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Synthesis, crystal structure, IR, ¹H NMR and theoretical calculations of 1,2,4-triazole Schiff base



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HIGHLIGHTS

- The calculated and experimental data on geometric parameters of the molecule were present.
- The FT-IR and ¹H NMR spectra of the molecule was studied through experiment and calculation.
- The HOMO-LUMO and NBO of the synthetic substance were being presented for the first time.

G R A P H I C A L A B S T R A C T

5-Propyl-4-amino-1,2,4-triazole Schiff base was characterized by X-ray single crystal diffraction technique. The molecular geometry was optimized using density functional theory (DFT/B3LYP) and hartree fock (HF) methods. From the optimized geometry of the molecule, vibrational frequencies, HOMO-LUMO and natural bond orbital (NBO) were calculated with B3LYP /6-311G+(d,p). In addition, gauge independent atomic orbital (GIAO) ¹H NMR chemical shift values was calculated with B3LYP/6-311G+(d,p) and HF/6-311G+(d,p).



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ABSTRACT

5-Propyl-4-amino-1,2,4-triazole Schiff base was characterized by FT-IR, ¹H NMR and X-ray single crystal diffraction techniques. The compound crystallizes in the triclinic space group *p*-1 with *z* = 2. The molecular geometry was optimized using density functional theory (DFT/B3LYP) and hartree fock (HF) methods with the 6-311G+(d,p) and 6-311G basis set in ground state. From the optimized geometry of the molecule, vibrational frequencies, HOMO–LUMO and natural bond orbital (NBO) were calculated with B3LYP/6-311G+(d,p) level. In addition, gauge independent atomic orbital (GIAO) ¹H NMR chemical shift values was calculated at B3LYP/6-311G+(d,p) and HF/6-311G+(d,p) level.

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1. Introduction

There is currently considerable interest given to 1,2,4-triazole derivatives due to their broad-spectrum activities. This kind of

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compounds have potential applications in the fields of pesticides and medicines possessing antifungal [1], antimicrobial [2–4], antitumor [5] and anticancer [6] properties. Especially, many 1,2,4-triazole compounds have been developed as marketed products, such as fluconazole, rizatriptan and terconnazole.

Schiff base derivatives of 1,2,4-triazoles have also been found to possess pharmacological activities [7–10]. In recently 10 years, our research group have designed and synthesized a series of 1,2,4-triazole Schiff bases. The results of biological activity test indicated that some compounds showed good antifungal activity and potential application value. With the aim to screen higher biological activity compounds, 5-propyl-4-amino-1,2,4-triazole Schiff base was synthesized by 1,2,4-triazolethione with p-methoxyacetophenone under refluxing. The crystal was got from ethanol and the crystal structure was obtained by X-ray diffraction. The crystallographic Data Center, CCDC-889088. In this paper, the crystal structure and theoretical study using the DFT/B3LYP and HF methods were reported firstly.

In recent years, computational chemical models are playing an ever increasing role in chemical research. HF and DFT methods are the common used methods in many reported references [11,12]. Among DFT calculation, Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) is the best predicting results for vibrational wave numbers for moderately lager molecule [13]. Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially in systems containing extensive electron conjugation and/or electron lone pairs [14]. Consequently, the geometry optimization of target compound was carried out using HF and DFT/B3LYP methods. Vibrational frequencies, natural bond orbitals and HOMO–LUMO were calculated by DFT/B3LYP method.

2. Experimental and theoretical methods

2.1. The preparation of single crystal

The synthetic rout of 5-propyl-4-amino-1,2,4-triazole Schiff base in this experiment is as Fig. 1 [15]. Thiocarbazide (0.047 mol) was added to n-butyric acid (0.05 mol) in a reaction flask, the mixture was refluxed for 5 h, then cooled to room temperature and filtration. The crude product thus obtained was crystallized from water. m.p.: 101.1–102.1 °C (Lit. [16] 101–103 °C). 5-propyl-4-amino-1,2,4-triazolethione (5 mmol) was added to a solution of p-methoxy acetophenone (5 mmol) in ethanol (20 ml) and glacial acetic acid (2 ml), the mixture was refluxed for 30 min. The reaction mixture was left standing overnight and then filtration. The crude product was crystallized from absolute ethanol, obtaining target compound as a white solid in a yield of 79%. The saturated solution of this compound dissolved in ethanol was stood at room temperature for half a month by slowing evaporation, yielding colorless single crystals suitable for X-ray analysis.

2.2. X-ray crystal structure determination

A colorless single crystal of the title compound with dimensions of 0.33 mm \times 0.27 mm \times 0.13 mm was selected for X-ray diffraction analysis. The X-ray diffraction data were collected on a Bruker SMART-APEX II CCD diffractometer [296(2)K] equipped with a graphite monochromated Mo K α radiation (λ = 0.71073 Å) by using $\omega - 2\theta$ scan technique at room temperature. A total of 3786 reflections were collected in the range of $1.73 < \theta < 25.10^\circ$, of which 2636 were independent with $R_{int} = 0.0162$ and 182 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods with SHEL-XS-97 [17], and refined using the full-matrix least squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms using SHELXL-97 [18]. All hydrogen atoms except H atom of N(2), which is confirmed in difference Fourier syntheses, were located theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Details of the data collection conditions and the parameters of refinement process are given in Table 1. The molecular structure and packing diagram are shown in Figs. 2 and 3. The main bond lengths and bond angles are shown in Table 2.

2.3. Computational details

The Hartree–Fock and density functional theoretical computations of synthesized compound were performed at the Hartree–Fock and Becke–Lee–Parr hybrid exchange correlation three-parameter functional (B3LYP) level with standard 6-311G and 6-311G+(d,p) basis set to derive the complete geometry optimization. The vibrational frequencies were calculated at B3LYP/6-311G+(d,p) level of theory for the optimized structure and the obtained frequencies were scaled by 0.9613 [19]. In addition, natural bond orbitals (NBO) was also investigated under B3LYP/6-311G+(d,p) optimized geometry. Furthermore, GIAO ¹H chemical shift values (with respect to TMS) were calculated using the HF and DFT/B3LYP method with the 6-311G+(d,p) basis set. All calculations reported in this work were carried out with the GAUSSIAN 03 program [20].

3. Results and discussion

3.1. Crystallography

From the Table 2, the bond lengths of 1.283 Å in title compound between atoms N(4) and C(6) is similar to those observed in other Schiff bases [21], indicating it is double bonds. The S(1)=C(5) bond length of 1.681 Å is intermediate between S=C(1.43 Å) and S–C (1.82 Å) may be due to the conjugation effects of 1,2,4-triazole in the molecules. The bond length of C(11)–O(1) 1.357 Å is shorter than bond length of C(14)–O(1) 1.419 Å because C(11) is the carbon in the benzene ring. From the molecular structure, it can be calculated that the dihedral angle between the triazole ring and benzene ring is 78.83°, which indicates that the two rings are not coplanar in the molecular structure. The X-ray analysis also reveals



Fig. 1. The synthetic route of the title compound.

Tab	ole	1				
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Crystal	data	and	structure	refinement	of	target	compound	1.
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Chemical formula	C ₁₄ H ₁₈ N ₄ OS
Formula weight (g mol ⁻¹)	290.38
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	p-1
a (Å)	7.7598(12)
b (Å	8.4874(12)
c (Å	12.4768(18)
α (°)	70.760(2)
β (°)	83.251(2)
γ (°)	75.398(2)
Volume (Å ³)	750.24(19)
Ζ	2
D_{calc} (Mg m ⁻³)	1.285
Absorption coefficient (mm ⁻¹)	0.217
F(000)	308
θ range (°)	1.73-25.10
Limiting indices	$-8 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 9$, $-14 \leqslant l \leqslant 13$
Reflections collected	3786
Reflections unique	2636 [R(int) = 0.0162]
Completeness to θ = 25.10	98.9%
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F^2	1.048
Final R indices $[l > 2\sigma(l)]$	$R_1 = 0.0424, wR_2 = 0.1243$
R indices (all data)	$R_1 = 0.0523, wR_2 = 0.1429$
Largest diff. peak and hole $(e \cdot \dot{A}^{-3})$	0.262 and -0.227



Fig. 2. The ORTEP diagram of target compound.

that, the substituted benzene ring and the triazole ring are on the opposite sides of the C=N double bond (Fig. 2). The torsion angle of N(3)-N(4)-C(6)-C(8) is 179.02°, which means that the C=N double bond is in the *E* configuration [9]. Molecule is linked through intermolecular N-H···S hydrogen bonds and the distance between the donor and acceptor atoms is 3.304 Å.

3.2. Optimized structure

The structure of title compound was optimized by the B3LYP and HF methods and the optimized structure was showed in Fig. 4. From Fig. 4, we can see that the benzyl ring and triazole ring are on the opposite side of the double bond, and two rings are not coplanar in the molecular structure. The optimized bond lengths, bond angles and torsion angles of this compound are calculated by HF and DFT methods with 6-311+G(d,p) and 6-311G basis sets are listed in Table 2. It could be seen from Table 2 that the computed bond lengths, bond angles and dihedral angles are in good agreement with experimental data. The average absolute deviations of bond lengths and bond angles are 0.01 Å, 0.80° for B3LYP/6-311G+(d,p), and 0.20 Å, 0.81° for B3LYP/6-311G, and 0.19 Å, 1.06° for HF/6-311G+(d,p), and 0.11 Å, 1.13° for HF/6-311G, respectively. Compared with the experimental values, the calculated results show that the lager basis sets 6-311G+(d,p) is more suitable than 6-311G at B3LYP method. There is no remarkable difference between the 6-311G+(d,p) and 6-311G basis set at HF method. According to these results, it may be concluded that the B3LYP/6-311G+(d,p) calculation well reproduce the geometry of the target Compound.

3.3. IR spectrum

Among the theoretical methods, DFT-based calculations, because of their reasonable computational costs and rather reliable results, are the most popular ones to predict the structure through comparison between predicted and experimental IR spectra [22]. The IR (KBr pellets) spectrum was recorded on a Brucker Equinox-55 spectrometer. Based on optimized geometries, the vibrational frequencies are calculated with the B3LYP functional and the 6-311G+(d,p) basis set, the observed and calculated data of the IR spectrum are given in Table 3 and Fig. 5. A comparison of the calculated and experimental frequencies is show a slightly difference, the calculated IR spectrum data were slightly lower than the experimental value. The suggested reasons were as following: first, theoretical DFT studies support the experimental works in particular in the vibrational analysis but these studies are generally limited to the simple harmonic approach known to provide an approximate description requiring the use of a scaling factor to obtain the vibrational frequencies [23]. Second, the computational data were gained when the dye molecules were in isolated state of vacuum condition, however, the experimental data were obtained when they were solid compound.

The bands observed at 2925 and 3097 cm⁻¹ in the IR spectrum are assigned to the C—H and N—H stretching modes. The theoretically compound frequencies for C—H and N—H stretching modes by B3LYP/6-311+G(d,p) method are 2894 and 3017 cm⁻¹, showing



Fig. 3. The packing diagram of target compound.

Table 2

The selected bond lengths (A), bond angles and torsion angles (°) for target compound determined by X-ray diffraction, DFT and HF calculations.

	X-ray	DFT/B3LYP				HF			
		6-311G+(d,p)	A.D.	6-311G	A.D.	6-311G+(d,p)	A.D.	6-311G	A.D.
Bond lengths									
O(1)-C(11)	1.357	1.385	0.03	1.386	0.03	1.340	0.02	1.366	0.01
O(1)-C(14)	1.419	1.424	0.01	1.455	0.04	1.402	0.02	1.429	0.01
S(1)-C(5)	1.681	1.669	0.01	1.712	0.03	1.677	0.00	1.722	0.04
N(1)-C(4)	1.309	1.301	0.01	1.319	0.01	1.272	0.04	1.287	0.02
N(1)-N(2)	1.377	1.370	0.01	1.399	0.02	1.359	0.02	1.379	0.00
N(2)-C(5)	1.346	1.359	0.01	1.364	0.02	1.329	0.02	1.333	0.01
N(3)-C(4)	1.385	1.387	0.00	1.397	0.01	1.377	0.01	1.385	0.00
N(3)-N(4)	1.422	1.394	0.03	1.413	0.01	1.387	0.04	1.398	0.02
N(4)-C(6)	1.283	1.293	0.01	1.309	0.03	1.268	0.02	1.283	0.00
Bond angles									
C(11)-O(1)-C(14)	118.81	118.94	0.13	119.45	0.64	120.26	1.45	121.71	2.90
C(4) - N(1) - N(2)	104.24	104.30	0.06	104.04	0.20	104.60	0.36	104.77	0.53
C(5)-N(2)-N(1)	114.00	114.72	0.72	114.32	0.32	113.89	0.11	113.44	0.56
C(5)-N(3)-C(4)	109.38	108.69	0.69	109.26	0.12	108.31	1.07	109.01	0.37
C(5)-N(3)-N(4)	124.42	126.52	2.10	126.89	2.47	126.59	2.17	127.02	2.60
N(1)-C(4)-N(3)	109.78	110.73	0.95	110.45	0.67	110.50	0.72	109.83	0.05
N(2)-C(5)-S(1)	129.41	128.43	0.98	128.10	1.31	127.85	1.56	127.54	0.89
Torsion angles									
N(3)-N(4)-C(6)-C(8)	179.02	-175.32	3.70	-175.90	3.12	-176.31	2.71	-177.06	1.96
N(2)-N(1)-C(4)-N(3)	1.00	1.79	0.79	1.58	0.58	1.65	0.65	1.39	0.39
N(4)-N(3)-C(4)-C(3)	12.40	14.60	2.20	13.18	0.78	14.15	1.75	12.72	0.32
C(14)-O(1)-C(11)-C(12)	-177.30	-179.43	2.13	-179.25	1.95	-179.25	1.95	-179.25	1.95



Fig. 4. The optimized structure of target compound within numbering of atoms obtained at B3LYP/6-311+G(d,p) level of theory.

Table 3					
Comparison	of selected	experimental	and calculated	vibrational spectrum.	

No.	Exp.		Calcd. B3LYF	P/6-311 g+(Vibratory feature	
	Freq. ^a	Int.(IR)	Non scaled	Scaled ^b	Int.(IR)	
1	3097	w	3139	3017	21.15	N—H
2	2925	m	3011	2894	56.98	C—H
3	1583	VS	1628	1564	337.51	C=N
4	1502	S	1488	1430	138.85	C=S
5	1317	S	1434	1378	118.91	C—H
6	1273	VS	1288	1153	324.77	N—H
7	1171	S	1197	1150	156.04	C—N
8	1030	m	1054	1013	40.81	С—О—С
9	831	m	848	815	50.86	С—Н

^a Frequencies in cm⁻¹.

^b Scaling factor using 0.9613; vs: very strong, s: strong, m: middle, w: weak.

excellent agreement with recorded spectrum as well as literature data [24,25]. The typical vibration frequency of N=C stretching mode at 1583 cm⁻¹, which was of lower field than the general vibration frequency of C=N (1690–1640 cm⁻¹), proving that the aryl ring and triazole ring which were near the C=N bound had strong conjugative effects [26]. The band observed at 1502 cm⁻¹ is assigned to the (S=C) stretching modes and there is no absorption at 2565–2550 cm⁻¹ (S–H), manifesting title compound is mainly exist in keto configuration, and this result is in agreement with the crystal structure. This S=C stretching mode was calculated at 1430 cm⁻¹ for B3LYP/6-311G+(d,p) level and compares well with the value reported previously(1500 cm⁻¹, 1452 cm⁻¹) [14]. The C–H out-of-plane bending vibration generally lie in the range 950–800 cm⁻¹ [27], the experimental value and calculational value are 831 cm⁻¹ and 815 cm⁻¹, respectively.

Table 4							
Theoretical and experimental	¹ H NMR (All	values in	ppm) f	or the t	arget	compoun	ć

Proton	Exp.	Calcd.							
		B3LYP/6-311g+(d	,p)	HF/6-311g+(d,p)					
	$\delta_{exp.}$	$\delta(^{1}H)$	A.D.	$\delta(^{1}H)$	A.D.				
3H(1C CH ₃)	0.97	0.79 0.86 1.25	0.18 0.11 0.28	1.03 1.07 1.08	0.06 0.10 0.11				
2H(2C CH ₂)	1.72	1.80 1.91	0.08 0.19	1.85 1.85	0.13 0.07				
3H(7C CH ₃)	2.35	2.00 2.02 2.42	0.35 0.33 0.07	1.98 2.12 2.32	0.37 0.23 0.03				
2H(3C CH ₂)	2.58	2.07 2.57	0.51 0.01	2.37 2.52	0.21 0.06				
1H(2N NH)	12.23	8.53	3.70	8.78	3.45				
3H(14C O-CH ₃)	3.88	3.61 3.61 3.99	0.27 0.27 0.11	3.66 3.68 4.10	0.22 0.20 0.11				
2H(10C 12C Ar—H)	6.98	6.81 7.05	0.17 0.07	7.45 7.07	0.47 0.07				
2H(9C 13C Ar—H)	8.01	7.78 8.85	0.23 0.74	8.24 9.34	0.23 1.33				

A.D. refers to the absolute deviation.

3.4. ¹H NMR spectrum

The ¹H NMR spectra was measured with a Varian unity INOVA-400 nuclear magnetic resonance and the chemical shifts were expressed in ppm relatively to TMS. The gauge-including atomic orbital (GIAO) 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 [14]. GIAO ¹H chemical shift values were calculated using the HF and DFT/B3LYP methods with the 6-311G+(d,p) basis set. The results of this calculation with respect to TMS are shown in Table 4. The experimental ¹H NMR data of target compound in CDCl₃ with TMS as internal standard was also displayed in Table 4 and the spectra of the ¹H NMR was presented in Fig. 6.

The proton chemical shift (¹H NMR) of organic molecules generally varies greatly with the electronic environment of the proton. Hydrogen attached or nearby electron-withdrawing atom or group can decrease the shielding and move the resonance of attached proton towards to a higher frequency, whereas electron-donating atom or group increases the shielding and moves the chemical shifts towards to a lower frequency [28]. The chemical shifts of aromatic protons of organic molecules are usually observed in the range of 7.00-8.00 ppm. The signals of the 4 aromatic protons of the target compound were reported at 6.98-8.01 ppm in CDCl₃ solvent, calculated at 6.81-8.85 ppm for B3LYP level and 7.07-9.34 ppm for HF level, respectively. The signal of the N-H protons in the experiment spectrum is 12.23 ppm, while this signal is observed computationally at 8.53 and 8.78 ppm for two methods due to this proton is active hydrogen. The chemical shift value of $3H(1C CH_3)$ is lower than the $3H(7C CH_3)$ and $3H(14C O-CH_3)$ due to the electronic charge density around of the triazole and benzene ring [29].

As can be seen from Table 4 and Fig. 6, the theoretical ¹H chemical shift results for the target compound are generally closer to the experimental observations except the active hydrogen. The comparison of mean absolute deviation is 0.38 ppm with B3LYP/ 6-311G+(d,p) level and 0.41 ppm with HF/6-311G+(d,p) level, indicating that the ¹H chemical shift obtained by B3LYP method show good correlation with the experimental values than HF method. Compared with the experimental chemical shifts, correlation graphics based on the calculations are presented in Fig. 7. The ¹H chemical shifts correlation values are 0.9960 and 0.9946 for B3LYP/6-311g+(d,p) and HF/6-311G+(d,p), respectively.

3.5. NBO charges

Natural atomic charges were calculated by B3LYP/6-311+G(d,p) method and the results are listed in Table 5. The magnitudes of all carbon atoms in the benzene ring are negative excepted C29 that connected to of oxygen atom. The charge value for S2 is negative and found to be -0.24467 at the B3LYP/6-311+G(d,p) level of calculation. Compared with all other N atoms in this molecular, N4 atom is having maximum negative charge at DFT/B3LYP methods. The magnitudes of the hydrogen atomic charges are found to be positive at the basis sets ranging from 0.172 to 0.419 at B3LYP/6-311+G(d,p) method. The charge value for H38 connected to of N4 atom is obviously more than other hydrogen atoms because of H38 has intra-molecular hydrogen bond with the S2 atom.



Fig. 5. Comparison of experimental and calculated spectra of target compound. (a) Calculated with B3LYP/6-311+G(d,p). (b) Experimental spectra.

Table 5

The charge distribution calculated by natural bond orbital (NBO) using B3LYP/6-311G+(d,p) method of target molecule.

Atoms	B3LYP(NBO)	Atoms	B3LYP(NBO)	Atoms	B3LYP(NBO)	Atoms	B3LYP(NBO)
01	-0.53352	C11	-0.38300	H21	0.22745	H31	0.22226
S2	-0.24467	H12	0.20445	H22	0.25014	C32	-0.15598
N3	-0.30180	H13	0.20418	H23	0.21676	H33	0.21023
N4	-0.39411	C14	-0.42830	C24	-0.14061	C34	-0.20956
N5	-0.30540	H15	0.21849	C25	-0.12691	H35	0.19490
N6	-0.31708	H16	0.22935	H26	0.23099	H36	0.17386
C7	-0.57315	C17	0.41473	C27	-0.28786	H37	0.17254
H8	0.20478	C18	0.21047	H28	0.21472	H38	0.41946
H9	0.19336	C19	0.33833	C29	0.34612		
H10	0.19408	C20	-0.64777	C30	-0.24196		

Tab	1.	C
IdD	Ie.	O.

Si	gnificant	donor-accer	ntor inter	actions of	f target	compound	and th	eir second	order	perturbation	energies
U 1	Simulatic	uonor uccc	ptor miter		i tui get	compound	und th	ch second	oraci	percurbation	CHCIGICS

Donor NBO (i)	Acceptor NBO (j)	E(2) (kcal/mol) ^a	$E(j) - E(i) (a.u.)^{b}$	<i>F</i> (<i>i</i> , <i>j</i>) (a.u.) ^c
BD(2) N5-C18	BD*(2) N3-C17	26.03	0.36	0.090
BD(2) C24-C25	BD*(2) N6-C19	18.79	0.27	0.066
BD(2) C24-C25	BD*(2) C27-C29	17.42	0.27	0.061
BD(2) C24-C25	BD*(2) C30-C32	22.70	0.28	0.072
BD(2) C27-C29	BD*(2) C24-C25	25.10	0.29	0.077
BD(2) C30-C32	BD*(2) C27-C29	22.38	0.28	0.072
LP(2) O1	BD*(2) C27-C29	31.34	0.34	0.098
LP(3) S2	BD*(2) N5-C18	95.94	0.11	0.098
LP(1) N4	BD*(2) N3-C17	23.81	0.28	0.075
LP(1) N4	BD*(2) N5-C18	68.77	0.20	0.115
BD*(2) N5-C18	BD*(2) N3-C17	17.98	0.08	0.046
BD*(2) N6-C19	BD*(2) C24-C25	144.17	0.01	0.072
BD*(2) C27-C29	BD*(2) C24-C25	252.71	0.01	0.082
BD*(2) C27-C29	BD*(2) C30–C32	277.67	0.01	0.083

^a E(2) means energy of hyperconjucative interactions.

^b Energy difference between donor and acceptor *i* and *j* NBO orbitals.

^c F(i,j) is the Fock matrix element between *i* and *j* NBO orbitals.

3.6. NBO analysis

Natural Bound Orbital (NBO) analysis give strong insight in the intra and inner molecular bonding and interaction among bonds, and also provide a convenient basis for investigation of charge transfer or conjugative interactions in molecular system. The second order Fock matrix was carried out to evaluate the donoracceptor interactions in the NBO analysis. For each donor (*i*) and acceptor (*j*), the stabilization energy $E^{(2)}$ associates with electron delocalization between *i* and *j* is estimated as [30]

$$E^{(2)} = -q_i(F_{ij}^2/\varepsilon_j - \varepsilon_i)$$



Fig. 6. Experimental ¹H chemical shift spectra of target compound.



Fig. 7. Correlation graphics between the experimental and theoretical ¹H NMR chemical shift values of target compound.



Fig. 8. Plots of the frontier orbitals of target compound by B3LYP/6-311G+(d,p) method.

where q_i is the donor orbital occupancy, ε_j and ε_i are diagonal elements and $F_{i,j}$ is the off diagonal NBO Fock matrix element.

In NBO analysis, large E(2) value shows the intensive interaction between electron-donors and electron-acceptors, and the greater the extent of conjugation of the whole system, the selected second-order perturbation theory analysis of the Fock matrix in NBO basis were presented in in Table 6. The interaction BD*(2) C27–C29 \rightarrow BD*(2) C30–C32 has the highest E(2) value around 277.67 kcal/mol and hence gives the strongest stabilization to the structure. Similarly, the interactions BD*(2) C27–C29 \rightarrow BD*(2) C24–C25, BD*(2) N6–C19 \rightarrow BD*(2) C24–C25 and the interaction initiated by lone pair of LP(3) S2, LP(1) N4 \rightarrow BD*(2) N5–C18 are giving stabilization to the structure because of their higher *E*(2) values.

3.7. Frontier molecular orbitals

Highest occupied molecular orbital (HOMO), which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand; lowest unoccupied molecular orbital (LUMO) can be thought the innermost orbital containing free places to accept electrons [31]. The HOMO–LUMO gap is used as a direct indicator of kinetic stability. A large HOMO–LUMO gap implies high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electrons to a high-lying LUMO or to extract electrons from a low-lying HOMO [32]. Meanwhile, a molecular with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [33].

The energy of the FMOs such an the highest occupied MO (HOMO) and the lowest (LUMO) have been calculated and the pictorial illustrations of the FMOs of title compound have been given in Fig. 8. The calculations indicate that target compound has 77 occupied molecular orbitals. It is clear from the figure that while the HOMO orbital is mainly delocalized on the benzene ring LUMO orbital is delocalized on triazole ring and S1 atom. The value of the energy separation between the HOMO and LUMO is 0.139 a.u.

4. Conclusions

In this paper, 5-propyl-4-amino-1,2,4-triazole-3-thione Schiff base was synthesized and characterized by spectroscopic (FT-IR and 1H NMR) and structural (single-crystal X-ray diffraction) techniques. The geometric parameters of target compound have been calculated using HF and DFT (B3LYP) method with the 6-311G and 6-311G+(d,p) basis sets and compared with the experimental findings. The results showed that the calculated geometric parameters obtained by B3LYP/6-311G+(d,p) method had a better agreement with the experimental data than HF method. FT-IR and 1H NMR spectra have been recorded and analyzed. The theoretically computed spectra were found good agreement with experimental FT-IR and 1H NMR spectra. The NBO, HOMO and LUMO energy of 5-propyl-4-amino-1,2,4-triazole-3-thione Schiff base in the ground state have been calculated by using density functional theory. The value of the energy gap between the HOMO and LUMO reveals that charge transfer may be taking place from the benzene ring to triazole ring.

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