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STRUCTURE AND DFT CALCULATIONS OF 2-{[3-METHYL-3-PHENYL-CYCLOBUTYL)-THIAZOL-2-YL]-HYDRAZONOMETHYL}-PHENOL

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The title compound 2-{[3-Methyl-3-phenyl-cyclobutyl)-thiazol-2-yl]-hydrazonomethyl}-phenol ($C_{21}H_{21}N_3S_1O_1$) crystallizes in the *P*-1 triclinic space group with $a = 5.8880(4)$, $b = 9.5618(5)$, $c = 17.0484(10)$ Å, $\alpha = 80.214(5)°$, $\beta = 80.532(5)°$, $\gamma = 80.116(5)°$. In addition to molecular geometry and packing from X-ray experiment, we have also calculated the molecular geometry and vibrational frequencies of the title compound in the ground state using density functional theory DFT (B3LYP) with the 6-31G(*d,p*) basis set. Apart from this, the structure of the title compound is characterized by ^{1}H NMR, ^{13}C NMR, IR and UV-vis. Spectra, and the experimental emission energies are compared with the HOMO—LUMO energy gaps calculated by the DFT method.

Keywords: crystal structure, IR spectroscopy, DFT calculations.

Various hydrazone compounds posses strong bactericidal, herbicidal, insecticidal, and fungicidal properties [1]. Some phenylhdrazone derivatives have been shown to be potentially DNA-damaging and are mutagenic agents [2]. In addition, hydrazones have been widely studied as chelating ligands for spectrophotometeric and fluorimetric determination of transition metal ions [3, 4]. It has been known that various thiazole derivatives show herbicidal, anti-inflammatory, anti-microbial, and anti-parasite activity [5] and also liquid crystal properties [6]. Because of their attractive properties, molecular and crystal structure analyses of hydrazone and thiazole compound have long been studied. On the other hand an alternative DFT method have been carried out for the equilibrium structure properties of a molecular system, such as geometry, vibrational frequency, electronic absorption spectra, etc. In this work, we have calculated the geometric parameters and vibrational frequencies of compound **I** in the ground state to distinguish the fundamentals from the experimental vibrational frequencies and geometric parameters using the DFT (B3LYP) method. The calculated geometric parameters and IR frequencies approximately agree with the experimental IR and X-ray values. Apart from this, the experimental emission energies were compared with the HOMO—LUMO energy gaps calculated by the DFT method.

EXPERIMENTAL

Measurements. FT-IR spectra were recorded on a KBr pellet with a Mattson 1000 FT-infrared spectrometer in the 4000—400 cm^{-1} range. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Mercury 400 MHz spectrometer.

Synthesis of the title compound. The compound was synthesized as shown in Scheme 1 by the following procedure. To a stirred solution of salicylaldehyde (10 mmol) in 30 ml of ethanol, thiosemi-

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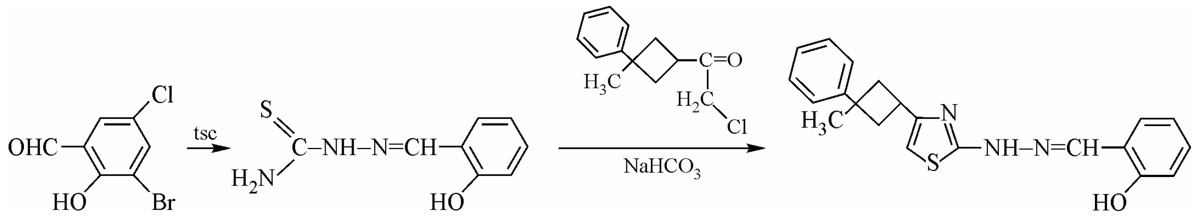

Scheme 1. Synthetic route for the synthesis of the target compound

carbazide (10 mmol) was added in portions. Subsequently, a solution of phenacyl chloride (10 mmol) in 20 ml of ethanol was added dropwise. After the addition of α-haloketone, the temperature was kept at 323—328 K for 2 h more. After cooling to room temperature the solution was made alkaline with an aqueous solution of NH_3 (5 %), and a light yellow precipitate separated. The precipitate was filtered off, washed with the aqueous NH_3 solution several times, and dried in air. Single crystals suitable for the crystal structure determination were obtained by slow evaporation of its ethanol solution. Yield: 76 %, melting point: 470 K. Characteristic IR bands: 3171 cm^{-1} ν(—OH), 3115 cm^{-1} ν(—N—H), 2957—2857 cm^{-1} ν(C—H aliphatics), 1616 cm^{-1} ν(C=N azomethine), 1578 cm^{-1} ν(C=N thiazole), 637 cm^{-1} ν(C—S—C thiazole). Characteristic ^1H NMR shifts (DMSO-d_6, δ, ppm): 1.46 (s, 3H, —CH_3 in cyclobutane), 2.34—2.50 (m, 4H, —CH_2— in cyclobutane), 3.57 (q, j = 8.78 Hz, 1H, >C—H in cyclobutane), 6.40 (s, 1H, =CH—S), 6.85 (dd, j_1 = 7.68 Hz, j_2 = 6.93 Hz, 2H, aromatics), 7.12—7.20 (m, 4H, aromatics), 7.27—7.31 (t, j = 7.68 Hz, 2H, aromatics), 7.53 (d, j = 7.32 Hz, 1H, aromatics), 8.19 (s, 1H, azomethine), 10.17 (s, 1H, —NH—D_2O exchangeable), 11.92 (s, 1H, —OH—D_2O exchangeable). Characteristic ^{13}C NMR shifts (DMSO-d_6, δ, ppm): 168.71, 156.72, 152.92, 152.17,

Table 1

Crystallographic data for **I**

Empirical formula	$C_{21}H_{21}N_3OS$
Formula weight	363.47
Temparature, K	296
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
a, b, c, Å	5.8880(4), 9.5618(5), 17.0484(5)
α, β, γ, Å	80.214(5), 80.532(5), 80.116(5)
Volume, $Å^3$	922.72(10)
Z	2
Calculated density, g/cm^3	1.308
μ, mm^{-1}	0.19
Crystal size, mm	0.52, 0.50, 0.14
θ range, deg.	26
Index ranges (h, k, l)	–7→7, –11→11, –21→21
Reflections collected	12883
Independent reflections (R_{int})	3628
Observed reflections [$I > 2\sigma(I)$]	2846
T_{min} / T_{max}	0.877 / 0.971
S	1.06
Final R indices [$I > 2\sigma(I)$]	0.038
wR indices [$I > 2\sigma(I)$]	0,099
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, $e\cdot Å^{-3}$	0.23 / –0.20

143.65, 131.00,128.85, 127.59, 125.90, 125.24, 120,63, 120.11, 116.76, 101.86, 40.85, 40.72, 38.95, 30.69.

X-ray crystallography. The data collection was performed at 296 K on a Stoe-IPDS-2 diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the SHELXL-97 program [7]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically. All hydrogen atoms of carbons were included using a riding model and refined isotropically with C—H = 0.93 Å (for phenyl groups), and C—H = 0.98 Å. $U_{iso}(H) = 1.2U_{eq}(C)$.

DFT calculations. Density functional theory (DFT) calculations of compound **I** have been performed using the GAUSSIAN 03 program [8]. The DFT (B3LYP) [9, 10] level with the 6-31G(*d,p*) basis set was used for the geometry optimization, frequency calculation, and orbital shapes. The ground-state geometries were obtained in the gas phase by full geometry optimization, starting from the structural data.

RESULTS AND DISCUSSION

Description of the crystal structure. Details of crystal parameters, data collection, structure solution, and refinement are given in Table 1. Title compound **I**, which is shown in Fig. 1, *a* with atom labeling, crystallizes in the *P*-1 triclinic space group. Hydrogen bonding geometries are listed in Table 2; selected bond distances and bond angles are shown in Table 3. Compound **I** contains thiazole, hydrazone, phenol, and cylobutane moities. The thiazole ring Cg2 (S1/C14/N1/C12/C13), the phenly ring Cg3 (C1—C6), and the phenol ring Cg4 (C16—C21) are planar. The dihedral angles between these planes are 74.44(5)°, 10.44(5)°, and 66.17(6)° for Cg3/Cg2, Cg2/Cg4, and Cg4/Cg3 respec-

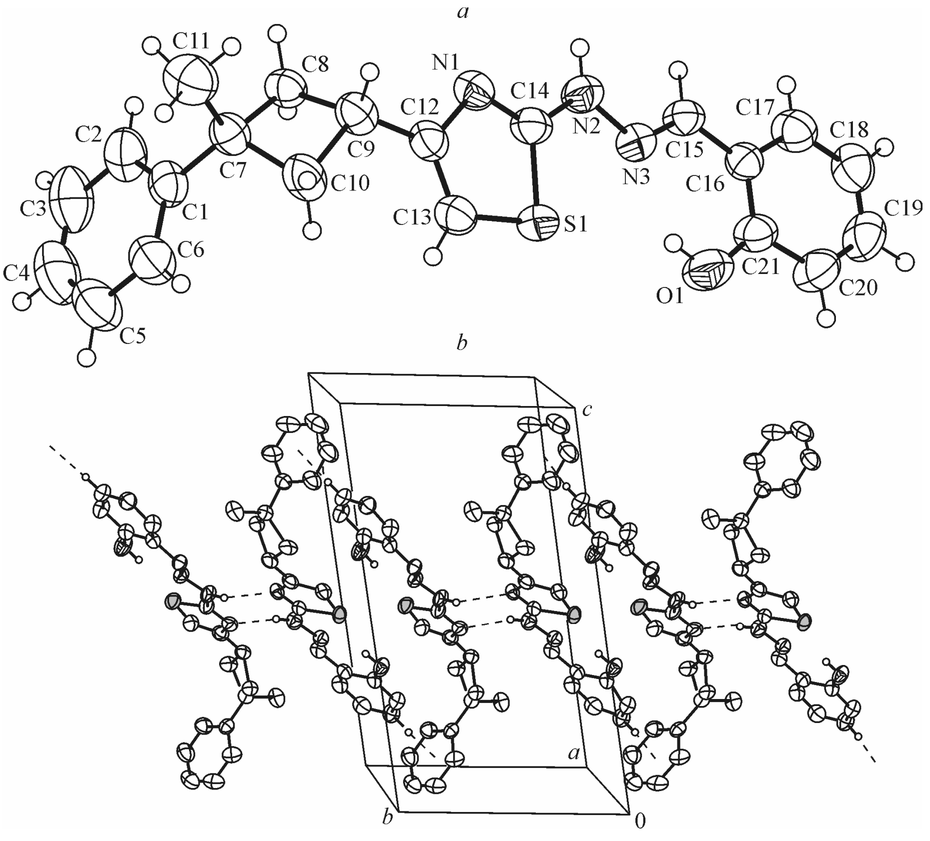

Fig. 1. Molecule of compound **I** showing the atom labelling scheme (*a*). A view of hydrogen bonding interacttions in compound **I** (*b*)

Table 2

Hydrogen bonding geometries for **I**

D—H...A/Cg	D—H, Å	H...A/Cg, Å	D...A/Cg, Å	D—H...A/Cg, deg.
N2—H2---N1[i]	0.86	2.24	3.0676(19)	161
C19—H19---Cg(3)[ii]	0.930	3.0967	3.845(2)	138.71

Symmetry code: [i] –*x*, 1–*y*, 1–*z*, [ii] –*x*, 2–*y*, 1–*z*.

Table 3

Optimized and experimental geometric parameters of the title compound

Bond lengths, Å	Experimental	Calculated (B3LYP)	Bond Angles, deg. Dihedral Angles, deg.	Experimental	Calculated (B3LYP)
S1—C14	1.733(18)	1.759	C7—C8—C9	89.25(13)	88.88
S1—C13	1.722(18)	1.752	C8—C9—C10	87.99(12)	88.62
N1—C14	1.319(2)	1.302	C9—C10—C7	90.02(13)	89.21
N1—C12	1.400(2)	1.388	C10—C7—C8	87.55(12)	87.88
N2—C14	1.347(2)	1.372	C13—S1—C14	88.82(9)	87.44
N2—N3	1.367(2)	1.352	C12—N1—C14	110.94(14)	110.40
N3—C15	1.273(2)	1.294	C14—N2—N3	113.69(13)	121.96
C9—C12	1.490(2)	1.497	N2—N3—C15	118.59(13)	118.62
C9—C8	1.552(2)	1.559	C14—N2—N3—C15	178.21(14)	–179.197
C9—C10	1.538(2)	1.549	S1—C14—N2—N3	–3.93(19)	–0.561
C7—C8	1.555(2)	1.564	N1—C14—N2—N3	176.58(15)	179.460
C7—C10	1.548(2)	1.565	O1—C21—C16—C15	3.62(26)	–0.006
C12—C13	1.342(3)	1.363			
C21—O1	1.348(2)	1.348			
S1—C14	1.733(18)	1.759			
S1—C13	1.722(18)	1.752			
N1—C14	1.319(2)	1.302			

tively. In the cyclobutane ring Cg1, the C8/C7/C10 plane forms a dihedral angle of 24.09(12)° with the C8/C9/C10 plane. Similar puckering of a cyclobutane ring has been reported (23.5°) [11]. The hydrazone group connecting 2-positions of the thiazole ring is aproximately planar with a 178.21(14)° torsion angle (C15—N3—N2—C14). Coumpound **I** has an O—H···N intramolecular hydrogen bond.The molecules of **I** are linked head-to-head by N—H···N hydrogen bonding. In this hydrogen bonding, the N2 atom of the hydrazone group at (*x*, *y*, *z*) acts as a donor to the N1 atom at (–*x*, 1–*y*, 1–*z*). This interaction results in a hydrogen bonded dimer of graph set motif R_2^2 (8) [12] ring at (0, 1/2, 1/2). R_2^2 (8) rings run parallel to the [100] direction at (*n*, 1/2, 1/2). Apart from this, the dimers are linked by the C—H...π intermolecular hydrogen bond. So, crystal packing is stabilized along the *b* axes (Fig. 2, *b*).

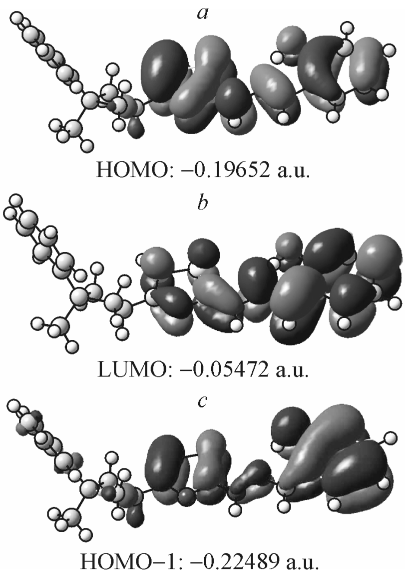
a
HOMO: –0.19652 a.u.
b
LUMO: –0.05472 a.u.
c
HOMO–1: –0.22489 a.u.

Fig. 2. Frontier orbitals in compound **I**

Table 4

Comparison of the selected IR spectral data (frequencies in cm^{-1}) *of* **I** *with the calculated spectral data in the gas phase*

Assignment	Experimental	B3LYP/6-31G(*d,p*)	Assignment	Experimental	B3LYP/6-31G(*d,p*)
ν(NH)	3115 w	3539	ν(C=N) in azomethine	1616 m	1679
ν(OH)	3171 s	3512	ν(C=N) in thiazole	1578 vs	1631
ν(CH) aromatic	3073 w—3058 w	3281—3171	ν(C=C) in thiazole	1490 w	1580
ν(CH) aliphatic	2957—2857 s	3126—3035			

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w = weak; m = medium; s = strong; vs = very strong.

DFT calculations. We have calculated the theoretical structural parameters and vibrational spectra of the title compound using the B3LYP method with the 6-31G(*d,p*) basis set. We have compared our calculations of title compound **I** with the experimental result. It should be noted that the experimental data belong to the solid phase, whereas the calculated data correspond to the isolated molecule in the gas phase. However, the selected experimental and computational bond distance and angles in Table 3 clearly show that both data only slightly differ from each other. According to our calculations, the DFT method correlates well for bond lengths. For example, the N2—N3 single bond length is 1.367 and 1.352 Å obtained from X-ray and DFT respectively, which matches well with literature value for the N—N single bond [13]. The largest difference between the experimental and calculated S1—C13 length is about 0.030 Å. However, the biggest deviation occurs in the C14—N2—N3 angle by ca 8.27° due to the N—H...N intermolecular hydrogen bonding.

In Table 4, the selected IR spectra for compound **I** are given together with the data obtained from DFT calculations and their assignments. From the analyses of the experimental data the absorption band centered at 3115 cm^{-1} is assigned to the ν_{str}(N—H) vibration of the hydrazone group. The strong band observed at 3171 cm^{-1} is attributed to the absorption of the ν_{str} (O—H) vibration of phenol. Both the ν_{str}(N—H) and ν_{str} (O—H) bands are shifted to the low frequency region due to the intermolecular N—H···N and intramolecular O—H···N hydrogen bonding respectively. In the 3073—3058 cm^{-1} region, stretching modes of aromatic CH hydrogen appear. The symmetric and asymmetric stretching modes of aliphatic CH hydrogen are observed in the 2957—2857 cm^{-1} region. The sharp band at 1616 cm^{-1} is due to the C=N (in azomethine) stretching. The very strong band observed at 1578 cm^{-1} belongs to C=N stretching (in thiazole), and the absorption band at 1490 cm^{-1} belongs to C=C stretching (in thiazole). In DFT calculations unscaled ν_{str}(O—H) and ν_{str}(N—H) frequencies are at 3512 cm^{-1} and 3539 cm^{-1} respectively. The differences between experiment and DFT calculations for ν_{str}(O—H) and ν_{str}(N—H) are greater than for the other vibrations. The reason for these differences is that crystal packing is mainly stabilized by the intra-intermolecular hydrogen bonds that is highly effective in the absorption bands [14].

We have also performed molecular orbital (MO) calculations to assign the emission bands. The calculations indicate that compound **I** has 96 occupied MOs. Fig. 2 shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) for **I**. The calculated value of the energy separation between HOMO and LUMO is 0.1418 a.u. (3.8586 eV) and is comparable with the experimentally measured emission energy value of 3.49 eV. Another emission band at 5.07 eV is attributed to the HOMO-1→LUMO transition that has a 0.17017 a.u. (4.6305 eV) energy gap. These emission bands of the molecule may be assigned to the n—π^* and π—π^* electronic transitions respectively. The deviation between the experimental and calculated energy gaps may be due to the intermolecular interactions and ground-state considerations in the DFT calculations.

Supplementary Data. CCDC 735311 contains the supplementary crystallographic data for 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; email: deposit@ccdc.cam.ac.uk].

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