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# Experimental and theoretical studies of (FTIR, FT-NMR, UV–Visible, X-ray and DFT) 2-(4-Allyl-5-pyridin-4-yl-4H-[1,2,4]triazol-3-ylsulfanyl)-1-(3-methyl-3-phenyl-cyclobutyl)-ethanone



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#### HIGHLIGHTS

• Theoretical modeling of the C<sub>23</sub>H<sub>24</sub>N<sub>4</sub>OS, in comparison to the experimental.

• The single crystal structure of the prepared compound has been investigated by different spectroscopic techniques.

• The crystal and the optimized molecular structures are characterized, and discussed.

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# ABSTRACT

The single crystal structure, 2-(4-Allyl-5-pyridin-4-yl-4H-[1,2,4]triazol-3-ylsulfanyl)-1-(3-methyl-3-phenyl-cyclobutyl)-ethanone, has been synthesized and characterized by IR, NMR, UV spectra and X-ray diffraction methods. In addition, the optimized structure, the vibrational assignments, the chemical shifts, the molecular orbital energies, molecular electrostatic potential maps and thermodynamic properties, ionization potential, electron affinity, electronegativity, global chemical hardness and chemical softness of the molecule have been investigated by using Density Functional Theory with B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets. UV-Visible spectrum of the compound was recorded and the electronic properties HOMO and LUMO energies were measured by time-dependent TD-DFT approach. The observed results of the compound have been compared with theoretical results and it is found that the experimental data show good agreement with calculated values. The single crystal structure of the compound crystallizes in the monoclinic system with space group C 2/c.

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# 1. Introduction

Compounds containing triazole subunits have been intensively studied owing to their diverse biological properties and also because of the ease of complexation [1–3]. 1,2,4-Triazole and its derivatives are an important class of ligands used as building tectons in constructing coordination complexes [4–6]. In particular, pyridyl-decorated triazole ligands are extensively studied, for example R-Isophthalate (R = -H,  $-NO_2$ , and -COOH) as modular building blocks for mixed-ligand coordination polymers incorporated with a versatile connector 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole 4-amino-3,5-bis(3-pyridyl)-4H-1,2,4-triazole, [7] and other groups [8,9]. In the published articles, such series of ligands

successfully behave as not only the extended exo-bidentate linkers with the terminal pyridyl groups but also as the promoter of a coordinative cycle with the central triazole upon metalation [9]. 1,2,4-Triazoles and their derivatives are found to be associated with various biological activities such as anticonvulsant, antifungal, anticancer, antiinflammatory and antibacterial properties. Several compounds containing 1,2,4-Triazole rings are well known as drugs. For example, fluconazole is used as an antimicrobial drug, while vorozole, letrozole and anastrozole are non-steroidal drugs used for the treatment of cancer and loreclezole is used as an anticonvulsant [10]. The crystal structure of 2-(4-Allyl-5-pyridin-4-yl-4H-[1,2,4]triazol-3-ylsulfanyl)-1-(3-methyl-3-phenyl-cyclobutyl)-ethanone is based on simple reaction between RSH and R'CH2Cl. In chemistry literature there are some example showing reactivity of between 4-(prop-2-en-1-yl)-5-(pyridin-4-yl)-4H-1,2,4-triazole-3-thioland2-chloro-1-(3-methyl-3-phenylcyclobutyl) ethanone [11–17].

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In this work, we report the experimental and the theoretical studies of single crystal structure ( $C_{23}H_{24}N_4OS$ ) and also, in the following we discuss IR, NMR, UV spectra of compound by using Density Functional Theory (DFT) calculations. The results calculated in all these methods were compared with the experimental results which yield good agreement between observed and calculated values.

# 2. Experimental

#### 2.1. General

IR spectrum was recorded on an ATI Unicam-Mattson 1000 FTIR spectrophotometer using KBr pellets. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained by using a Bruker 300 MHz spectrometer. The UV spectrum of the compound was recorded on a Schimadzu UV-1700 spectrometer in CHCl<sub>3</sub> solvent.

#### 2.2. Synthesis of the title compound

The compound was synthesized as shown in Scheme 1 by the following procedure. To a stirred solution of 4-allyl-5-(pyridine-4-yl)-4H-1,2,4-triazole-3-thiol (10 mmol) and potassium carbonate (10 mmol) in 30 mL of absolute ethanol, 2-chloro-1-(3-methyl-3phenylcyclobutyl) ethanone (10 mmol) in 10 mL of absolute ethanol was added dropwise and stirring was continued for 2 h. more at room temperature. The solvent was evaporated in vacuo to dryness. Residue was triturated with water and filtered. Suitable single crystals for crystal structure determination were obtained by slow evaporation of its ethanol solution. Yield: 88%, melting point: 366 K. Characteristic IR bands: 3095–3018 cm<sup>-1</sup> v(aromatics), 2973–2864 cm<sup>-1</sup> v(aliphatics), 1708 cm<sup>-1</sup> v(C=O), 1650 cm<sup>-1</sup> v(C=N pyridine), 1606 cm<sup>-1</sup> v(C=N triazole or C=C alken). Characteristic <sup>1</sup>H NMR shifts (CDCl<sub>3</sub>,  $\delta$ , ppm): 1.46 (s, 3H, –CH<sub>3</sub> in cyclobutane), 2.28–2.33 (m, 2H, --CH<sub>2</sub>- in cyclobutane), 2.43–2.50 (m, 2H,  $-CH_2$  - in cyclobutane), 3.737 (q, J = 8.78 Hz, 1H, >C -H in cyclobutane), 4.34 (s, 2H, S–CH<sub>2</sub>–), 4.73 (t, J = 2.2 Hz, 2H, –N–CH<sub>2</sub>–), 4.86 (d, *J* = 17.2 Hz, 1H, H<sub>A</sub>H=C-, on ethylene group), 5.25 (d, *J* = 10.6 Hz, 1H, H<sub>B</sub>H=C–, on ethylene group), 5.90–6.01 (m, 1H, –H<sub>C</sub>=CH<sub>2</sub>–, on ethylene group), 7.12-7.18 (m, 3H, aromatics), 7.28-7.32 (m, 2H, aromatics), 7.65 (d, J = 1.6 Hz, 2H, C=CH aromatics on pyridine ring), 8.75 (d, J = 1.5 Hz, 2H, N=CH aromatics on pyridine ring). Characteristic <sup>13</sup>C NMR shifts (CDCl<sub>3</sub>,  $\delta$ , ppm): 204.13, 153.69, 152.64, 150.85, 150.63, 134.37, 130.92, 128.32, 125.67, 124.56, 122.11, 118.66, 47.05, 41.27, 39.08, 38.47, 36.69, 30.36.

#### 2.3. Single crystal XRD

The data collection was performed at 293 K on a Stoe-IPDS-2 image plate detector using a graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Data collection and cell refinement were performed using X-AREA [18] and X-RED32 [18]. The structure was solved by direct methods using SHELXS-97 [19] and refined by a full-matrix least-squares procedure using the program SHELXL-97 [19]. Molecular graphics were performed using ORTEP-3 [20]. All non-hydrogen atoms were easily found from the difference

#### Table 1

Crystal	lographic	data	of (	( <b>1</b> )	)
Ci y Stui	iographic	uuuu	01		<i>.</i>

Empirical formula	$C_{23}H_{24}N_4OS$
Molecular weight	404.53
Temperature, T (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Crystal size (mm <sup>3</sup> )	$0.720 \times 0.530 \times 0.340$
Space group	C 2/c
a (Å)	36.1594(14)
b (Å)	5.7537(2)
<i>c</i> (Å)	33.1187(12)
α (°)	90
β (°)	142.261(16)
γ(°)	90
Volume, $V(Å^3)$	4217.3(3)
Ζ	8
T <sub>min</sub> , T <sub>max</sub>	0.9901, 0.9955
Calculated density (Mg m <sup>-3</sup> )	1.425
$\theta$ Range (°)	1.84-27.22
Index ranges	$h = -42 \rightarrow 42, k = -6 \rightarrow 6, l = -38 \rightarrow 37$
Measured reflections	25,264
Independent reflections	3711
Observed reflections $(I > 2\sigma)$	3044
Goodness-of-fit on F <sup>2</sup>	1.057
R1 indice $(I > 2\sigma)$	0.0472
wR2 indice $(I > 2\sigma)$	0.1308
$\Delta ho_{ m min}$ , $\Delta ho_{ m max}$ (e/Å <sup>3</sup> )	-0.119, 0.103

Fourier map and refined anisotropically. The all hydrogen atoms were included using a riding model and refined isotropically with CH = 0.93 Å (for phenyl group), CH<sub>2</sub> = 0.97 Å, CH<sub>3</sub> = 0.96 Å and CH = 0.98 Å  $U_{iso}$ (H) = 1.2 U<sub>eq</sub> (1.5 for methyl group). Relevant crystal data and details of the structure determinations are given in Table 1.

# 2.4. Computational methodology

The molecular structures of the title compound in the ground state (*in vacuo*) were optimized by DFT methods to include correlation corrections with the 6-31G(d) and 6-311G(d, p) basis sets. In DFT calculations, hybrid functionals are also used, including the Becke's three-parameter functional (B3) [21], which defines the exchange functional as the linear combination of Hartree–Fock, local, and gradient-corrected exchange terms. The B3 hybrid functional was used in combination with the correlation functionals of Lee et al. [22].

Then vibrational frequencies for optimized molecular structures have been calculated. 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 chemical shifts are calculated within GIAO approach [23,24] applying B3LYP method with 6-31G(d) and 6-311G(d, p) basis sets. The isotropic shielding values were used to calculate the isotropic chemical shifts  $\delta$  with respect to tetramethylsilane (TMS).  $\delta_{iso}(X) = \sigma_{TMS}(X) - \sigma_{iso}(X)$ , where  $\delta_{iso}$  is isotropic chemical shift and  $\sigma_{iso}$  is isotropic shielding. UV–Visible spectra, electronic transitions, vertical excitation energies and oscillator strengths were computed with the time dependent (TD) DFT method. Besides of these, the lowest unoccupied molecular orbital (LUMO)



Scheme 1. Synthetic route for the synthesis of the target compound.

highest occupied molecular orbital (HOMO) energy differences for these species were calculated with this method. All the calculations were performed using the Gaussview molecular visualization program [25] and Gaussian 03 program on a personal computer [26].

The molecular electrostatic potential (MEP) was evaluated to research the reactive sites of the title compound using B3LYP/6-311G(d, p) level. In addition, electronic absorption spectra were calculated using the time-dependent DFT (TD-DFT) method.

### 3. Results and discussion

# 3.1. Description of the crystal structure using XRD

The single crystal structure is shown in Fig. 1. The title compound (1) crystallizes in the monoclinic space group C 2/c with eight molecules in the unit cell but the asymmetric unit in the crystal structure contains only one.

The crystal structure ( $C_{23}H_{24}N_4OS$ ) contains pyridine, triazole, phenyl and cyclobutane rings. The pyridine, triazole and phenyl rings are planar with maximum deviations of -0.0051(17), 0.0074(13) and -0.0042(16) Å, respectively. The dihedral angles between the pyridine ring A(N1/C1–C5), the triazole ring B(N2–N4/C6–C7), the cyclobutane ring C(C13–C16) and D(C18–C23) are 44.15(11)° A/B, 83.23(12)° A/C, 62.72(09)° A/D, 53.40(13)° B/C, 26.05(12)° B/D and 36.25(15)° C/D.

In the cyclobutane ring C, the dihedral angle between C14—C15—C16 plane and C14—C13—C16 plane is 25.91(44)°. The value found in this study is in agreement with literature values such as 24.02(22)° [27], 25.74(15)° [13] and 24.3° [28]. As can be seen in Table 2, in the triazole ring, due to conjugations of electrons, the N3—N4 single bond length is shorter than reported values [29,30]. The crystal structure exhibits intra–inter molecular interactions. In the crystal packing, there are two intra-molecular C—H...O1/N2 and an intermolecular C—H...N hydrogen bonding, details of which are given in Table 3. Intra molecular hydrogen bonding, the atom C13 of cyclobutane ring at (x, y, z) acts as hydrogen-bond donor, via atom H13, to atom N4 of the triazole ring at (1/2 - x, -1/2 + y, 1/2 - z). This dimers stabilize crystal packing in three dimensional space (see Fig. 2).

#### 3.2. Theoretical studies using DFT method

#### 3.2.1. Optimized structure

The optimized molecular geometries are calculated by using B3LYP/6-31G(d) and B3LYP/6-311G(d, p) methods. Some selected geometric parameters experimentally obtained and theoretically calculated by B3LYP/6-31G(d) and B3LYP/6-311G(d, p) methods

at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

#### Table 2

Selected geometrical parameters of the title compound (1) with X-ray structure and DFT method.

	Experimental	B3LYP 6- 31G(d)	B3LYP 6-311G(d, p)
Bond lengths (Å)			
01–C12	1.213(3)	1.216	1.210
C11-C12	1.507(3)	1.531	1.528
S1-C11	1.803(2)	1.830	1.829
S1C7	1.749(2)	1.766	1.766
N1-C3	1.331(4)	1.337	1.335
N1-C4	1.327(3)	1.341	1.339
N2-C6	1.361(3)	1.379	1.378
N2-C7	1.371(3)	1.376	1.376
N2-C8	1.473(3)	1.463	1.463
N3-C6	1.315(3)	1.323	1.319
N3-N4	1.381(3)	1.369	1.366
N4-C7	1.301(3)	1.317	1.312
Bond angles (°)			
C4-N1-C3	116.2(2)	116.6	116.7
C11-C12-C13	116.5(2)	114.9	114.7
C11-C12-01	121.6(2)	122.7	122.7
C12-C11-S1	115.7(2)	115.3	115.4
C11-S1-C7	100.6(1)	98.7	98.5
S1-C7-N2	125.3(2)	124.0	124.0
S1-C7-N4	124.2(2)	125.2	125.2
C7-N2-C6	104.6(2)	103.9	103.9
N2-C6-N3	110.3(2)	109.9	109.8
C6-N3-N4	107.2(2)	108.1	108.1
N3-N4-C7	107.5(2)	107.3	107.4
N4-C7-N2	110.4(2)	110.8	110.7
N2-C8-C9	117.3(2)	114.8	115.0
Torsion angles (°)			
C18-C15-C16-C13	137 7(2)	1361	135.6
C15 - C16 - C13 - C12	_139 3(2)	_136.8	-136.4
C16-C13-C12-C11	-80.9(3)	_88 3	_85.1
C13 - C12 - C11 - S1	168.6(2)	169.6	169.6
C12 - C11 - S1 - C7	89 5(2)	73.2	73.1
01-C12-C11-S1	-87(3)	-91	-95
C11-S1-C7-N4	77 0(2)	58.8	58.8
C11-S1-C7-N2	-1046(2)	-1213	-1205
S1-C7-N4-N3	179 9(2)	-179.4	-178 7
S1-C7-N2-C6	-1793(2)	-180.0	179 3
N2-C8-C9-C10	-2.7(5)	-2.2	-1.4

# Table 3 Hydrogen bond interactions of the title compound (1) (Å, °).

Hydrogen bond (Å, °)	D—H	НА	DA	D—HA
C13—H13N4 <sup>i</sup>	0.98	2.49	3.387(3)	153
C8—H8AO1	0.97	2.29	3.220(6)	161
C10—H10AN2	0.93	2.55	2.883(5)	102

Symmetry code: (i): 1/2 - x, -1/2 + y, 1/2 - z.





**Fig. 2.** A diagram showing the C—H...N intermolecular hydrogen bonds in the title compound. Only those H atoms involved in the hydrogen bonding interactions are shown. [Symmetry code: (i):1/2 - x, -1/2 + y, 1/2 - z.]

are listed in Table 1 and compared with X-ray results. We noted that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase. In the solid state, the existence of the crystal field along with the intermolecular interactions have connected the molecules together, which result in the differences of bond parameters between the calculated and experimental values. It is well known that DFT optimized geometric parameters are usually good agreement with experimental values and more accurate than Hartree-Fock and semi-empirical methods, due to inclusion of electron correlation. The largest differences between experimental and calculated bond lengths, bond angles and torsion angles are about 0.027 Å and 0.026 Å, 2.5° and 2.3°, 18.2° and 18.2° for B3LYP/6-31G(d) and B3LYP/6-311G(d, p), respectively. Both the optimized bond lengths and bond angles provided by B3LYP/6-311G(d, p) method are the closest to the experimental values (see Table 1).

#### 3.2.2. Vibrational spectra

IR spectrum is obtained using an ATI Unicam-Mattson 1000 FTIR spectrophotometer using KBr pellets and IR spectrum of this structure is shown in Fig. 3. Harmonic vibrational frequencies were calculated by using B3LYP/6-31G(d) and B3LYP/6-311G(d, p) levels. The experimental and calculated frequencies show differences. The first reason is that the experimental spectrum has been recorded for the compound in the solid state, while the computed spectra correspond to isolated molecule in the gas phase. The second reason is the fact that the experimental values correspond to anharmonic vibrations, whereas the calculated values are harmonic vibrations [31]. To describe the observed modes, we calculate harmonic vibrational frequencies and compare theoretical and experimental results (see Table 4).

The characteristic v(CH) stretching vibrations of heteroaromatic structures are expected to appear in 3000–3100 cm<sup>-1</sup> [27]. In the present study, v(CH) symmetric and asymmetric stretching modes are observed in the range of 3019–3089 cm<sup>-1</sup>. The experimental C=O stretching mode is observed at 1707 cm<sup>-1</sup>. In the pyridine and triazole rings, CN and C=N stretching vibrations are observed at 1510/1263 cm<sup>-1</sup> and 1606 cm<sup>-1</sup>, respectively. Also, v(SC)stretching mode is observed at 674 cm<sup>-1</sup>. The other stretching, bending, twist, rocking, scissorsing modes can be seen in Table 4. Despite the differences between observed and calculated values, the general agreement is good.

#### 3.2.3. Molecular electrostatic potential

Electrostatic potential maps, also known as electrostatic potential energy maps, or molecular electrical potential surfaces, illustrate the charge distributions of molecules three dimensionally. The purpose of finding the electrostatic potential is to find the reactive site of a molecule. These maps allow us to visualise variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another. Molecular electrostatic potential (MESP) mapping is very useful in the investigation of the molecular structure with its physiochemical property relationships [32].

The molecular electrostatic potential, V(r), at a given point r(x, y, z) in the vicinity of a molecule, is defined in terms of the



Fig. 3. FTIR spectrum of the title compound.

 Table 4

 Vibrational frequencies of the title compound (1) with experimental and DFT/B3LYP

 Methods.

Frequencies	Experimental	B3LYP 6-	B3LYP 6-311G(d,
		31G(d)	p)
$v_{as}(CH_2)$ all.	3108	3224	3252
υ <sub>s</sub> (CH) pyr.	3089	3152	3178
υ <sub>as</sub> (CH) pyr.	3055	3146	3172
$v_s(CH)$ phe.	3040	3189/3154	3209
$v_{as}(CH)$ phe.	3019	3177-3169	3197-3189
$\upsilon_{s}(CH_{2}) + \upsilon_{s}(CH)$ all.	2968	3145	3174
$\upsilon_{s}(CH_{2}) + \upsilon_{as}(CH)$ all.	2959	3135	3161
$v_{as}(CH_2)$ cyc.	2951	3121-3105	3142-3126
$v_{as}(CH_2)$	2933	3098	3117
$v_{as}(CH_3)$	2915	3092/3083	3118/3107
$v_{as}(CH_2)$ all.	2859	3087	3112
$\upsilon_{s}(CH_{2}) + \upsilon(CH)$ cyc.	2818	3062-3059/	3081-3078/3069
5( 2) ( ) 5		3048	,
v.(CH2) all.	_	3054	3074
$v_{\rm c}(\rm CH_2)$	-	3050	3067
$v_{c}(CH_{2})$	_	3019	3040
$\nu(C=0)$	1707	1784	1804
v(C=C)	1606	1710	1733
v(CC) phe	1557	1646	1664
$\nu(CC)$ pvr	1534	1639	1655
v(CN) pyr	1510	1594	1610
$\delta(CH)$ phe	1494	1529	1548/1493
$O(CH_{2}) + O(CH_{2}) CVC$	1465	1503/1493	1529_1520
$\delta(CH)$ pyr + $\delta(NCN)$	1405	1/06	1509
tri	1455	1450	1505
$O(CH_{a})$ all	1429	1491	1513
$\rho_s(CH_2)$ and $\rho_s(CNC)$ pyr	1423	1451	1/71
$p_s(CH) + \delta(CH) $ pyr.	1403	1433	1471
$p_s(CH_2) \neq o(CH)$ all.	1333	1445	1407
$p_s(CH_2)$	1374	1422	1432
$p_t(Cn_3)$	1545	1412	1455
$\mathcal{O}(\mathbf{C} = \mathbf{N})$ (II).	1000	1412	1444/1425
$O(CH_2)$ dll. $f(CL_1)$ all $h \to (CN_1)$ tri	1298	1395	1425/1410
$\mathcal{L}(CH_2)$ all. $\neq \mathcal{D}(CN)$ (II.	1205	1376	1392
0(CH)	1220	1375	1390
$U(C_{phe}, C_{cyc}) + O(CH_2)$ CVC.	1206	1321	1335
$\delta(CH_2)$	1188	1293	1309
$t(CH_2)$ all. + $\delta(NCN)$ tri.	1171	1286	1297
U(CNC) DVL	1135	1268	1290
$t(CH_2) + \rho_t(CH)$ cvc.	1092	1249	1267/1095
$t(CH_2)$ all.	1074	1220	1226
$\rho_{\rm c}(\rm CH)$ phe.	1062	1203	1215
$f(CH_2) + O_1(CH_2) CVC$	1027	1174	1167/1122
$\nu(NN)$ tri	982	1137/1091	1144
$\theta$ (phe)	945	1017	1057/1017
$O_{\rm c}(\rm CH)$ pyr	926	1114	1122
$\theta(\mathbf{pvr})$	883	1010	1012
t(CH) phe	868	1001	994
t(CH) pvr	831	992/852	989
$\theta(cyc)$	766	981	1006/988
$\delta(CH_{\alpha})$ all	740	953	950
$\delta(CCS)$	728	762	766
$\delta(NCN)$ out of plane	701	725	778/721
v(SC)	674	723	728
v(se)	0/4	124	120

all.: allyl, pyr.: pyridin, phe.: phenyl, cyc.: cyclobutyl, tri: triazole,  $\rho_t$ : rocking, t: twist,  $\delta$ : bending,  $\rho_s$ : scissorsing,  $\upsilon_s$ : symmetric stretching,  $\upsilon_{as}$ : asymmetric stretching,  $\theta$ : breathing.

interaction energy between the electrical charge generated from the molecule's electrons and nuclei and a positive test charge (a proton) located at r. For the system studied, the V(r) values were calculated as described previously using the following equation [33]:

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \rho(r') / |r' - r| d^3 r'$$
(1)

where  $Z_A$  is the charge of nucleus A located at  $R_A$ ,  $\rho(r')$  is the electronic density function of the molecule, and r' is the dummy



Fig. 4. The total electron density surface mapped with electrostatic potential of the title compound by B3LYP/6-311G(d, p).

integration variable. The MEP is related to the electronic density and is a very useful descriptor in understanding sites of electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions [34–36]. The electrostatic potential V(r) is also well suited for analyzing processes based on the "recognition" of one molecule by another, such as in drug–receptor and enzyme– substrate interactions, because it is through their potentials that the two species first "see" each other [37,38]. Being a real physical property, V(r) can be determined experimentally by diffraction or computational methods [39].

Total SCF electron density surface mapped with molecular electrostatic potential (MESP) of the title compound (1) are shown in Fig. 4. The molecular electrostatic potential surface MESP which is a 3D plot of electrostatic potential mapped onto the iso-electron density surface simultaneously displays molecular shape, size and electrostatic potential values. The colour scheme for the MESP surface is red-electron rich or partially negative charge; blue-electron deficient or partially positive charge; light blue-slightly electron deficient region; yellow-slightly electron rich region, respectively. Areas of low potential, red<sup>1</sup>, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Nitrogen has a higher electronegativity value would consequently have a higher electron density around them. Thus the spherical region that corresponds to nitrogen atom would have a red portion on it. The MESP of the compound clearly indicates the electron rich centres of nitrogen and oxygen atoms. The contour map of electrostatic potential of the compound has been constructed by the DFT method and is shown in Fig. 5 also confirms the different negative and positive potential sites of the molecule in accordance with the total electron density surface.

3.2.4. Natural bond orbital analysis

The charges of the atoms determined by natural bond orbital (NBO) analysis by B3LYP/6-31G(d) and B3LYP/6-311G(d, p) methods are presented in Table 5. The more positive charges on C12 and C6 carbon atoms are due to the highly electronegative nitrogen and oxygen attachment with that carbon atom. This is caused by the electronegativity of nitrogen and oxygen atoms. When compared the charges of the aromatic ring carbon atoms, less positive

 $<sup>^{1}\,</sup>$  For interpretation of color in Fig. 4, the reader is referred to the web version of this article.



**Fig. 5.** The contour map of electrostatic potential of the total density of the title compound by B3LYP/6-311G(d, p).

 Table 5

 The charges of the atoms determined from natural bond orbital analysis (NBO) by B3LYP method.

Atoms	B3LYP 6-	B3LYP6-	Atoms	B3LYP 6-	B3LYP 6-
	31G(d)	311G(d, p)		31G(d)	311G(d, p)
S1	0.2937	0.2461	H2	0.2468	0.2161
N1	-0.4483	-0.4486	H3	0.2245	0.1824
N2	-0.4004	-0.4133	H4	0.2262	0.1841
N3	-0.2857	-0.2906	H5	0.2614	0.2274
N4	-0.3070	-0.3171	H8A	0.2870	0.2479
01	-0.5528	-0.5664	H8B	0.2610	0.2202
C1	-0.0725	-0.0627	H9	0.2372	0.1985
C2	-0.2679	-0.2418	H10A	0.2238	0.1919
C3	0.0243	0.0680	H10B	0.2292	0.1956
C4	0.0211	0.0655	H11A	0.2722	0.2320
C5	-0.2355	-0.2049	H11B	0.2879	0.2480
C6	0.3571	0.3586	H13	0.2556	0.2143
C7	0.1762	0.2234	H14A	0.2576	0.2211
C8	-0.2939	-0.2178	H14B	0.2384	0.2006
C9	-0.2392	-0.1872	H16A	0.2374	0.1989
C10	-0.4323	-0.3733	H16B	0.2456	0.2059
C11	-0.6854	-0.5822	H17A	0.2265	0.1917
C12	0.5969	0.6053	H17B	0.2375	0.2008
C13	-0.3448	-0.2974	H17C	0.2400	0.2034
C14	-0.4381	-0.3745	H19	0.2349	0.2024
C15	-0.0599	-0.0304	H20	0.2367	0.2008
C16	-0.4298	-0.3612	H21	0.2364	0.2010
C17	-0.6625	-0.5621	H22	0.2361	0.2003
C18	-0.0353	-0.0307	H23	0.2317	0.1991
C19	-0.2288	-0.2043			
C20	-0.2245	-0.1858			
C21	-0.2392	-0.2047			
C22	-0.2254	-0.1871			
C23	-0.2318	-0.2075			

charge is observed in the C3 and C4 carbon atoms which is attached to the highly electronegative nitrogen (N1) atom.

#### 3.2.5. NMR spectra

The "gauge-independent atomic orbital" (GIAO) method has proven to be quite accepted and accurate, in particular when applied in the context of highly correlated ab initio methods, such as perturbation theory and coupled cluster theory. Both approaches are computationally expensive and time consuming and often cannot be applied to larger molecular systems. Density Functional Theory (DFT) shielding calculations are rapid and applicable to large systems, but the paramagnetic contribution to the shielding trends to be overestimated. In this sense, theoretical calculations of the chemical shifts may be used as an aid for the assignment of the experimental data. The results of these calculations are tabulated in Table 6. The theoretical <sup>13</sup>C and <sup>1</sup>H chemical shift values (with respect to TMS) of the title compound are compared to the experimental <sup>13</sup>C and <sup>1</sup>H chemical shift values. The <sup>13</sup>C chemical shift values (with respect to TMS) are observed to be 204.13–30.36 ppm range and it is found that these values are at the 198.795–31.889 ppm range by the B3LYP/6-31G(d) level and 213.946–34.518 ppm range by the B3LYP/6-311G(d, p) level. <sup>13</sup>C NMR spectra of the title compound show the signals at 153.69 and 150.85 ppm related to C(6) and C(7) atoms next to the N atoms of the five-membered triazole ring. This signals are calculated as 149.329 and 162.148 ppm for the C(6) atom and 152.474 and 164.694 ppm for the C(7) atom by using the B3LYP/6-31G(d) and B3LYP/6-311G(d, p) levels, respectively. The chemical shift values of C12 atom next to oxygen atom are observed as 204.13 ppm in the <sup>13</sup>C NMR spectra.

Besides of the <sup>13</sup>C chemical shift values, the <sup>1</sup>H chemical shift values are observed in the range of 8.75–1.46 ppm and the <sup>1</sup>H chemical shift values (with respect to TMS) have been calculated as 8.739–1.208 ppm with B3LYP/6-31G(d) level and 9.031–1.203 ppm with B3LYP/6-311G(d, p) level.

#### 3.2.6. Thermodynamic properties

In this study, we calculated total energy, dipole moment, zeropoint vibrational (ZPVE) energy and the standard thermodynamic parameters such as standard heat capacity  $C_{\rm vib}$ , standard entropy  $S_{\rm vib}$  and standard enthalpy  $H_{\rm vib}$  of the title compound at 298.15 K temperature and 1 atm pressure by using B3LYP/6-31G(d) and B3LYP/6-311G(d, p) levels. As can be seen in Table 7, the ZPVE and  $E_{\text{total}}$  of the molecular structure obtained by the B3LYP/6-311G(d, p) method are much lower than that obtained by the B3LYP/6-31G(d) method. They are at 268.131 kcal  $mol^{-1}$  and 284.851 kcal mol<sup>-1</sup>, 270.133 kcal mol<sup>-1</sup> and 286.809 kcal mol<sup>-1</sup> by using B3LYP/6-311G(d, p) and B3LYP/6-31G(d) methods, respectively. The results of the energies, dipole moment, enthalpy, entropy, heat capacity, and ZPVE provide helpful information to further study the title compounds. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermochemical fields.

#### 3.2.7. Electronic absorption spectra

The excited states were taken into account for the TD-DFT method based on the B3LYP/6-311G(d, p) and B3LYP/6-31G(d) levels including chloroform solvent in order to investigate the properties of electronic absorption. The energies of four important molecular orbitals of the title compound **(1)**: the second highest and highest occupied MO's (HOMO and HOMO–1), the lowest and the second lowest unoccupied MO's (LUMO and LUMO+1) were calculated and are presented in Table 8.

It is known that photon energy *E* is given by:

$$E = hc/\lambda \tag{2}$$

where *h* is the Planck's constant, *c* is the light velocity in vacuum, and  $\lambda$  is the wavelength of light. For molecular maximum absorption spectrum, *E* can be replaced with molecular orbital energy level difference ( $\Delta E$ ); thus, Eq. (3) changes to [40]:

$$\Delta E = hc/\lambda \tag{3}$$

The calculations were also performed with CHCl<sub>3</sub> solvent effect. The energy gap between HOMO and LUMO is a critical parameter in determining molecular electrical transport properties [32]. The experimental and calculated UV–Vis absorption spectrums are shown in Fig. 6. Experimentally, electronic absorption spectrum of the title compound in CHCl<sub>3</sub> solvent shows two bands at 274 and 256 nm. One of the absorption bands at 274 nm is caused by the  $n \rightarrow \pi^*$  transition and the other band at 256 nm is due to  $\pi \rightarrow \pi^*$  transitions. The  $\pi \rightarrow \pi^*$  transitions are expected to occur relatively at lower wavelength, due to the consequence of the extended aro-

d experimental <sup>13</sup> C and <sup>1</sup> H isotropic chemical shifts ( $\delta_{iso}$ ) (with respect to TMS all values in ppm) for the title compound.								
Exp.	B3LYP 6-31G(d) $(\delta_{iso})$	B3LYP 6-311G(d, p) $(\delta_{iso})$	Atoms	Exp.	B3LYP 6-31G(d) $(\delta_{iso})$	B3LYP 6-311G(d, p) $(\delta_{iso})$		
134.27	129.336	141.801	H2	7.65	7.287	7.628		
122.11	114.579	125.167	H3	8.75	8.673	8.963		
152.64	144.131	157.168	H4	8.75	8.739	9.031		
152.64	144.578	157.643	H5	7.65	7.802	8.162		
122.11	117.650	128.619	H8A	4.73	5.604	5.841		
153.69	149.329	162.148	H8B	4.73	4.482	4.703		
150.85	152.474	164.694	H9	5.90-6.01	6.334	6.609		

H10A

H10B

H11A

H11B

H14A

H14B

H16A

H16B

H17A

H17B

H17C

H19

H20

H21

H22

H23

Δ

H13

4.86

5.25

4.34

4 3 4

3.74

2.33

2.28

2.50

2.43

1.46

1.46

1.46

7.28-7.32

7.12-7.18

7.12-7.18

7.12-7.18

7.28-7.32

4.930

5.481

3.628

4 2 9 3

3.328

2.859

1.912

2.639

2 1 9 7

1.782

1.250

1.208

7 0 1 6

7.209

7.124

7.227

6.960

Table 6								
Theoretical and experimental	<sup>13</sup> C and <sup>1</sup> H is	sotropic chemica	l shifts (δ <sub>iso</sub> )	(with respect to	o TMS all	values in ppm)	for the title	e comp

53.838

145.166

121.104

54 553

213.946

42.444

35.824

45.003

45 345

34.518

161.743

130.713

131.643

134.488

130.859

Table 7

Atoms C1 C2 C3 C4 C5 C6 C7

C8

C9

C10

C11

C12

C13

C14

C15

C16

C17

C18

C19

C20

C21

C22

C23

The calculated thermodynamic parameters of compound (1) using by B3LYP/6-311G(d, p), B3LYP/6-31G(d) methods.

49.289

129.461

110.094

50 715

198.795

39.386

33.559

41.194

41.418

31.889

145.376

118.494

121.827

119.178

121.755

118.379

39.08

130.92

118.66

41 27

204.13

47.05

36.69

38.47

36 69

30.36

150.63

124.56

128.32

125.67

128.32

124.56

Thermodynamic parameters (298 K and 1 atm)	B3LYP/6- 31G(d)	B3LYP/6- 311G(d, p)	
SCF energy (Hartree) Total energy (thermal), $E_{total}$ (kcal mol <sup>-1</sup> ) Heat capacity at const. volume, $C_{vib}$ (cal mol <sup>-1</sup> K <sup>-1</sup> ) Entropy, $S_{vib}$ (cal mol <sup>-1</sup> K <sup>-1</sup> ) Enthalpy, $H$ (kcal mol <sup>-1</sup> ) Vibrational energy, $E_{vib}$ (kcal mol <sup>-1</sup> ) Zero-point vibrational energy, $E_0$ (kcal mol <sup>-1</sup> )	-1583.251 286.809 101.164 188.227 17.269 285.032 270.133	-1583.566 284.851 101.604 188.461 17.313 283.074 268.131	
Rotational constants (GHz) A B C Dipole moment (Debye)	0.264 0.063 0.059 5.593	0.267 0.062 0.059 5.576	

B3LYP/6-31G(d) 3 Absorbance 2 1 Ω 150 200 250 300 350 400 Wavelength(nm)

Fig. 6. The experimental and the calculated UV-Vis absorption spectra of the title compound.

maticity of the benzene, triazole and pyridine rings. Then the  $n \rightarrow \pi^*$ transition is more significant due to the presence of lone pair of electrons in the oxygen and nitrogen atoms in the molecular structure. Some frontier molecular orbitals are shown in Fig. 7. As shown from Fig. 7, the electron clouds of the HOMO and HOMO-1 are delocalized all of the molecule and benzene moiety, respectively.

This orbitals are seem to be the  $\pi$ -bonding type orbital. LUMO is found mainly delocalized on triazole and pyridine rings but LUMO+1 is found mainly delocalized on carbonyl group. The energy gap of HOMO-LUMO explains the eventual charge transfer

Table 8

The calculated absorption wavelength ( $\lambda$ ), excitation energies ( <i>E</i> ), oscillat	or strength ( <i>f</i> ) and frontier orbital energies of compound (1) by TD-DFT method.
--	--

Methods	λ (nm)	<i>E</i> (eV)	f	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm LUMO}~(\rm eV)$	$E_{\text{HOMO}-1}$ (eV)	$E_{LUMO+1}$ (eV)
B3LYP 6-31G(d)	282.95 278.17 271.37	4.3819 4.4571 4.5689	0.2786 0.0790 0.0176	-6.430	-1.488	-6.572	-0.835
B3LYP 6-311G(d, p)	285.08 276.86 274.51	4.3490 4.4782 4.5165	0.3320 0.0140 0.0170	-6.631	-1.723	-6.817	-1.023
Experimental	274 256						



5.092

5.683

3.846

4 382

3.297

2.842

1.842

2.654

2 1 0 5

1.756

1.259

1.203

7 2 7 7

7.497

7.389

7.508

7.229

Experimental

B3LYP/6-311G(d,p)



compound by B3LYP/6-311G(d, p).

interaction within the optimized molecule, and this gap is found to be 4.942 eV and 4.908 eV by using B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets. Besides of these properties of the molecule, we have calculated ionization potential, electron affinity, electronegativity, chemical hardness and chemical softness of the molecule with DFT. The energy HOMO is sometimes considered as an approximation to the ionization potential while the energy LUMO is considered as an approximation to the electron affinity. The ionization potentials of the molecule are 6.430 and 6.631 eV for B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets, respectively. The electron affinity of the molecule are 1.488 and 1.723 eV for B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets, respectively. The electronegativity of the molecule are 3.959 and 4.177 eV for B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets, respectively. The chemical hardness of the molecule are 2.471 and 2.454 eV for B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets, respectively. The chemical softness of the molecule are 0.202 and 0.204 eV for B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets, respectively.

# 4. Conclusion

In this study, we investigate X-ray structure, IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR of the title compound. In addition to the experimental studies, most of the properties of the molecular structure have been calculated by using B3LYP/6-31G(d) and B3LYP/6-311G(d, p) basis sets. Single crystal structure has been compared the optimized molecular structure. The X-ray structure is found to be very slightly different from its optimized structures. The results show that the optimized bond lengths are slightly longer than the experimental values, and the optimized bond angles are slightly different from the experimental ones. It was noted that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase. Also, the other experimental results are in good agreement with the theoretical results.

### Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 808472. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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