

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

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**Abstract** The molecular geometry, vibrational frequencies, gauge including atomic orbital (GIAO)  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift values and several thermodynamic parameters of 5-(2-Hydroxyphenyl)-4-(p-tolyl)-2,4-dihydro-1,2,4-triazole-3-thione in the ground state have been calculated by using the Hartree-Fock (HF) and density functional method (DFT/B3LYP) with 6–31G(d), 6–31 + G(d,p) and LANL2DZ basis sets. The results of the optimized molecular structure are presented and compared with the experimental X-ray diffraction. The computed vibrational frequencies are used to determine the types of molecular motions associated with each of the experimental bands observed. Also, calculated  $^1\text{H}$  chemical shift values compared with the experimental ones. The data of the title compound display significant molecular structure and IR, NMR analysis provide the basis for future design of efficient materials having the of 1,2,4-triazole core.

**Keywords** 5-(2-Hydroxyphenyl)-4-(p-tolyl)-2,4-dihydro-1,2,4-triazole-3-thione · DFT · HF · GIAO ·  $^1\text{H}$  ·  $^{13}\text{C}$  NMR · IR spectra · Structure elucidation · Vibrational assignment

## 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 4,5-disubstituted 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 is to describe and characterize the molecular structure, vibrational properties and chemical shifts on 5-(2-Hydroxyphenyl)-4-(p-tolyl)-2,4-dihydro-1,2,4-triazole-3-thione 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 shift. 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 also increases. To optimize computing-time the DFT level was used. It was proposed that the single-point calculation of magnetic shielding by DFT methods was combined with a fast and reliable geometry-optimization procedure at the molecular mechanics level [18].

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

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[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  $^{13}\text{C}$  c.s. calculations [22] in all those cases in which the electron correlation contributions were not negligible.

In previous publication, IR and  $^1\text{H}$  NMR spectra (in the DMSO- $d_6$  solution) and the crystal structure of the title compound had been studied [7]. To the best of our knowledge, no estimates of theoretical results for the title compound have been reported so far. In this study, the geometrical parameters, fundamental frequencies and GIAO  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of the title compound in the ground state have been calculated by using the HF and DFT (B3LYP) method with 6–31G(d), 6–31 + G(d,p) and LANL2DZ basis sets. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift-molecular structure relationship. And so, these calculations are valuable for providing insight into molecular analysis.

### Computational details

The molecular structures of the title compound in the ground state (in vacuo) are optimized HF and B3LYP with 6–31G(d), 6–31 + G(d,p) and LANL2DZ basis sets. Then vibrational frequencies for optimized molecular structures have been calculated. The vibrational frequencies for these species are scaled by 0.8929 and 0.9613, 0.89 and 0.96, 0.9393 and 0.9978, respectively. The geometry of the title compounds, together with that of tetramethylsilane (TMS) is fully opti-

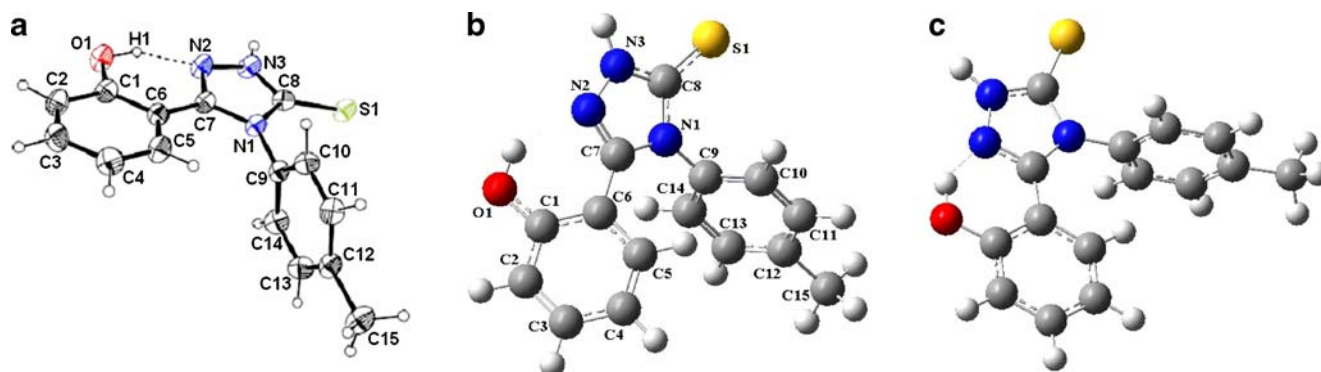
mized.  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are calculated within GIAO approach [20, 21] applying B3LYP and HF method [27] with 6–31G(d) [28], 6–31 + G(d,p) [29] and LANL2DZ [30–32] basis sets. Generally, reliable predictions of optimized geometrical parameters, frequencies and chemical shifts require several elements: adequate basis sets, sufficient electron correlation effects. Besides, the choice of the basis set is also a critical point in any computational study on molecular properties. In order to investigate the basis set effect on result, we take in to account 3 types of basis functions: (i) 6–31G(d) for checking polarization function effect, (ii) 6–31 + G(d,p) for checking both polarization function and diffuse effects, and (iii) LANL2DZ for checking examine some effective core potentials. The theoretical chemical shift values of  $^1\text{H}$  and  $^{13}\text{C}$  were obtained by subtracting the GIAO isotropic magnetic shielding (IMS) values [33, 34]. For instance, the average  $^{13}\text{C}$  IMS of TMS are taken into account for the calculation of  $^{13}\text{C}$  c.s. of any X carbon atom, and so c.s. can be calculated using the following equation  $\text{CS}_x = \text{IMS}_{\text{TMS}} - \text{IMS}_x$ . All the calculations are performed by using Gauss-View molecular visualisation program [35] and Gaussian 98 program package on personal computer [36].

### Results and discussion

#### Geometrical structure

The atomic numbering scheme for the title compound crystal [7] and the theoretical geometric structure of the title compound are shown in Fig. 1a–b. The crystal structure of the title compound is monoclinic and space group is C2/c. The crystal structure parameters of the title compound are  $a=26.524$  (3) Å,  $b=11.3288$  (18) Å,  $c=9.2310$  (11) Å,  $\beta=104.643(9)^\circ$  and  $V=2683.7(6)$  Å<sup>3</sup> [7].

The optimized parameters (bond lengths and angles, and dihedral angles) of the title compound have been obtained at the HF and B3LYP methods with the basis sets. These results



**Fig. 1** (a) The experimental geometric structure of the title compound ( $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$ ) [7] (b) The theoretical geometric structure of the title compound ( $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$ ) (with HF/6–31G(d) level). (c) The theoret-

ical geometric structure of the title compound ( $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$ ) (with B3LYP/LANL2DZ level)

are listed in Table 1 and compared with the experimental data of the title compound. The molecular structure of the title compound is non-planar and is shown in Fig. 1a–b. An intramolecular O–H···N hydrogen bond [O–H 0.82 Å, H···N

1.88 (3) Å and O–H···N 141.6 (2)°] exists between the hydroxyphenyl group and the triazole N atom [7]. The bond distance and angle are only found to be 1.682 Å and 142.4° for B3LYP/LANL2DZ level. However, the other calcula-

**Table 1** Optimized and experimental geometries parameters of the title compound (C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>OS) in the ground state

Parameters	Exp. [7]	Calculated					
		HF			B3LYP		
		6–31G(d)	6–31 + G(d,p)	LANL2DZ	6–31G(d)	6–31 + G(d,p)	LANL2DZ
<b>Bond lengths (Å)</b>							
S(1)–C(8)	1.671(3)	1.672	1.673	1.719	1.665	1.665	1.709
O(1)–C(1)	1.353(3)	1.339	1.338	1.365	1.349	1.352	1.376
N(1)–C(9)	1.445(3)	1.433	1.434	1.439	1.454	1.437	1.445
C(6)–C(7)	1.464(4)	1.475	1.476	1.473	1.465	1.466	1.467
C(12)–C(15)	1.507(4)	1.511	1.510	1.514	1.510	1.511	1.517
C(8)–N(1)	1.382(3)	1.371	1.370	1.384	1.401	1.417	1.401
C(8)–N(3)	1.336(4)	1.327	1.327	1.342	1.358	1.375	1.359
C(7)–N(2)	1.308(3)	1.279	1.277	1.301	1.310	1.343	1.317
O(1)–H	0.820	0.951	0.948	0.959	1.005	0.982	1.005
N(3)–H	0.860	0.994	0.993	0.991	1.009	1.009	1.009
C(2)–H	0.930	1.074	1.074	1.070	1.085	1.085	1.085
C(3)–H	0.930	1.075	1.076	1.072	1.087	1.086	1.087
C(4)–H	0.930	1.074	1.074	1.071	1.086	1.085	1.086
C(5)–H	0.930	1.072	1.072	1.068	1.082	1.082	1.082
C(10)–H	0.930	1.074	1.074	1.071	1.086	1.085	1.086
C(11)–H	0.930	1.076	1.076	1.073	1.088	1.087	1.088
C(13)–H	0.930	1.075	1.076	1.072	1.088	1.087	1.088
C(14)–H	0.930	1.074	1.075	1.072	1.086	1.085	1.086
C(15)–H	0.960	1.085	1.085	1.084	1.097	1.095	1.097
<b>Bond angles (°)</b>							
C(8)–N(1)–C(9)	121.2 (8)	123.9	123.9	122.9	122.5	122.3	121.8
O(1)–C(1)–C(6)	123.4 (2)	124.0	124.0	124.0	123.9	123.7	123.3
N(2)–C(7)–C(6)	121.4 (2)	122.8	122.9	122.3	121.8	121.8	120.9
N(3)–C(8)–S(1)	128.4 (2)	127.1	127.1	127.1	127.9	127.9	127.9
C(11)–C(12)–C(15)	122.0 (3)	120.5	120.6	120.7	120.9	120.7	120.7
N(2)–N(3)–H	123.3	121.1	121.3	121.0	120.9	121.0	120.8
C(1)–O(1)–H	109.5	111.3	111.7	115.0	109.2	109.6	110.9
H–C(15)–H	109.5	107.6	108.1	108.1	108.1	108.1	110.1
C(12)–C(13)–H	119.5	119.8	119.8	119.8	119.6	119.6	119.5
C(9)–C(10)–H	119.5	119.9	119.9	119.9	119.8	119.8	119.8
C(6)–C(5)–H	119.2	119.4	119.4	119.9	119.4	119.5	119.9
<b>Dihedral angles (°)</b>							
O(1)–C(1)–C(2)–C(3)	-177.9 (3)	-179.0	-179.0	-178.9	-178.3	-178.4	-179.9
O(1)–C(1)–C(6)–C(5)	177.6 (3)	178.2	178.2	177.9	177.4	177.6	179.9
O(1)–C(1)–C(6)–C(7)	-1.2 (4)	-0.3	-0.1	-0.4	-1.8	-1.4	-0.002
C(1)–C(6)–C(7)–N(2)	9.2 (4)	32.3	32.4	19.9	18.2	16.5	0.008
C(1)–C(6)–C(7)–N(1)	-170.7 (3)	-146.3	-146.3	-159.1	-161.2	-162.9	-179.9
N(2)–N(3)–C(8)–S(1)	-177.9 (2)	-179.8	-179.9	-179.7	-179.7	-179.9	-180.0
C(8)–N(1)–C(9)–C(10)	95.0 (3)	74.4	75.4	77.2	75.3	78.1	88.8
C(10)–C(11)–C(12)–C(15)	177.8 (3)	178.8	178.6	178.4	178.6	178.6	178.3
C(15)–C(12)–C(13)–C(14)	-178.7 (3)	-178.5	-178.3	-178.2	-178.9	-178.3	-178.3
C(2)–C(1)–O(1)–H	-	166.4	166.0	168.9	173.4	173.3	179.9
C(6)–C(1)–O(1)–H	-	-14.4	-14.9	-11.6	-6.8	-6.9	-0.005
S(1)–C(8)–N(3)–H	-	-1.9	-1.6	-0.8	-1.8	-1.4	-0.002
C(7)–N(2)–N(3)–H	-	-178.4	-178.7	-179.2	-178.6	-179.1	-180.0

tions are not observed. Also, this difference is illustrated in Fig. 1c. The dihedral angle between the five-membered 2,4-dihydro-1,2,4-triazole ring and the hydroxyphenyl group is  $10.18 (1)^\circ$ . The p-tolyl moiety were almost perpendicular to both the 2,4-dihydro-1,2,4-triazole group and the hydroxyphenyl group, with dihedral angles of  $84.42 (1)$  and  $85.54 (1)^\circ$ , respectively [7]. The orientation of the substituents with respect to the 1,2,4-triazole ring is determined by the torsion angles C1-C6-C7-N2 [ $9.2 (4)^\circ$ ], N2-N3-C8-S1 [ $-177.1 (2)^\circ$ ], C8-N1-C9-C10 [ $95.0 (3)^\circ$ ] and C10-C11-C12-C15 [ $177.8 (3)^\circ$ ] [7]. These torsion angles have been calculated at  $32.3^\circ$ ,  $-179.8^\circ$ ,  $74.4^\circ$  and  $178.8^\circ$  for HF/6-31G(d) level,  $18.2^\circ$ ,  $179.7^\circ$ ,  $75.3^\circ$  and  $178.6^\circ$  for B3LYP/6-31G(d) level, respectively.

The different substituents dependent on the 1,2,4-triazole ring is defined by the bond lengths N1-C9 [ $1.445 (3) \text{ \AA}$ ] and C6-C7 [ $1.464 (4) \text{ \AA}$ ] [7]. Herein these bond lengths have been calculated at  $1.433 \text{ \AA}$  and  $1.475 \text{ \AA}$  for HF/6-31G(d) level, and  $1.454 \text{ \AA}$  and  $1.465 \text{ \AA}$  for B3LYP/6-31G(d) level. In previous works, the S = C bond length was found to be  $1.6797(19) \text{ \AA}$  [37] and  $1.669(2) \text{ \AA}$  for the different substituent dependent on the 1,2,4-triazole ring [38]. In the triazole ring, the bond lengths of C = N and N-N were obtained to be  $1.295(2) \text{ \AA}$  and  $1.376(2) \text{ \AA}$  [37], and  $1.313(2) \text{ \AA}$  and  $1.377(2) \text{ \AA}$  [38]. In the present paper, these distances are  $1.270$  and  $1.355 \text{ \AA}$  for HF/6-31 + G(d,p) level,  $1.317$  and  $1.364 \text{ \AA}$  for B3LYP/6-31 + G(d,p) level. In the triazole ring, the C(7)-N(2) double bond distance is significantly shorter than the C(8)-N(1) and C(8)-N(1) bonds. This statement is attributed to the presence of delocalization between the lone pair on atom N(3) and C(8) = S(1) double bond, and also to electronic factors associated with the large electron density substituents. In this relation, these results are consistent with the respect to the different 1,2,4-triazole derivatives [37, 38]. Furthermore, C(8)-N(1)-C(9) and O(1)-C(1)-C(6) bond angles for the title compound were observed to be  $121.8 (2)^\circ$  and  $123.4 (2)^\circ$  [7], these angle values have been calculated at  $123.9^\circ$ ,  $122.5$ ,  $124.0^\circ$ ,  $123.9$  by using HF and B3LYP with 6-31G(d) basis set, respectively, as can be seen in Table 1. The optimized geometric parameter other values of the title compound are shown in Table 1. For the optimized geometric parameters, various methods including HF method estimated some bond lengths well to some extent [39–43]. We noted that the experimental results belong to the solid phase and theoretical calculations belong to the gaseous phase. As a result, the B3LYP method for geometric parameters is much closer to experimental data.

#### Assignments of the vibration modes

Based on optimized geometries, the vibrational frequencies have been performed by the same methods and basis sets as. Our calculations of the title compound are compared to the

experimental results. The bands calculated in the measured region  $4000\text{--}400 \text{ cm}^{-1}$  arise from the vibrations of O-H, N-H stretching, methyl asymmetric and symmetric stretching, and the internal vibrations, etc. of the title compound. The vibrational bands assignments have been made by using Gauss-View molecular visualisation program [35]. Theoretical and experimental results of the title compound are shown in Table 2. Most bands observed in infrared spectra of the title compound belong to p-tolyl and 2-hydroxy phenyl groups' modes, only some of them may be assigned to group ring C-H (symmetric/asymmetric) and C-C stretching. These bands have been calculated at  $3053\text{--}2864$ ,  $3029\text{--}2836$ ,  $3250\text{--}3009$  and  $1626\text{--}1581$ ,  $1612\text{--}1566$ ,  $1703\text{--}1636 \text{ cm}^{-1}$  for HF levels, and  $3122\text{--}2928$ ,  $3115\text{--}2917$ ,  $3236\text{--}3033$  and  $1605\text{--}1524$ ,  $1593\text{--}1512$ ,  $1659\text{--}1550 \text{ cm}^{-1}$  for B3LYP levels. In the triazole, the N-H and C = N stretching modes were observed to be  $3448$ ,  $1504 \text{ cm}^{-1}$  [38],  $3240$  and  $1622 \text{ cm}^{-1}$  [7] as experimentally, and  $3483$  and  $1508 \text{ cm}^{-1}$  for B3LYP/6-311G(d,p) level, and  $3483 \text{ cm}^{-1}$  for HF/6-311G(d,p) level [38]. Here these modes are found to be  $3507$  and  $1638 \text{ cm}^{-1}$  for HF/6-31G(d) level, and  $3332$  and  $1613 \text{ cm}^{-1}$  for B3LYP/6-31G(d) level. Also, the other levels of calculations can be seen in Table 2. These results indicated some band shifts with regard to the different substituent-triazole ring.

Other essential characteristic vibrations of the title compound are O-H, N-H, N-S = C, C = N, N-C, N-N, S = C stretching. Some of these modes, corresponding to the experimental modes, such as O-H, N-H, C = N and N-S = C stretching were observed to be  $3390$ ,  $3240$ ,  $1622$  and  $1502 \text{ cm}^{-1}$  [7]. These modes have been calculated at  $3597$ ,  $3507$ ,  $1638$ ,  $1495$  using HF/6-31G(d) level and  $3533$ ,  $3332$ ,  $1613$   $1483 \text{ cm}^{-1}$  using B3LYP/6-31G(d) level, these result from different substituent atoms or atom groups in the molecular structure. For other assignment of internal vibrations of the title compound can be seen Table 2 and Fig. 2.

Calculated infrared intensity (Rel. intensity) allows determination of the strength of the transition. Note that experimental IR spectra are generally reported in either percent transmission or absorbance unit. Apparently, these mentioned can be seen in Fig. 2. In Hartree-Fock, all the vibrational frequencies are overestimated and in agreement with the 10–20% error in the average of overall the frequencies [44, 45]. This overestimation depends on the type of the vibrational mode and the wavenumber range. In general, the DFT methods have the wavenumbers relatively close to the experimental result. According to the different molecular structures which have many electrons, this statement can be changed. In our results, the O-H and N-H stretching modes are estimated with the  $\sim 8.0$  and  $\sim 10.0\%$  error in the average for HF levels and  $\sim 6.0$  and  $\sim 4.0\%$  error in the average for B3LYP levels. The other modes are estimated in the smaller error range. Besides, as can be seen Fig. 2, simulated infrared spectra are generally closer to percent transmission in the experimental IR spectrum.

**Table 2** Comparison of the observed and calculated vibrational spectra of the title compound (C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>OS)

Assignments	FT-IR [7] (cm <sup>-1</sup> )	HF						B3LYP					
		6-31G(d)		6-31 + G(d,p)		LANL2DZ		6-31G(d)		6-31 + G(d,p)		LANL2DZ	
		Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>
$\nu$ O-H str.	3390	3597	0.72	3639	0.7	3723	0.63	3533	0.37	3536	0.35	3706	0.32
$\nu$ N-H str.	3240	3507	0.57	3499	0.55	3694	0.74	3332	1	3350	1	3266	0.01
$\nu$ ring C-H str.	-	3053	0.02	3029	0.01	3250	0.01	3122	0.01	3115	0.01	3236	0.03
$\nu$ ring C-H str.	-	3038	0.04	3012	0.03	3228	0.05	3100	0.01	3087	0.02	3223	0
$\nu$ ring C-H str.	-	3035	0.01	3008	0.01	3212	0.01	3097	0.04	3087	0	3218	0.03
$\nu$ ring C-H str.	-	3028	0.03	3003	0.03	3210	0.07	3091	0.02	3081	0.01	3218	0.03
$\nu$ ring C-H str.	3086	3026	0.05	3002	0.02	3207	0.04	3087	0.04	3079	0.03	3197	0.01
$\nu$ ring C-H str.	3074	3009	0.02	2985	0.01	3191	0.02	3070	0.02	3062	0.01	3194	0.04
$\nu$ ring C-H str.	3059	3007	0.04	2983	0.04	3185	0.06	3068	0.04	3058	0.03	3191	0.02
$\nu$ ring C-H str.	3036	3005	0.05	2981	0.04	3184	0.04	3067	0.03	3057	0.03	3186	1
$\nu_{as}$ CH <sub>2</sub> sym str.	3017	2934	0.02	2908	0.06	3098	0.09	3008	0.04	2999	0.04	3135	0.05
$\nu_{as}$ CH <sub>3</sub> sym str.	2992	2915	0.08	2889	0.06	3080	0.09	2984	0.05	2973	0.03	3109	0.05
$\nu_s$ CH <sub>3</sub> sym str.	2922	2864	0.11	2836	0.11	3009	0.15	2928	0.08	2917	0.07	3033	0.07
$\nu$ N = C + ring C-C str.	1622	1638	0.54	1625	0.55	1709	0.36	1613	0.15	1599	0.14	1668	0.15
$\nu$ ring C-C str.	1619	1626	0	1612	0	1703	0.01	1605	0.01	1593	0.02	1659	0.01
$\nu$ ring C-C str.	1584	1610	0.18	1596	0.13	1667	0.08	1575	0.18	1562	0.04	1625	0
$\nu$ ring C-C str.	-	1589	0.03	1575	0.02	1663	0.22	1573	0.08	1560	0.16	1619	0.18
$\nu$ ring C-C str.	1540	1581	0.16	1566	0.17	1636	0.15	1524	0.22	1512	0.2	1550	0.09
$\nu$ N-ring C str.	1514	1518	0.39	1505	0.41	1587	0.32	1504	0.14	1491	0.14	1545	0.18
$\nu$ N-S = C str.	1502	1495	1	1483	1	1556	0.36	1483	0.36	1467	0.27	1515	0.02
$\beta$ ring CH bend.	1487	1487	0.7	1474	0.55	1545	0.02	1462	0.02	1439	0.25	1515	0.31
$\beta$ CH <sub>3</sub> bend.	1422	1463	0.03	1439	0.02	1542	0.1	1459	0.01	1437	0.35	1513	0.03
$\beta$ CH <sub>3</sub> bend.	-	1459	0.02	1437	0.08	1540	1	1453	0.33	1433	0.02	1498	0.11
$\beta$ ring CH bend.	-	1454	0.07	1435	0.02	1518	0.03	1443	0.81	1431	0.45	1469	0.64
$\beta$ ring CH bend.	1404	1403	0.03	1388	0.03	1482	0.02	1400	0.03	1386	0.01	1445	0.03
$\rho_w$ CH <sub>3</sub> wag.	-	1400	0	1380	0.13	1466	0.01	1398	0.09	1381	0.07	1441	0.1
$\nu$ N-C str.	1390	1391	0.14	1377	0	1447	0.11	1387	0	1363	0.01	1437	0.01
$\rho$ O-H + C-H rock.	-	1343	0.37	1325	0.28	1408	0.39	1365	0.42	1354	0.35	1415	0.32
$\nu$ N-C str.	1327	1318	0.53	1308	0.53	1384	0.04	1306	0.06	1294	0.03	1363	0.01
$\rho$ ring C-H rock.	1309	1302	0.06	1289	0.04	1373	0.43	1298	0.19	1289	0.26	1360	0.1
$\nu$ C-OH str.	1283	1275	0.44	1262	0.42	1320	0.28	1296	0.09	1288	0.07	1343	0
$\nu$ N-S = C str.	1265	1240	0.09	1229	0.07	1299	0.14	1289	0.09	1279	0.05	1332	0.34
$\rho$ O-H + C-H rock.	1253	1224	0.1	1212	0.13	1292	0.01	1251	0.37	1238	0.34	1283	0.19
$\nu$ S = C str.	-	1204	0.49	1196	0.5	1270	0.05	1227	0.41	1215	0.32	1276	0.27
$\nu$ C-CH <sub>3</sub> str.	-	1184	0.03	1174	0.02	1258	0.04	1223	0.1	1213	0.18	1259	0.25
$\rho$ O-H + C-H rock.	-	1172	0.12	1162	0.12	1248	0.4	1193	0.02	1183	0.03	1244	0.01
$\rho$ C-H rock.	-	1165	0.01	1157	0.05	1240	0.03	1180	0.26	1173	0.24	1217	0.01
$\rho$ C-H rock.	-	1162	0.04	1152	0.01	1234	0.28	1165	0.03	1155	0.02	1208	0.06
$\rho$ C-H rock.	-	-	-	1116	0.08	1197	0.47	1151	0.06	1142	0.06	1194	0.18
$\rho$ C-H rock.	-	1123	0.08	1088	0.05	1172	0.06	1123	0.01	1115	0.01	1156	0
$\nu$ N-N str.	-	1095	0.06	1081	0.22	1156	0.01	1103	0.02	1093	0.02	1148	0.02
$\nu$ ring C-C str.	-	1088	0.25	1059	0	1130	0.07	1097	0.05	1090	0.06	1113	0.06
$\nu$ ring C-C str.	1050	1068	0	1046	0.04	1126	0.04	1062	0.01	1056	0.01	1091	0
$\nu$ C-ring C str.	-	1053	0.05	1036	0.02	1101	0.01	1034	0.04	1020	0.02	1085	0.04
$\beta$ CH <sub>3</sub> bend.	-	1048	0.02	1009	0.03	1080	0	1028	0.03	1020	0.03	1055	0.03
$\beta$ ring bend.	-	1017	0.03	1003	0.05	1068	0.01	1012	0	1006	0.01	1044	0.02
$\beta$ ring bend.	-	1011	0.04	996	0	1064	0.01	984	0.01	979	0.01	1028	0
$\beta$ ring CH out of plane bend.	-	1000	0	982	0	1061	0.07	981	0	969	0	1019	0
$\beta$ ring CCC bend.	-	986	0.02	979	0.02	1050	0.03	945	0.03	952	0	1015	0

**Table 2** (continued)

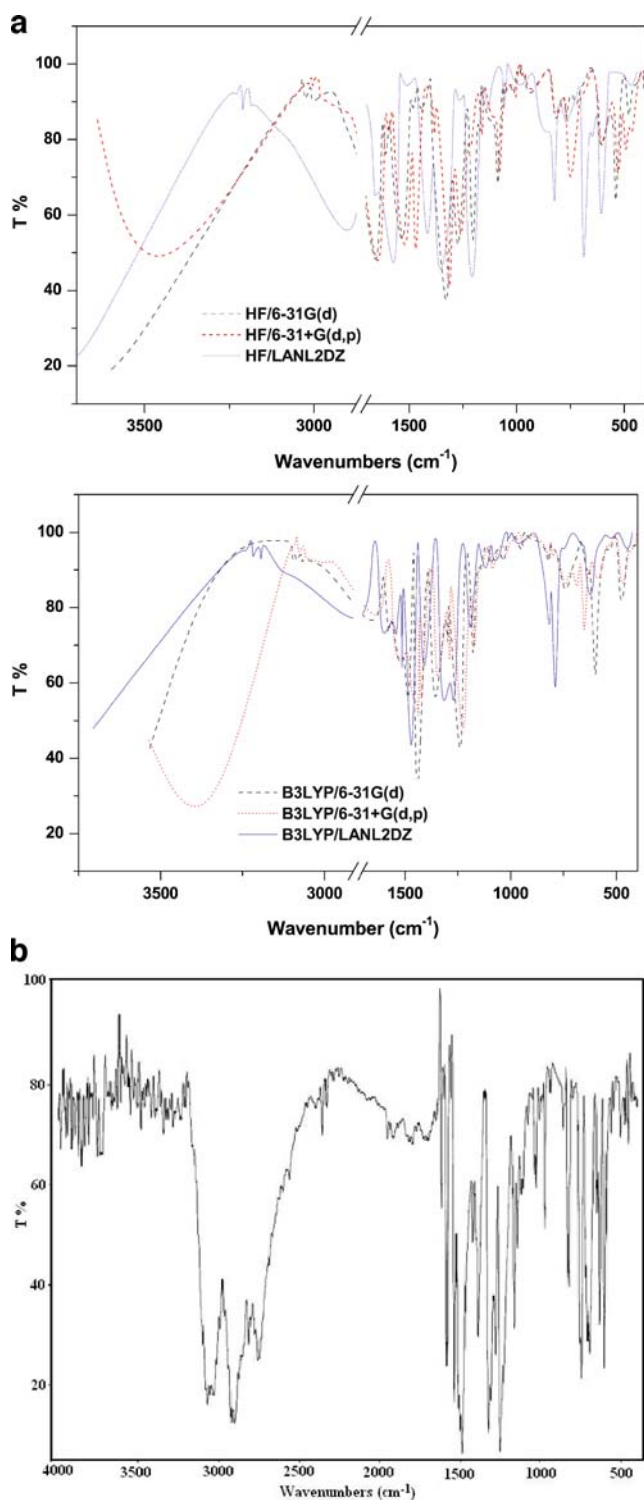
Assignments	FT-IR [7] (cm <sup>-1</sup> )	HF						B3LYP					
		6–31G(d)		6–31 + G(d,p)		LANL2DZ		6–31G(d)		6–31 + G(d,p)		LANL2DZ	
		Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>	Scaled freq. <sup>a</sup>	I <sub>Rel. int.</sub> <sup>b</sup>
$\beta$ ring CH out of plane bend.	955	981	0	970	0.01	1044	0	944	0	942	0.02	1014	0.01
$\beta$ CH <sub>3</sub> bend.	-	977	0	967	0.01	1042	0	927	0	941	0.01	996	0
$\beta$ ring CH out of plane bend.	-	974	0.02	959	0.01	1037	0	924	0	925	0.01	993	0
$\beta$ ring CH out of plane bend.	-	966	0	947	0.04	1003	0.03	913	0.01	922	0	970	0.02
$\beta$ hetero-ring bend.	-	952	0.05	867	0.01	949	0.02	839	0.01	840	0.01	901	0
$\beta$ ring CH out of plane bend.	-	873	0.01	838	0	916	0	818	0.05	814	0.04	877	0
$\beta$ ring CH out of plane bend.	-	844	0	827	0.07	900	0.08	814	0	811	0	860	0.03
$\rho_w$ ring CH wag.	-	832	0.05	808	0.07	849	0.09	805	0.03	802	0.04	837	0.06
$\beta$ ring HC-CH-CH bend.	-	813	0.07	772	0.02	836	0.08	787	0.01	782	0.01	813	0.17
$\beta$ ring HC-CH-CH bend.	758	778	0.02	-	-	821	0.29	744	0.09	742	0.08	809	0.01
$\rho_w$ ring CH wag.	748	770	0.09	765	0.11	815	0.02	714	0.05	727	0.05	788	0.41
$\rho_w$ ring HC-C-OH wag.	720	754	0.2	750	0.19	775	0.07	706	0.04	703	0.04	771	0
$\rho_w$ ring HC-CN-C in plane wag.	709	718	0.06	713	0.06	771	0.08	684	0.03	684	0.09	749	0.03
$\rho_w$ ring HC-CN-C out of plane wag.	696	712	0.03	708	0.04	712	0.03	669	0	667	0	720	0
$\rho_w$ hetero-ring HN-S = C wag.	651	676	0.02	669	0.03	700	0.01	647	0.04	653	0.2	692	0
$\beta$ ring bend.	-	664	0	660	0	692	0.58	628	0.06	637	0.03	665	0.02
$\beta$ ring bend.	635	627	0.01	622	0.02	665	0.04	623	0.03	624	0.06	647	0.01
$\rho_w$ ring HC-CH <sub>3</sub> -CH in plane wag.	-	617	0.13	613	0.13	648	0.13	597	0.31	619	0.02	643	0.07
$\rho_w$ ring HC-CH <sub>3</sub> -CH out of plane wag.	606	588	0.08	585	0.08	622	0.1	590	0.07	588	0.08	612	0.09
$\beta$ ring bend.	-	547	0.04	544	0.02	612	0.38	551	0.01	549	0.01	604	0.2
$\rho_w$ N-H wag.	-	543	0.26	537	0.15	575	0.01	531	0.03	533	0.02	566	0.01
$\rho_w$ N-H + ring C-H wag.	-	528	0.12	522	0.16	573	0.01	-	-	-	-	555	0
$\rho_w$ ring C-H wag.	-	511	0.01	507	0.02	535	0.01	512	0	509	0	527	0.01
$\rho_w$ O-H wag.	-	492	0.01	494	0.15	508	0.01	492	0.01	488	0.01	498	0
$\rho_w$ O-H + ring C-H wag.	-	480	0.09	480	0.06	487	0.02	483	0.11	482	0.07	483	0
$\beta$ O-H bend.	-	464	0.2	464	0.11	461	0.03	455	0.06	455	0.06	459	0.02
$\rho$ C-OH rock.	-	443	0.03	441	0.02	-	-	451	0.01	447	0.02	-	-
$\beta$ ring bend.	-	413	0	411	0	443	0.01	409	0.02	410	0.02	437	0.02
$\tau$ hetero-ring-CH <sub>3</sub>	-	409	0.03	408	0.02	439	0.01	405	0.01	404	0	424	0

<sup>a</sup> Scaled frequencies are in unit (1/cm); <sup>b</sup> I<sub>rel. inten.</sub> are in unit km mol<sup>-1</sup>.

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.



**Fig. 2** (a) Simulated (HF and B3LYP levels) IR spectra of the title compound ( $C_{15}H_{13}N_3OS$ ) (b) FT-IR spectrum of the title compound ( $C_{15}H_{13}N_3OS$ ) [7]

Thus, GIAO  $^{13}C$  and  $^1H$  c.s. calculations have been carried out using the B3LYP with 6–31G(d), 6–31 + G(d,p) and LANL2DZ basis sets for the optimized geometry. The results of these calculations are tabulated in Table 3. The

theoretical  $^1H$  chemical shift values (with respect to TMS) of the title compound are generally compared to the experimental  $^1H$  chemical shift values [7]. These results are shown in Table 3.  $^1H$  chemical shift values were experimentally observed [7] but  $^{13}C$  chemical shift values were not observed. Besides, experimental  $^1H$  chemical shift values were not available for individual hydrogen. Therefore, only  $^1H$  chemical shift values are compared to theoretical results. We have calculated  $^1H$  chemical shift values (with respect to TMS) of 9.61–2.39, 9–42–2.55 and 8.14–1.78 ppm with HF levels, and 8.98–2.16, 10.24–2.12 and 7.57–1.65 ppm with B3LYP levels. These variations were observed to be 13.95–2.1 ppm [7], these values are depicted in Table 3, and so the accuracy ensures reliable interpretation of spectroscopic parameters. Also, the difference is related to bond lengths in the between hydrogen and other atoms. As can be seen from Fig. 1, molecular structure of the title compound includes hydroxyl and methyl bounded to aromatic rings. The hydroxyl group include oxygen atom which shows electronegative property, and so H atom contribute to the downfield resonance. Besides, the H chemical shift of SH was experimentally observed to be 13.95 ppm [7]. This statement was not theoretically distinguished. This statement results from thiol-thione tautomerism at the triazole ring. In different substituent-1,2,4-triazole, the H chemical shift of N-H were observed to be 11.33–13.56 ppm [46]. This chemical shift has been obtained to be  $\sim 8.7$  and  $\sim 8.1$  ppm via all calculations. The other aromatic-H was observed to be 6.92–7.64 ppm [7]. This statement has been calculated 6.49–7.91, 7.03–8.42 and 6.72–8.03 using HF levels, and 6.24–7.36, 6.60–7.69 and 6.42–7.66 using B3LYP levels. Furthermore, the  $^{13}C$  chemical shift values (with respect to TMS) for all calculations have range  $\sim 185.0$  from  $\sim 22.0$  ppm in the average. The chemical shift values of C1 and C8 atoms bounded hydroxyl group and sulphur atom have been calculated at 160.98 and 190.76, 154.70 and 184.90, and 161.93 and 204.07 ppm HF levels and 151.69 and 166.73, 155.77 and 170.58, and 158.36 and 182.61 ppm B3LYP levels, respectively (in Table 3). 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. Average chemical shift values of the other aromatic-C atoms have been found to be  $\sim 120.0$ ,  $\sim 117.0$  and  $\sim 127.0$  ppm via HF levels and  $\sim 114.0$ ,  $\sim 107.0$  and  $\sim 113.0$  via B3LYP levels. As can be seen from Table 3, theoretical  $^1H$  chemical shift results of the title compound are generally closer to the experimental  $^1H$  chemical shift data.

Thermodynamic parameters of the title compound

Several thermodynamic parameters have been calculated using HF and B3LYP with the same basis sets as and are

**Table 3** Theoretical and experimental  $^{13}\text{C}$  and  $^1\text{H}$  isotropic chemical shifts (with respect to TMS, all values in ppm) for the title compound ( $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$ )

Atom	Exp. (ppm) [7] (DMSO- $d_6$ )	Calculated chemical shift (ppm)					
		HF			B3LYP		
		6–31G(d)	6–31 + G(d,p)	LANL2DZ	6–31G(d)	6–31 + G(d,p)	LANL2DZ
C1	-	160.98	154.70	161.93	151.69	155.77	158.36
C2	-	115.28	112.75	123.83	111.84	115.07	121.06
C3	-	137.21	133.45	142.43	125.21	128.45	132.23
C4	-	113.18	111.63	121.62	110.80	113.90	119.27
C5	-	132.36	129.91	137.54	121.81	124.68	127.81
C6	-	104.53	103.80	110.13	103.66	108.60	108.0
C7	-	157.52	149.11	158.81	144.03	147.27	152.18
C8	-	190.76	184.90	204.07	166.73	170.58	182.61
C9	-	130.51	127.85	134.72	128.01	132.22	134.73
C10	-	132.82	130.09	139.73	124.63	127.52	132.32
C11	-	128.44	125.06	134.45	123.97	126.98	130.92
C12	-	140.44	139.60	148.17	133.78	139.06	141.11
C13	-	128.20	124.50	134.09	123.96	127.14	131.02
C14	-	130.51	127.29	136.49	122.09	125.17	129.16
C15	-	20.51	17.67	21.79	22.10	23.83	26.59
H <sub>3</sub> (-CH <sub>3</sub> -Ar)	2.1	2.63	3.16	2.47	2.63	2.79	2.31
		2.49	2.79	2.06	2.24	2.43	1.84
		2.39	2.55	1.78	2.16	2.12	1.65
H2 (Ar-H)	6.92–7.64	7.23	7.79	7.73	6.76	7.25	7.29
H3 (Ar-H)	6.92–7.64	7.69	8.08	7.75	7.05	7.26	7.26
H4 (Ar-H)	6.92–7.64	6.49	7.03	6.84	6.24	6.60	6.52
H5 (Ar-H)	6.92–7.64	6.90	7.47	6.72	6.30	6.79	6.42
H10 (Ar-H)	6.92–7.64	7.91	8.42	8.03	7.36	7.69	7.60
H11 (Ar-H)	6.92–7.64	7.69	8.21	8.03	7.32	7.69	7.66
H13 (Ar-H)	6.92–7.64	7.45	7.79	7.58	7.15	7.47	7.42
H14 (Ar-H)	6.92–7.64	7.23	7.45	6.99	6.77	7.04	6.95
H (OH)	10.02	9.61	7.95	6.52	8.98	10.24	7.57
H (NH)	-	8.54	9.42	8.14	7.97	8.75	7.57
H (SH)	13.95	-	-	-	-	-	-

**Table 4** Calculated energies (a.u), zero-point vibrational energies ( $\text{kcal mol}^{-1}$ ), rotational constants (GHz), entropies ( $\text{cal mol}^{-1} \text{K}^{-1}$ ) and dipole moment (D) for the title compound ( $\text{C}_{15}\text{H}_{13}\text{N}_3\text{OS}$ )

Parameters	HF			B3LYP		
	6–31G(d)	6–31 + G(d,p)	LANL2DZ	6–31G(d)	6–31 + G(d,p)	LANL2DZ
Dipole moment	5.0729	4.9842	5.2645	3.9421	3.9709	4.3397
Zero-point vibrational energy	157.858	156.590	161.702	157.632	160.31481	161.15033
Total energy	-1211.31775	-1211.36704	-823.45067	-1211.09967	-1217.15465	-828.88075
Rotational constants	0.39559	0.39608	0.40495	0.40279	0.40607	0.40883
	0.27598	0.27465	0.26150	0.26463	0.26166	0.25096
	0.17748	0.17730	0.17048	0.17074	0.17004	0.16477
Entropy						
	Rotational	30.589	30.329	31.752	34.185	34.208
	Translational	38.444	38.109	39.823	42.884	42.820
	Vibrational	49.902	49.629	51.443	53.952	59.462
	Total	118.935	118.067	123.018	131.021	136.490



given in Table 4. Accurate predictions of zero-point vibrational energy (ZPVE) and the entropy ( $S_{\text{vib}}(T)$ ) require scaling the data [44]. The total energies and the change in the total entropy of the title compound at room temperature at different basis sets and theoretical methods are also presented. In previously works, the dipole moment and ZPE energies values of some molecules which included 1,2,3/1,2,4-triazole core were obtained to be  $\sim 3.0$ – $6.0$  D and  $\sim 155.0$ – $476.0$  kJ mol<sup>-1</sup> [47, 48]. These results are important to test the reliability of our results. As regard as, the results of the energies, dipole moment, entropy and ZPE can be used to the new synthesis of some molecules which include 1,2,4-triazole core.

## Conclusions

In this study, to test the HF and DFT level of theory with different basis sets reported, computed and experimental geometric parameters, vibrational frequencies, chemical shifts and several thermodynamic parameters of the title compound have been compared. To fit the theoretical frequency, zero-point vibrational energy and the entropy results with experimental ones for HF and B3LYP levels, we have multiplied the data. Multiplication factors results gained seemed to be in a good agreement with experimental ones. The B3LYP levels which have level of theory to include the effects of electron-correlation have shown better fit to the experimental ones than those of HF levels in terms of evaluate geometric parameters, vibrational frequencies and chemical shifts. An intramolecular O-H $\cdots$ N hydrogen bond occurs between the hydroxyphenyl group and the triazole N atom. Besides, the triazole ring is attributed to the presence of delocalization between the lone pair on atom N(3) and C(8) = S(1) double bond, and also to electronic factors associated with the large electron density substituents. Further variation in different positions of the aromatic-substituent groups and the  $\pi$ -conjugation network containing the 1,2,4-triazole ring in the core structure is necessary for reaching a concrete inference.

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