, IR  $\upsilon$  (cm<sup>-1</sup>): 3281-3100 (OH), 1628 (C=N), 1260 (C=S), 975-910 (HC=CH<sub>2</sub>), <sup>1</sup>H-NMR (400 MHz, DMSO-d6, ppm):  $\delta$  4.80 (d, J=7.32, 2H, CH<sub>2</sub>-CH=CH<sub>2</sub>), 5.20-5.22 (m, 2H Ar-CH<sub>2</sub>-CH=CH<sub>2</sub>), 5.82 (dq, J=7.33, 1.10, 1H, Ar-CH<sub>2</sub>-CH=CH<sub>2</sub>), 6.78-6.80 (m, 2H, H<sub>1</sub>, H<sub>3</sub>), 7.21-7.23, 2H, H<sub>2</sub>, H<sub>4</sub>), 10.45 (br, 1H, OH).

### 2.2. Crystallographic analysis

Data collection was performed on a STOE IPDS II image plate detector using MoK<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å) .Intensity data were collected in the  $\theta$  range 2.26°-28.00° at 293 °K. Data collections: Stoe X-AREA [27]. Cell refinement: Stoe X-AREA [27]. Data reduction: Stoe X-RED [27]. The structure was solved by direct methods

Comparison of the observed and calculated vibrational spectra of 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione (C<sub>11</sub>H<sub>11</sub>N<sub>3</sub>OS).

Assignments	FT-IR(cm <sup>-1</sup> ) with KBr	Scaled frequencies (6-31G(d)) (cm $^{-1}$ ) and relative Intensity (I $_{\rm IR},$ km/mol)) and relative intensity (I , km/mol)			and		
		HF	I <sub>IR</sub>	BLYP	I <sub>IR</sub>	B3LYP	I <sub>IR</sub>
O-H str.	3281	3676	0.34	3548	0.53	3581	0.50
ν N-H str.	3250	3508	0.50	3535	0.47	3541	0.26
$\nu_{as}$ CH <sub>2</sub> str. (Ar-CH <sub>2</sub> -CH= <u>CH<sub>2</sub></u> )	3118	3044	0.06	3142	0.09	3119	0.07
v ring C-H str.	3090	3034	0.05	3119	0.08	3112	0.05
ν ring C-H str.	3066	3019	0.06	3114	0.09	3100	0.05
v ring C-H str.	3052	3011	0	3103	0.07	3090	0.02
$\nu$ C-H str. (Ar-CH <sub>2</sub> - <u>CH</u> =CH <sub>2</sub> )	3039	3009	0	3089	0.03	3075	0
v ring C-H str.	3028	2994	0.03	3087	0.01	3071	0.03
$V CH_2 SII. (AI-CH_2-CH=CH_2)$	2984	2971	0.05	3000	0.04	3037	0.04
$v_{as}$ CH <sub>2</sub> str. (Ar-CH <sub>2</sub> -CH=CH <sub>2</sub> )	2909	2908	0.01	2964	0.02	2937	0.02
$v C=C str (Ar-CH_2-CH=CH_2)$	2320	1678	0.04	1655	0.01	1647	0.04
v = C + ring C - C str	1628	1654	0.37	1597	0.16	1621	0.01
v N=C + ring C-C str.	1020	1612	0.10	1561	0.16	1569	0.08
v ring C-C str.	1584	1601	0.07	1505	0.26	1508	0.10
$\nu$ ring C-C str.+ $\beta$ CH bend.	_	1503	0.39	1469	0.56	1462	0.28
$\nu$ N-C=S str.	1500	1499	1	1452	0.27	1436	0.11
$\rho_w$ CH <sub>2</sub> wag.(Ar- <u>CH</u> <sub>2</sub> -CH=CH <sub>2</sub> )	1309	1457	0.14	1447	0.09	1430	0.23
$\rho_{\rm w}$ CH <sub>2</sub> wag.(Ar- <u>CH<sub>2</sub></u> -CH=CH <sub>2</sub> )	-	1449	0.24	1433	0.09	1419	0.07
$\rho_s$ CH <sub>2</sub> scis. (Ar-CH <sub>2</sub> -CH= <u>CH<sub>2</sub></u> )	-	1430	0.04	1419	1	1396	1
ν N-C str.	1390	1394	0.19	1362	0.24	1360	0.15
ν N-C str.	1327	1354	0.41	1339	0.37	1330	0.17
$\rho_{\rm W}$ CH <sub>2</sub> wag.(Ar- <u>CH</u> <sub>2</sub> -CH=CH <sub>2</sub> )	-	1352	0.11	1335	0.02	1301	0.14
$\rho$ O-H+C-H rock.	-	1309	0.41	1301	0.07	1291	0.16
$\beta$ CH bend. (Ar-CH <sub>2</sub> - <u>CH</u> =CH <sub>2</sub> )	-	1283	0.01	1285	0.06	1272	0.09
v C-C STF.	-	1269	0.06	1277	0.27	1265	0.18
v C-On Su.	1265	1202	0.04	1242	0.28	1254	0.24
0 - H + C - H rock		1225	0.50	1228	0.52	1178	0.14
v = C  str.	1260	1186	0.20	1174	0.51	1156	0.19
$\rho$ O-H+C-H rock.	1253	1157	0.12	1158	0.03	1144	0.11
v S=C str.	_	1131	0.11 0.10	1154	0.11	1141	0.05
$\rho$ ring C-H rock.	-	1103	0.20	1119	0.29	1101	0.48
ν N-N str.	-	1091	0.07	1095	0.01	1079	0.19
ν ring C-C str.	-	1070	0.03	1054	0.11	1044	0.02
v ring C-C str.	-	1041	0.02	1035	0.10	1015	0.02
$\gamma$ CH out of plane bend.(Ar-CH <sub>2</sub> - <u>CH</u> =CH <sub>2</sub> )	-	1026	0.01	1018	0.07	992	0.03
$\nu$ ring C-C str.+ $\beta$ CH bend.	-	1014	0	1004	0.09	979	0.04
$\gamma$ ring CH out of plane bend.	-	996	0.13	951	0.04	950	0.11
γ hing ch out of plane bend.	-	972	0.09	950	0 15	955	0 01
v ring CH out of plane bend		963	0.02	912	0.15	906	0.01
$\rho$ CH <sub>2</sub> rock (Ar-CH <sub>2</sub> -CH=CH <sub>2</sub> )	-	921	0.02	906	0.04	898	0.02
$\rho$ CH <sub>2</sub> rock. (Ar-CH <sub>2</sub> -CH=CH <sub>2</sub> )	-	896	0.01	887	0.12	884	0.09
$\gamma$ ring CH out of plane bend.	_	860	0.05	837	0	820	0
$\beta$ ring HC-CH-CH bend.	-	813	0.11	818	0.07	801	0.09
$\tau$ hetero-ring-CH <sub>2</sub>	-	767	0.23	754	0.14	746	0.07
$ ho_w$ ring CH wag.	748	761		744	0.15	733	0.14
$ ho_{ m w}$ ring HC-C-OH wag.	719	748	0.02	711	0.03	727	0.07
$\rho_{\rm w}$ ring HC-C-OH wag.	-	732	0.02	683	0.03	700	0.02
$\rho_w$ hetero-ring HN-S=C wag.	651	684	0.02	660	0.05	660	0.02
$\beta$ ring CCC bend.	635	662	0.01	643	0.05	659	0.02
$\rho_t \operatorname{CH}_2 \operatorname{twis.} (\operatorname{Ar-CH}_2-\operatorname{CH}_2)$	-	597	0.01	597	0.08	587	0.06
$\rho_t \operatorname{CH}_2 \operatorname{twis.} (\operatorname{Ar-CH}_2-\operatorname{CH}_2)$	-	560	0.05	562	0.01	548	0.01
$\rho_w$ N-H wag.	-	558	0.02	544	0.04	541	0.03
$\rho_{\rm W}$ N-H wag.+ ring C-H wag	-	544	0.34	526	0.08	514	0.06
$\rho_{\rm W}$ N-H wag.+ ring C-H wag	-	521	0.03	512	0.07	503	0.12
$\rho_{\rm w}$ mig CH wag.	-	499	0.05	493	0.15	472	0.06
$\mu$ C-OH IUCK.		409	0.01	402	0.25	432	0.20
$\rho$ CH <sub>2</sub> rock (Ar-CH <sub>2</sub> -CH=CH <sub>2</sub> )	-	386	0.01	303	0.01	380	0.05
$\beta \text{ OH bend}$		370	0.01	375	0.25	368	0.10
$\rho_{\rm W}$ O-H + ring C-H wag	_	339	0.01	361	0.06	358	0.20
$\beta$ OH wag.	-	303	0.01	322	0.08	330	0.05
$\beta$ OH wag.	-	263	0.15	277	0.03	292	0.01

using SHELXS-97 [28] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least- squares refinement based on F<sup>2</sup> using SHELXL-97 [28]. Molecular drawings were obtained using ORTEP-III[29].

# 3. Computational methods

Molecular geometry is restricted and all the calculations are performed without specifying any symmetry for the title molecule

Theoretical and experimental  $^{13}C$  and  $^{1}H$  isotropic chemical shifts (with respect to TMS, all values in ppm) for 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione ( $C_{11}H_{11}N_3OS$ ).

		Calculated chemical shift (ppm)		
Atom	Experimental (ppm) (DMSO-d <sub>6</sub> )	HF	BLYP 6-31G(d)	B3LYP
C1	168.1	153.69	145.89	150.13
C2	117.88	111.03	108.27	110.32
C3	135.51	137.02	124.36	128.78
C4	116.01	115.67	111.90	115.19
C5	134.77	134.77	124.52	127.73
C6	115.45	107.96	104.10	106.91
C7	160.13	151.10	142.40	151.06
C8	182.33	178.76	159.27	170.32
C9	46.64	44.05	50.71	50.78
C10	129.29	129.45	122.21	128.50
C11	119.47	116.85	115.58	111.76
H2 (Ar-H)	6.78-7.23	7.24	6.82	6.93
H3 (Ar-H)	6.78-7.23	8.28	7.46	7.67
H4 (Ar-H)	6.78-7.23	7.44	6.91	7.14
H5 (Ar-H)	6.78-7.23	7.89	7.05	7.38
H9a (Ar- <u>CH</u> 2-CH=CH2)	4.80	3.68	3.78	3.89
H9b (Ar- $\underline{CH}_2$ -CH=CH <sub>2</sub> )	4.80	4.51	4.74	4.72
H10 (Ar-CH <sub>2</sub> - <u>CH</u> =CH <sub>2</sub> )	5.82	6.42	6.67	6.65
H11a (Ar-CH <sub>2</sub> -CH= <u>CH</u> <sub>2</sub> )	5.20-5.22	5.67	5.51	5.26
H11				
H11b (Ar-CH <sub>2</sub> -CH= <u>CH</u> <sub>2</sub> )	5.20-5.22	5.36	5.45	5.28
H(OH)	10.45	5.19	4.51	5.56
H(NH)	10.45	9.66	9.40	9.64

by using Gaussian 03w Program package [30] on a personal computer. The molecular structures of the title compound in the ground state (in vacuo) are optimized HF, BLYP and B3LYP with 6-31G(d) basis set. Vibrational frequencies for optimized molecular structures have been calculated. Three sets of vibrational frequencies for these species are calculated with these methods and then scaled by 0.8929, 0.994 and 0.9613, respectively. The geometry of the title compounds, together with that of tetramethylsilane (TMS) is fully optimized. <sup>1</sup>H and <sup>13</sup>C NMR c.s. values are calculated within GIAO approach [20,21] applying B3LYP and HF method [31] with 6-31G(d) [32] basis set. The theoretical c.s. values of <sup>1</sup>H and <sup>13</sup>C were obtained by subtracting the GIAO isotropic magnetic shielding (IMS) values [33,34]. For instance, the average <sup>13</sup>C IMS of TMS are taken into account for the calculation of <sup>13</sup>C c.s. of any X carbon atom, and so c.s. can be calculated using the following equation  $CS_x = IMS_{TMS} - IMS_x$ . In order to describe conformational flexibility of the title molecule, the selected torsion angle, T(C5-C6-C7-N2), was varied from -180° to 180° in every 10° and the molecular energy profile as a function of the selected torsional degree of freedom is obtained by performing single point calculations on the calculated potential energy surface, and the molecular energy profile was obtained at the HF/6-31G(d) level. For the calculations of the MEP [35–38], using B3LYP/6-31G (d) level, was used. The thermodynamic properties of the title compound at different temperatures were calculated on the basis of vibrational analyses, using HF/6-31G(d) level.

# 4. Results and discussion

#### 4.1. Crystal and molecular structure

The atomic numbering scheme for the title compound  $(C_{11}H_{11}N_3OS)$  and the theoretical geometric structure of the title compound are shown in Fig. 2a-b-c.

The crystal structure of the title compound is monoclinic and space group is P2<sub>1</sub>/c,  $M_w$ =233.29, a=9.0907 (5) Å, b=9.1288 (7) Å, c=13.6222 (7) Å,  $\alpha$ =90°,  $\beta$ =98.442 (4),  $\gamma$ =90° and V=2683.7(6)Å<sup>3</sup>, F(000)=488, D<sub>x</sub>=1.386 g/cm<sup>3</sup>. Additional information for the structure determinations are given in Table 1.

The optimized parameters of the title compound (bond lengths and angles, and dihedral angles) by HF, BLYP and B3LYP methods with 6-31G(d) as the basis set are listed in Table 3 and compared with the experimental crystal structure for the title compound. The molecular structure of the title compound is non-planar and is shown in Fig. 2a-b-c. The hydroxyphenyl ring (C1-C2-C3-C4-C5) form dihedral angle were observed to be 79.25° with the 1,2,4-triazole ring. These dihedral angle have been found to be  $84.54^{\circ}$  HF/6-31G(d) level, and  $63.04^{\circ}$  for BLYP/6-31G(d) level, and 61.781 for B3LYP/6-31G(d) level. These experimental and theoretical results have shown non-planar of the title compound. The crystal structure contains intermolecular N-H...S and O-H...N interactions. In the title compound, atom N3 in the molecule at (x, y, z) acts as hydrogen-bond donor, via atoms H3 to atoms S1 at (-x+1, -y, -z+2) and atom O1 in the molecule at (x, y, z) acts as hydrogen-bond donor, via atoms H1 to atoms N2 at (-x, -y+1/2, -y+1/2)-z+3/2) (Fig. 3). The experimental N3...S1 and O1...N2 intermolecular contact distance values are 3.28, 2.87 Å, respectively, N-H...S and O-H...N bond angle values are 170°, 173.5° respectively. The full geometry of intermolecular interactions is given in Table 2.

In order to compare the theoretical results with the experimental values, root mean square error (RMSE) is used. Calculated RMSE for bond lengths and bond angles are 0.011Å and 1.01° for HF 6-31G(d) method, 0.012Å and 3.19° for BLYP 6-31G(d) method and 0.015Å and 1.66° for B3LYP 6-31G(d), respectively.

A logical method for globally comparing the structures obtained with the theoretical calculations is by superimposing the molecular skeleton with that obtained from X-ray diffraction, giving a RMSE of 0.164 Å for HF, 0.274 Å for method BLYP and 0.235 for B3LYP (Fig. 4). According to these results, it may be concluded that the HF calculation well reproduce the geometry of the title compound.

The orientation of the substitutents with respect to the 1,2,4-triazole ring is determined by the experimental dihedral angles C5-C6-C7-N2 [ $-75.76(13)^{\circ}$ ], C8-N1-C9-C10 [ $-77.20(19)^{\circ}$ ], N2-N3-C8-S1 [ $-177.31(12)^{\circ}$ ], C7-C6-C1-O1 [ $-2.2(2)^{\circ}$ ] and C6-C7-N1-C9 [ $0.2(2)^{\circ}$ ]. These dihedral angles have been calculated at -81.852,



Fig. 1. Chemical structure of the title compound.

-88.289, -179.501, -0.520 and -1.268° (HF/6-31G(d)), and -53.609, -78.935, -178.087, 1.289 and -1.162° (BLYP/6-31G(d)), and -5.419, -79.672, -177.922, -1.286 and -2.647° (B3LYP/6-31G(d)), respectively.

The different substitutents dependent on the 1,2,4-triazole ring is defined by the experimental bond lengths N1-C9 [1.466(18) Å], C6-C7 [1.472(18) Å] and S1 = C8 [1.679(14)]erein these bond lengths were calculated at 1.462, 1.481 and 1.683 Å (for HF/6-31G(d)), and 1.485, 1.482 and 1.683 Å (for BLYP/6-31G(d)), and 1.473, 1.469 and 1.720 Å (for B3LYP/6-31G(d)). In previous works, the S = C bond length was found to be 1.6797(19) Å [39] and 1.669(2) Å for the different substituent dependent on the 1,2,4-triazole ring [40]. In the triazole ring, the bond lengths of C=N and N-N were obtained to be 1.295(2) Å and 1.376(2) Å [39], and 1.313(2) Å and 1.377(2) Å [40]. In present paper, we have calculated at 1.273 Å and 1.356 Å using HF/6-31G(d) method, and 1.327 Å and 1.382 Å using BLYP/6-31G(d) method, and 1.324 Å and 1.395 Å using B3LYP/6-31G(d) method and the data are shown in Table 3. For the optimized geometric parameters. In present work, according BLYP and B3LYP methods, the HF method for optimized geometric parameters (bond lengths, bond and dihedral angles) is much closer to experimental data.

Molecular energy profiles with respect to rotations about the selected torsion angle is presented in Fig. 5. According to the results,



Fig. 2. (a) The experimental geometric structure of the title compound (b) The theoretical geometric structure of the title compound (with HF/6–31G(d) level). (c) The theoretical geometric structure of the title compound (with B3LYP/6–31G(d) level).



**Fig. 3.** Part of the crystal structure of the title compound, showing the intermolecular interactions (dashed lines). For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

the low energy domains for T(C5-C6-C7-N2) are located at-80 and 70° having energy of-1058.645 and-1058.646 a.u., respectively. Energy difference between the most favorable and unfavorable conformers, which arises from rotational potential barrier calculated with respect to the selected torsion angle, was calculated as 0.341 a.u.



**Fig. 5.** Molecular energy profile against the selected torsional degree of freedom at HF/6-31G(d) level.

#### 4.2. Assignments of the vibration modes

Harmonic vibrational frequencies of the title compound were calculated by using both HF and DFT (BLYP and B3LYP) method with 6-31G(d,p) basis set. Three sets of vibrational frequencies for these species are calculated with these methods and then scaled by 0.8929, 0.994 and 0.9613, respectivelyBy using Gauss-View [41] molecular visualization program, the vibrational bands assignments have been made. To facilitate assignment of the observed peaks, we have analyzed vibrational frequencies and compared our calculation of the title compound with their experimental results and shown in Table 4. The agreement between the experimental and calculated frequencies is quite good in general.

The bands calculated in the measured region 4000-400 cm<sup>-1</sup> arise from the vibrations of O-H, N-H stretching, and the internal vibrations, etc. of the title compound. Most bands observed in infrared spectra of the title compound belong to hydroxy phenyl groups' modes, only some of them may be assigned to group ring C-H (symmetric/asymmetric) and C-C stretching bands were observed to be 3090-3028 and 1628-1584 as experimentally and compares well with the value reported previously [3110-



Fig. 4. Atom-by-atom superimposition of the structures calculated (red) [a=HF; b=BLYP; c=B3LYP with 6-31G(d)] over the X-ray structure (black) for the title compound. Hydrogen atoms omitted for clarity.



Fig. 6. (a) Simulated (HF, BLYP and B3LYP levels) IR spectra of the title compound (b) FT-IR spectrum of the title compound.

3003, 1666-1535 cm<sup>-1</sup>, 42]. These modes have been calculated at 3034-2994 and 1654-1503 cm<sup>-1</sup> for HF/6-31G(d) level, and 3119-3087 and 1597-1469 cm<sup>-1</sup> for BLYP/6-31G(d) level, 3112-3071 and 1621-1462 cm<sup>-1</sup> for B3LYP/6-31G(d) level and compares well with the value reported previously [3052-3007 and 1639-1492 cm<sup>-1</sup> for HF/6-31G(d) level, 3130-3088 and 1597-1469 cm<sup>-1</sup> for BLYP/6-31G(d) level, and 3107-3071 and 1609-1474 cm<sup>-1</sup> for B3LYP/6-31G(d) level, 42]. The twisting, wagging, rocking, and scissoring bands of CH<sub>2</sub> are tabulated in Table 4.

In the triazole, the N-H and C=N stretching modes were observed to be 3250,  $1628 \text{ cm}^{-1}$  as experimentally and compares well with the value reported previously [3260,1666-1535 cm<sup>1</sup>, 42]. These modes were calculated at 3508 and  $1654 \text{ cm}^{-1}$  for HF/6-31G(d), 3535 and 1597 cm<sup>-1</sup> for BLYP/6-31G(d) level, and 3541 and 1647 cm<sup>-1</sup> for B3LYP 6-31G(d) level and compares well with the value reported previously [3507 and 1639-1610 cm<sup>-1</sup> for HF/6-

31G(d) level, 3534 and 1597-1574 cm<sup>-1</sup> for BLYP/6-31G(d) level, and 3527 and 1609-1584 cm<sup>-1</sup> for B3LYP/6-31G(d) level, 42].

Other essential characteristic vibrations of the title compound are O-H, N-C=S stretching modes were observed to be 3281 and 1500 as experimentally compares well with the value reported previously [3330,1210 cm<sup>1</sup>, 42]. These modes were calculated at 3676 and 14994 cm<sup>-1</sup> for HF/6-31G(d), 3548 and 1452 cm<sup>-1</sup> for BLYP/6-31G(d) level, and 3581and 1436 cm<sup>-1</sup> for B3LYP 6-31G(d) level and compares well with the value reported previously [3598 and 1204 cm<sup>-1</sup> for HF/6-31G(d) level, 3579 and 1210 cm<sup>-1</sup> for BLYP/6-31G(d) level, and 3617 and 1222 cm<sup>-1</sup> for B3LYP/6-31G(d) level, 42]. Also, the other levels of calculations can be seen in Table 4. These results indicated some band shifts with regard to the different substituent-triazole ring.

Calculated infrared intensity (Rel. intensity) allows determination of the strength of the transition. Note that experimental IR



Fig. 7. Correlation graphics of calculated and experimental frequencies of the title compound.



Fig. 8. Molecular electrostatic potential map calculated at B3LYP/6-31G(d) level.

spectra are generally reported in either percent transmission or absorbance unit. Apparently, these mentioned can be seen in Fig. 6. The simulated infrared spectra, where the intensity (km/mol) is plotted against the harmonic vibrational frequencies, and experimental infrared spectra are shown in Fig. 6.

In Hartree-Fock, all the vibrational frequencies are overestimated and in agreement with the 10–20% error in the average of overall the frequencies [43,44]. To make comparison with experiment, we present correlation graphic in Fig. 7 based on the calculations. As we can seen from correlation graphic in Fig. 7, experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a better correlation for DFT than HF. Only with DFT methods are the wavenumbers relatively close to the experimental, BLYP being the best for this purpose.

#### 4.3. Assignments of the chemical shift values

DFT and HF methods differ in that no electron correlation effects are taken into account in HF. DFT methods treat the electronic energy as a function of the electron density of all electrons simultaneously and thus include electron correlation effect. Explicitly, we have considered also of interest to investigate the influence of the level used for the geometry optimization on the final value of the title compound when GIAO <sup>13</sup>C and <sup>1</sup>H c.s. calculations have been performed. Thus, GIAO <sup>13</sup>C and <sup>1</sup>H c.s. calculations obtained at HF/6-31G(d), BLYP/6-31G(d) and B3LYP/6-31G(d) levels of theory for the three optimized geometries. The <sup>13</sup>C and <sup>1</sup>H c.s. values (with respect to TMS) have been calculated for the optimized structures of the title compound and generally compared to the experimental <sup>1</sup>H c.s. values.

These results are shown in Table 5. <sup>13</sup>C and <sup>1</sup>H c.s. values were experimentally observed, Therefore, <sup>13</sup>C and <sup>1</sup>H c.s values were only compared to theoretical results. We have calculated <sup>1</sup>H c.s. values (with respect to TMS) of 9.66-3.68 ppm with HF level, 9.40-3.78 ppm with BLYP level and 9.64-3.89 ppm with B3LYP level, however, the experimental results were observed to be 10.45-4.80 ppm, these values are shown in Table 5, and so the accuracy ensures reliable interpretation of spectroscopic parameters. As can be seen from Fig. 1, molecular structure of the title compound includes hydroxyl bounded to aromatic rings. The hydroxyl



Fig. 9. Molecular orbital surfaces and energy levels given in parentheses for the HOMO – 1, HOMO, LUMO and LUMO + 1 of the title compound computed at B3LYP/6-31G(d) level.

Calculated energies (a.u), zero-point vibrational energies (kcal mol<sup>-1</sup>), rotational constants (GHz), entropies (cal mol<sup>-1</sup> K<sup>-1</sup>) and dipole moment (D) of the title compound.

Parameters	HF	BLYP 6-31G(d)	B3LYP
Dipole moment (D)	7.6840	3.5284	6.6962
Zero-point vibrational energy(kcal mol <sup>-1</sup> )	129.17902	128.62513	127.99808
Total energy (a.u.)	-1058.64522	-1063.16906	-1063.42554
Rotational constants	0.85705	0.82282	0.81990
	0.33853	0.33567	0.34101
	0.28711	0.26088	0.26512
Entropy (cal mol <sup>-1</sup> K <sup>-1</sup> )			
Rotational	29.289	35.005	32.834
Translational	37.923	45.125	42.362
Vibrational	40.397	50.661	44.286
Total	107.609	130.791	119.482

group include oxygen atom which shows electronegative property, and so H atom contribute to the downfield resonance. Besides, the H c.s. of O-H and N-H was experimentally observed to be 10.45 ppm. The O-H and N-H were observed in the same band. In different substituent-1.2.4-triazole, the H c.s. of O-H was observed to be 10.10 ppm [42]. The other aromatic-H was observed to be 6.78-7.23, 4.80, 5.82, and 5.20-5.22 ppm. This statement was calculated 7.24-8.28, 3.68-4.51, 6.42 and 5.19-5.36 using HF levels, 6.82-7.46, 3.78-4.74, 6.67 and 5.45-5.51 using BLYP levels and 6.93-7.14, 3.89-4.72, 6.65 and 5.26-5.28 using B3LYP levels. Furthermore, we have calculated <sup>13</sup>C c.s. values (with respect to TMS) of 153.69-44.05 ppm with HF level, 159.27-50.71 ppm with BLYP level and 150.13-50.78 ppm with B3LYP level. The c.s. values of C1 and C8 atoms bounded hydroxyl group and sulphur atom were calculated at 153.69 and 178.76 ppm with HF level, 145.89 and 159.27 ppm with BLYP level and 150.13 and 170.32 ppm with B3LYP level, respectively (Table 5). This statement is attributed to the presence of delocalization between the lone pair on atom N(3) and C(1) = S(1) double bond, and also to electronic factors associated with the large electron density substituents. As can be seen from Table 5, theoretical <sup>1</sup>H c.s. results of the title compound are generally closer to the experimental c.s. data.

# 5. Other molecular properties

# 5.1. Molecular electrostatic potential

Molecular electrostatic potential (MEP) is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions [45–47]. To predict reactive sites for electrophilic attack for the title compound, MEP was calculated at the B3LYP/6-31G(d) optimized geometry. The negative (red) regions of MEP were related to electrophilic reactivity and the positive (blue) ones to nucleophilic reactivity shown in Fig. 8. As easily can be seen in Fig. 8, this molecule has two possible sites for electrophilic attack. The negative regions are mainly over the S1atom and N3 atom. For the title compound, negative regions were calculated: the MEP value around S1 is more negative than that of N3 atom. Thus, the calculations suggested that the preferred site for electrophilic attack is the S1 atom, followed from the N3 atom.

Namely, the title compound can act as multidentate ligand to bind one or two metal centers, so resulting in interesting metal complexes with different coordination geometries.

#### 5.2. Frontier molecular orbitals

The frontier molecular orbitals play an important role in the electric and optical properties, as well as in UV–Vis spectra and chemical reactions [48]. Fig. 9 shows the distributions and energy levels of the HOMO – 1, HOMO, LUMO and LUMO + 1 orbitals com-

# Table 7

Thermodynamic properties of the title compound at different temperatures at HF/6-31G(d) level.

T(K)	$C_{p,m}^{o} \longleftrightarrow (cal.mol^{-1}.K^{-1})$	$S_m^{o}  (cal.mol^{-1}.K^{-1})$	$H_m^{o} \rightleftharpoons (kcal.mol^{-1})$
200.0	37.04	94.69	4.37
298.1	50.51	119.86	9.13
300.0	56.13	2125.56	10.02
400.0	71.66	144.46	16.63
500.0	84.66	162.34	24.67
600.0	95.11	179.09	33.87
700.0	103.49	194.71	44.02
800.0	110.32	209.26	54.92
900.0	115.96	222.82	66.44
1000.0	120.68	235.50	78.48

puted at the B3LYP/6-31G(d) level for the title compound. The calculations indicate that the title compound has 61 occupied molecular orbitals. Both the highest occupied molecular orbitals (HOMOs) and the lowest-lying unoccupied molecular orbitals (LUMOs) are mainly localized on the rings indicating that the HOMO-LUMO are mostly the  $\pi$ -antibonding type orbitals. As seen from Fig. 9, in the HOMO-1 and HOMO, electrons are mainly delocalized on the S atom and the triazole ring. However, when electron transitions take place, some electrons will enter into the LUMO and LUMO + 1, then, in the LUMO and LUMO + 1, the electrons will mainly be delocalized on triazole ring and phenyl ring. Namely, electron transitions are corresponding to the  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electron transitions. The value of the energy separation between the HOMO and LUMO is 4.325 eV and this large energy gap indicates that the title structure is quite stable.

#### 5.3. Thermodynamic parameters of the title compound

Several thermodynamic parameters were calculated using HF, BLYP and B3LYP with 6-31G(d) basis set and calculated these parameters of the title compound are given in Table 6. Accurate prediction of zero-point vibrational energy (ZPVE) and the entropy (Svib(T)) scaling the data [43]. The total energies and the change in the total entropy of the title compound at room temperature at different theoretical methods were also presented. In Table 6 demonstrates several thermodynamic parameters of the title compound without of results of experimental.

Besides, based on the vibrational analysis at HF/6-31G(d) level and statistical thermodynamics, the standard thermodynamic functions: heat capacity ( $C_{p,m}^{o}$ ), entropy ( $S_{m}^{o}$ ), and enthalpy ( $H_{m}^{o}$ ) were obtained and listed in Table 7. The scale factor for frequencies is 0.8929, which is a typical value for the HF/6-31G(d) level of calculations.

As will be seen from Table 7, the standard heat capacities, entropies and enthalpies increase at any temperature from 200.0 K to 1000.0 K since increasing temperature causes an increase in the intensities of molecular vibration. For the title compound, the correlation equations between these thermodynamic properties and temperature T are as follows:

$$C_{p,m}^0 = -4.73318 + 0.22852T - 1.04158 \times 10^{-4}T^2,$$

$$S_m^0 = -46.68312 + 0.27435T - 8.70058 \times 10^{-5}T^2$$
,

$$H_m^0 = -5.64045 + 0.80609T - 4.68402 \times 10^{-5}T^2.$$

These equations will be helpful for the further studies of the title compound.

## 6. Conclusions

In this study, 4-allyl-5-(2-hydroxyphenyl)-2,4-dihydro-3H-1,2,4-triazole-3-thione was synthesized and characterized by IR, and X-ray single-crystal diffraction. The comparisons between to test the different HF, BLYP and B3LYP levels of theory with 6-31 G(d) basis set reported, computed and experimental the geometric parameters, vibrational frequencies and chemical shifts of the title compound were compared. However, these results did not adequately reproduce the experimental pattern of vibrational frequencies with the accuracy desired, and thus to reduce the error it is necessary to scale the vibrational frequencies. Thus, to fit the theoretical frequencies results with experimental ones for HF, BLYP and B3LYP methods, we scaled the data. Scaled results seemed to be in a good agreement with experimental ones. It is seen from the theoretical results, the results of HF method showed a better fit to experimental ones than DFT in evaluating geometrical parameters and vibrational frequencies, and chemical shifts.

#### Supplementary data

CCDC-737467 contains the supplementary crystallographic data for the compound reported in this paper.

These data can be obtained free of charge at www.ccdc.cam. ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

#### Acknowledgement

This study was supported financially by the Research Centre of Ondokuz Mayıs University (Project No: F-461).

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