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# Experimental and Computational Study on Molecular Structure, Natural Bond Orbital Analysis, Vibrational and Electronic Investigations of 1h-1,2,4-Triazole-3-Thiol and 2-Amino-1,3,4-Thiadiazole

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# ABSTRACT

The FT-IR and FT-Raman spectra of 1h-1,2,4-triazole-3-thiol (HTZT) and 2-amino-1,3,4thiadiazole (ATDZ) have been measured in the regions 400-4000 and 50 - 3500 cm-1 respectively. Utilizing the observed FT-IR and FT-Raman data, a complete vibrational assignment and analysis of the fundamental modes of the title compounds were carried out. The vibrational frequencies which were determined experimentally are compared with those theoretical frequencies from force field calculation based on B3LYP/6-311++G(d,p) method. Stability of the compound arising from hyperconjugative interactions and charged localization has been analysed using natural bond orbital analysis. The 1H and 13C nuclear magneticresonance (NMR) chemical shifts of the compounds were calculated by the gauge independentatomic orbital (GIAO) method and compared with experimental results. HOMO-LUMO analyses have been done for the title compounds.

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# Introduction

Recently, more attention has been focused on 1,2,4-triazole and 1,3,4-thiadiazole derivatives due to their usefulness in different areas of biological activities and as industrial intermediates. 1,2,4-triazole derivatives are known to exhibit antimicrobial [1-5], antitubercular [6], anticancer [7,8], anticonvulsant [9] anti-inflammatory and analgesic properties [10]. The arrangement of three basic nitrogen atoms in triazole ring induces the antiviral activities in the compounds containing triazole ring [11]. A series of 1,2,4-triazole derivatives have been extensively employed in agriculture as herbicides [12]. Certain 1,2,4-triazole also find applications in the preparation of photographic plates, polymers and as analytical agents [13]. The mercapto-substituted 1,2,4-triazole ring systems have been studied rather well, and so for a great variety of biological activities have been reported for them, such as antibacterial [14], antifungal [15-17], anticancer [18], anti HIV [19], etc.,

The 1,3,4-thiadiazole-2-amino derivate are mainly of great pharmacological and medicinal interest because they exhibit a wide range of anticancer activity [20-25], together with in vivo conditions [26-28], and the mechanism of action attributed to each derivative are strongly depending on the type of modifications of 1,3,4-thiadiazole ring [29-31]. To the best of our knowledge, no detailed spectroscopic investigation has been made on the title compound consideration of the above factors motivated us to undertake this detailed spectroscopic investigation.

The aim of the present work is to describe and characterized the molecular structure, vibrational spectra, electronic quantum chemical investigation and chemical shifts on the title compounds such as 1h-1,2,4-triazole-3-triazole-3-thiol (HTZT) and 2-amino-1,3,4-thiadiazole (ATDZ). For this purpose, geometry optimization of both titled structures and its corresponding frequencies were calculated by using the DFT/B3LYP and DFT/LSDA combinations. The molecular force fields were calculated by using a generalized valence force field (GVFF) together with the SQM methodology [32]. It is also planned to have theoretical determination of atomic charges, HOMO-LUMO energy gaps, thermodynamic properties and NBO analysis of the title compound using DFT methods.

# Experimental

The fine polycrystalline sample of 1h-1,2,4-triazole-3-thiol (HTZT) and 2-amino-1,3,4-thiadiazole (ATDZ) were purchased from commercial sources and they were used as such without further purification. The room temperature Fourier transform infrared spectra of the title compound was measured in the region 4000-400 cm<sup>-1</sup> at a resolution of  $\pm 1$  cm<sup>-1</sup> using a JASCO FT/IR-6300 spectrometer. KBr pellets were used in the spectral measurements. Boxcar apodization was used for 250 averaged interferograms collector for both the sample and background.

The FT-Raman spectrum of the title compound was recorded on a BRUKER RFS 100/S model interferometer equipped with FRA-106 FT-Raman accessory in the 3500-50 cm<sup>1</sup> Stokes region using the 1064 nm line of Nd:YAG laser for excitation, operating at 150 mW power. The reported wave numbers are believed to be accurate within  $\pm 4 \text{ cm}^{-1}$ .

## Computational details

The entire calculations are performed at B3LYP levels using GAUSSIAN 09W [33] program package, invoking gradient geometry optimization [34]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at B3LYP level, adopting the standard 6-311++G(d,p) basis set, for better description of polar bonds of acid groups. The optimized structural parameters are used in the vibrational frequency calculations at DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of title compounds were used for harmonic-vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. We have utilized the

gradient corrected density functional theory [35] with the Becke's three-parameter hybrid functional (B3) [36] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [37], accepted as a cost-effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structures.By combining the results of the GAUSSVIEW program [38] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate forms complete set and matches quite well with the motions observed using the GAUSSVIEW program.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of standard internal coordinates of HTZT and ATDZ were defined in Tables 1 and 2.

Table 1. Definition of internal coordinates of 1h-1,2,4triazole-3-thiol

| No(i)  | S ymbol     | Туре  | Definition                           |
|--------|-------------|-------|--------------------------------------|
| Stretc | hing        |       |                                      |
| 1      | Ri          | C-S   | C3-S7                                |
| 2-5    | Ri          | C-N   | C3-N2, C3-N4, C5-N4, C5-N1           |
| 6      | Pi          | N-N   | N1-N2                                |
| 7      | Di          | C-H   | С5-Н9                                |
| 8      | Ti          | N-H   | N1-H6                                |
| 9      | Qi          | S-H   | S7-H8                                |
| Bendir | ng          |       |                                      |
| 10-14  | βi          | Ring  | N1-N2-C3, N2-C3-N4, C3-N4-C5, N4-C5- |
|        |             |       | N1, C5-N1-N2                         |
| 15     | αί          | NNH   | N2-N1-H6                             |
| 16     | αί          | CNH   | C5-N1-H6                             |
| 17-18  | γi          | NCH   | N1-C5-H9, N4-C5-H9                   |
| 19-20  | δi          | NCS   | N2-C3-S7, N4-C3-S7                   |
| 21     | θi          | CSH   | С3-S7-H8                             |
| Out-of | f-plane ber | nding |                                      |
| 22     | ωi          | N-H   | H6-N1-N2-C5                          |
| 23     | ωi          | C-H   | H9-C5-N1-N4                          |
| 24     | ωi          | C-S   | S7-C3-N2-N4                          |
| 25     | ωi          | S-H   | H8-S7-C3-(N2,N4)                     |
| Torsio | n           |       |                                      |
| 26-30  | τί          | τRing | N1-N2-C3-N4, N2-C3-N4-C5, C3-N4-C5-  |
|        |             |       | N1, N4-C5-N1-N2, C5-N1-N2-C3         |

For numbering of atoms refer Fig.1

Table 2. Definition of internal coordinates of 2-amino-1,3,4-

| thiadiazole |  |
|-------------|--|
| unawazore   |  |

| No(i)   | Symbol     | Туре  | Definition                        |
|---------|------------|-------|-----------------------------------|
| Stretch | ing        |       |                                   |
| 1-2     | Ri         | C-S   | S1-C2, S1-C5                      |
| 3-5     | Ri         | C-N   | C2-N3, C5-N4, C2-N6               |
| 6       | Pi         | N-N   | N3-N4                             |
| 7       | Di         | C-H   | С5-Н9                             |
| 8-9     | Ti         | N-H   | N6-H7, N6-H8                      |
| Bending | 3          |       |                                   |
| 10-14   | βi         | Ring  | S1-C2-N3, C2-N3-N4, N3-N4-C5, N4- |
|         |            |       | C5-S1, C5-S1-C2                   |
| 15-16   | αί         | NCH   | N4-C5-H9                          |
|         | αί         | SCH   | S1-C5-H9                          |
| 17-18   | γi         | CNH   | C2-N6-H8, C2-N6-H8                |
| 19      | бі         | HNH   | H7-N6-H8                          |
| Out-of- | plane bend | ing   |                                   |
| 20      | ωi         | C-H   | H9-C5-N4-S1                       |
| 21      | ωi         | C-N   | N6-C2-S1-N3                       |
| Torsion |            |       |                                   |
| 22-26   | τί         | τRing | S1-C2-N3-N4, C2-N3-N4-C5, N3-N4-  |
|         |            |       | C5-S1, N4-C5-S1-C2, C5-S1-C2-N3   |

For numbering of atoms refer Fig.2

From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates are summarized in Tables 3 and 4.

| Table | 3 | . Definition | of | local  | symmetry    | coordinates | of | 1h |
|-------|---|--------------|----|--------|-------------|-------------|----|----|
|       |   | 1            | 2  | A_trie | zola_3_thia | 1           |    |    |

|     | 1,4,4               | -11 12/010-3-11101  |
|-----|---------------------|---|
| No  | Symbol <sup>a</sup> | Definition <sup>b</sup>   |
| 1   | CS                  | R <sub>1</sub>  |
| 2-5 | CN                  | <b>r</b> <sub>2</sub> , <b>r</b> <sub>3</sub> , <b>r</b> <sub>4</sub> , <b>r</b> <sub>5</sub> |
| 6   | NN                  | P <sub>6</sub>  |
| 7   | СН                  | D <sub>7</sub>  |
| 8   | NH                  | T <sub>8</sub>  |
| 9   | SH                  | Q9  |
| 10  | R bend 1            | $\beta_{10}+a(\beta_{11}+\beta_{14})+b(\beta_{12}+\beta_{13})$                                |
| 11  | R bend 2            | $(a-b) (\beta_{11}-\beta_{14}) + (1-a) (\beta_{12}-\beta_{13})$                               |
| 12  | bNH                 | $(\alpha_{15}-\alpha_{16})/\sqrt{2}$  |
| 13  | bCC                 | $(\gamma_{17}-\gamma_{18})/\sqrt{2}$  |
| 14  | bCS                 | $(\delta_{19} - \delta_{20})/\sqrt{2}$  |
| 15  | bSH                 | $\theta_{21}$   |
| 16  | ωNH                 | ω <sub>22</sub>   |
| 17  | ωCH                 | ω <sub>23</sub>   |
| 18  | ωCS                 | ω <sub>24</sub>   |
| 19  | ωSH                 | ω <sub>25</sub>   |
| 20  | $\tau R$ torsion 1  | $b(\tau_{26}+\tau_{30}) + a(\tau_{27}+\tau_{29}) + \tau_{28}$                                 |
| 21  | $\tau R$ torsion 2  | $(a-b) (\tau_{30} - \tau_{26}) + (1-a) (\tau_{29} - \tau_{27})$                               |
|     | a_Car               | $1449 h - C_{22} 729$   |

a=Cos 144°, b=Cos 72°

<sup>a</sup> The internal coordinates used her are defined in Table 1. <sup>b</sup> These symbols are used for description of normal modes by PED in

Table 6

 

 Table 4. Definition of local symmetry coordinates of 2amino-1,3,4-thiadiazole

| No  | Symbol <sup>a</sup> | <b>Definition</b> <sup>b</sup>   |
|-----|---------------------|--|
| 1-2 | CS                  | R <sub>1</sub> , R <sub>2</sub>  |
| 3-5 | CN                  | $r_3, r_3, r_5$  |
| 6   | NN                  | P <sub>6</sub>   |
| 7   | CH                  | D <sub>7</sub>   |
| 8   | NH2 ss              | $(T_8 + T_9) / \sqrt{2}$   |
| 9   | NH2ass              | $(T_8 - T_9)/\sqrt{2}$   |
| 10  | R bend 1            | $\beta_{10} + a(\beta_{11} + \beta_{14}) + b(\beta_{12} + \beta_{13})$ |
| 11  | R bend 2            | (a-b) $(\beta_{11}-\beta_{14}) + (1-a)(\beta_{12}-\beta_{13})$         |
| 12  | bNH                 | $(\alpha_{15} - \alpha_{16})/\sqrt{2}$                                 |
| 13  | bCN                 | $\gamma_{17}, \gamma_{18}$   |
| 14  | NH2rock             | $(\gamma_{17} - \gamma_{18})/\sqrt{2}$                                 |
| 15  | NH2twist            | $(\gamma_{17} + \gamma_{18})/\sqrt{2}$                                 |
| 16  | NH2sciss            | $(2 \pi_{19} - \pi_{17} + \pi_{18}) / \sqrt{2}$                        |
| 17  | NH2wag              | δ <sub>19</sub>  |
| 18  | ωCH                 | ω <sub>20</sub>  |
| 19  | ωCN                 | ω <sub>21</sub>  |
| 20  | $\tau R$ torsion 1  | $b(\tau_{22}+\tau_{26}) + a(\tau_{23}+\tau_{25}) + \tau_{24}$          |
| 21  | $\tau$ R torsion 2  | (a-b) $(\tau_{26} - \tau_{22}) + (1-a) (\tau_{25} - \tau_{23})$        |
|     | a=Co                | os 144°, b=Cos 72°   |

 $a=\cos 144^\circ$ ,  $b=\cos 72^\circ$ 

<sup>a</sup> The internal coordinates used her are defined in Table 2. <sup>b</sup> These symbols are used for description of normal modes by PED in Table 6.

# Results and discussion

#### **Molecular Geometry**

Molecular modeling is a powerful technique which describing the mechanism of interaction and/or following up physical changes in many systems and molecules. Molecular modeling simulates structures and reactions numerically, based in full or in part on the fundamental laws of physics [39,40]. The first task for the computational work is to determine the

optimized geometrics of the studied molecule. The energetically most stable optimized geometry obtained by B3LYP/6-311++G(d,p) method and the scheme of numbering the atoms of the molecules HTZT and ATDZ are shown in Figs 1 and 2, respectively.



Fig 1. Optimized molecular structure of 1h-1,2,4-triazole-3thiol along with numbering of atom





Molecular symmetry can predict or explain many molecular chemical properties such as dipole moment and allowed spectroscopic transitions. The optimized structural parameters bond length and bond angle for the thermodynamically preferred geometry of HTZE and ATDZ determined at B3LYP/6-311++G(d,p) and LSDA/6-311++G(d,p) methods are presented. In accordance with atom numbering scheme of the molecules shown in Figs 1 and 2 from the data shown in Table 5, it is seen that both B3LYP and LSDA methods of theory in general estimate same values of bond lengths and angles.

# Vibrational Assignments

The 21 normal modes of HTZT and ATDZ are distributed among the symmetry species as

1'3N - 6 = 15A' + 6A''

In agreement with Cs symmetry. The A' modes are stretching and in-plane vibrations while A" modes are correspond to out-of-plane vibrations. The combined FT-IR and FT-Raman spectra of the title compounds under investigation are shown in Figs 3-6.



Fig 3. Observed FT-IR Spectra of 1h-1,2,4-triazole-3-thiol



Fig 4. Observed FT-Raman spectra of 1h-1,2,4-triazole-3thiol



**Fig 5. Observed FT-IR Spectra of 2-amino-1,3,4-thiadiazole** The observed and calculated frequencies using B3LYP and LSDA method using 6-311++G(d,p) along with their relative intensities, probable assignments and potential energy distribution (PED) of HTZT and ATDZ are summarised in Tables 6 and 7, respectively.

## C-H Vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region for the ready identification of C-H stretching vibration [41]. In this region, bands are not affected appreciably by the nature of the substituent. In aromatic, compounds, C-H in-plane bending frequencies appear

in the range of 1300-1000 cm<sup>-1</sup> and C-H out-of-plane bending vibration in the range 1000-750 cm<sup>-1</sup> [41, 42]. Heterocyclic compound containing C-H vibration absorption bands are usually weak, in many cases it is too weak for detection.



Fig 6. Observed FT-Raman spectra of 2-amino-1,3,4thiadiazole

The assignments of carbon-hydrogen stretching modes are straight forward on the basis of the scaled *ab initio* predicted frequencies as well "group frequencies". In the present work the FT-IR and FT-Raman vibrational frequencies observed at 3100 and 3081 cm<sup>-1</sup> for HTZT and FTIR band at 3093 cm<sup>-1</sup> for ATDZ have been assigned to C-H Stretching vibrations, respectively, these modes were computed at 3106 and 3109 cm<sup>-1</sup> by the B3LYP/6-311++G(d,p) and LSDA/6-311++G(d,p) method, respectively. These are pure modes since their PED contribution 100%. The C-H in-plane and out-of-pane bending vibrations have also been identified and presented in Tables 6-7 respectively for HTZT and ATDZ.

#### NH<sub>2</sub>Vibrations

One can expect six internal modes of vibrations for NH<sub>2</sub> group of atoms, namely, the asymmetric stretching, symmetric stretching, the symmetric planar deformation or scissoring, the anti-symmetric planar deformation or rocking, the symmetric non-planar deformation or wagging, and the anti-symmetric non-planar deformation or torsion modes of vibrations. According to Scorates [43], the frequencies of amino group appear around 3500-3300 cm<sup>-1</sup> for NH<sub>2</sub> stretching 1700-1600 cm<sup>-1</sup> for scissoring and 1150-900cm<sup>-1</sup> for rocking deformations. NH<sub>2</sub> asymmetric and symmetric stretching fundamentals of ATDZ have been observed, in FT Raman and FTIR band at 3320, 3319 and 3112 cm<sup>-1</sup>, respectively. The scaled NH<sub>2</sub> asymmetric stretching modes are calculated at 3322 and 3317  $cm^{-1}$  by B3LYP/6-311++G(d,p) and LSDA/6-311++G(d,p), respectively. The scaled NH<sub>2</sub> symmetric stretching modes are calculated at 3116 and 3113 cm<sup>-1</sup> by B3LYP/6-311++G(d,p) and LSDA/6-311++G(d,p), respectively. These are used range of appearance for NH<sub>2</sub> stretching vibration [44, 45] in addition, the NH<sub>2</sub> group has scissoring, rocking, wagging and torsional modes of vibration. The NH<sub>2</sub> scissoring frequency is found at 1624 and cm<sup>-1</sup> by B3LYP/6-311++G(d,p)and 1617 LSDA/6-311++G(d,p), respectively and they match with the FT-IR and FT-Raman bands observed at 1620 and 1613 cm<sup>-1</sup>. The NH<sub>2</sub> rocking mode is assigned in the FT-IR band at 1023 cm<sup>-1</sup>. It is consistent with the computed wave numbers of 1025 and 1021 cm-1 by B3LYP and LSDA methods. The NH<sub>2</sub> wagging predicted at 890 and 886 cm<sup>-1</sup> by B3LYP and LSDA are in very

good agreement with the observed range at 898 and 909 cm<sup>-1</sup> in the FT-IR and FT-Raman spectra respectively. The twisting modes predicted by B3LYP and LSDA methods are in good agreement with the recorded value and presented in Tables 6 and 7.

## S-H Vibrations

Many earlier workers [45,48] studied the position of S-H stretching absorption band and able to show that a number of mercaptons butyl, propyl and isoamyl mercaptons gave a well-defined but rather a weak absorption in the region 2650-2550 cm<sup>-1</sup>. Accordingly, in the present study, the FTIR band at 2688 cm<sup>-1</sup> would be assigned to the S-H stretching fundamental of HTZT. The respective peaks for in-plane and out-of-plane bending vibrations of these groups are listed in Table 6. *C-S Vibrations* 

The absorption of C-S group with other substituent's usually appears between 1250 and 1020 cm<sup>-1</sup> [43]. Consideration of these factors leads to assign the FTIR and FT-Raman bands at 1176 and 1180 cm<sup>-1</sup> in HTZT to C-S vibration. The in-plane and out-of-plane bending vibration of C-S group were also found well within the characteristic region.

The C-S stretching bands [45,48] are observed in the range  $800 \pm 130 \text{ cm}^{-1}$ , usually with moderate intensity. In the present study, the FT-Raman and FTIR bands at 654 and 616 cm<sup>-1</sup> are assigned to C-S stretching vibration for ATDZ the scaled computed wave number for this vibration are 650, 649, 613 and 612 cm<sup>-1</sup> by B3LYP and LSDA method with 6-311++G(d,p) basis sets, which is in good agreement with the recorded spectral data.

#### C-N Vibrations

One expects to find infrared absorption and Raman scattering as a result of these vibrations in the region 1600-1050 cm<sup>-1</sup> [49]. In the present study, the band observed at 1481, 1414, 1324, 1261 and 1281 cm<sup>-1</sup> in FTIR and FT-Raman are assigned to C-N stretching vibration for HTZT. Similarly, the FT-Raman and FTIR bands observed at 1499, 1345, 1338and 1146 cm<sup>-1</sup> are attributed to C-N stretching vibration for ATDZ. The in-plane and out-of-plane vibration of ATDZ are shown in Table 7.

#### Thermodynamic parameters

In addition to the vibrational assignments, several calculated thermodynamic parameters of HTZT and ATDZ employing B3LYP and LSDA methods with 6-311++G(d,p) basis set are presented in Table 8. The Self-consistent field (SCP) energy, zero point vibrational energies (ZPVE), rotational constant, enthalpy and entropy as well as heat capacity for molecular systems were also determined.

Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Therefore it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centres of positive and negative charges. Dipole moments are strictly determined for neutral molecules. For charged systems, its value depends on the choice of origin and molecular orientation. The larger total dipole moment of HTZT and ATDZ molecule is due to the formation of intra molecular hydrogen bonding and steric interaction between the substituents. The temperature dependence of thermodynamic properties heat capacity at constant (Cp), entropy (S) and enthalpy change ( $\Delta$ Ho-T) for both the compounds were also B3LYP/6-311++G(d,p) determined by and LSDA/6-311++G(d,p) methods and are listed in Table 9.

| 50177 | 3 | 6 | 1 | 9 | 9 |  |
|-------|---|---|---|---|---|--|
|-------|---|---|---|---|---|--|

|          |               | unuu          | iuzoie   |               |               |
|----------|---------------|---------------|----------|---------------|---------------|
|          | 1h-1,2,4-tria | zole-3-thiol  |          | 2-amino-1,3,  | 4-thiadiazole |
| Value    | B3LYP         | LSDA          | Value    | B3LYP         | LSDA          |
|          | 6-311++G(d,p) | 6-311++G(d,p) |          | 6-311++G(d,p) | 6-311++G(d,p) |
|          | Bond Length ( | Å)            |          | Bond Length ( | Å)            |
| N1-N2    | 1.36          | 1.34          | S1-C2    | 1.76          | 1.74          |
| N1-C5    | 1.35          | 1.34          | S1-C5    | 1.76          | 1.74          |
| N1-H6    | 1.01          | 1.02          | C2-N3    | 1.30          | 1.31          |
| N2-C3    | 1.32          | 1.32          | C2-N6    | 1.37          | 1.35          |
| C3-N4    | 1.37          | 1.35          | N3-N4    | 1.37          | 1.34          |
| C3-S7    | 1.77          | 1.74          | N4-C5    | 1.29          | 1.29          |
| N4-C5    | 1.32          | 1.32          | C5-H9    | 1.08          | 1.09          |
| C5-H9    | 1.08          | 1.09          | N6-H7    | 1.01          | 1.02          |
| S7-H8    | 1.35          | 1.36          | N6-H8    | 1.01          | 1.02          |
|          | Bond Angle (  | <i>'</i> )    |          | Bond Angle (  | <i>'</i> )    |
| N2-N1-C5 | 110.33        | 110.75        | C2-S1-C5 | 85.42         | 85.67         |
| N2-N1-H6 | 119.89        | 119.72        | S1-C2-N3 | 114.00        | 113.63        |
| C5-N1-H6 | 129.78        | 129.54        | S1-C2-N6 | 122.48        | 123.12        |
| N1-N2-C3 | 101.79        | 101.81        | N3-C2-N6 | 123.41        | 123.18        |
| N2-C3-N4 | 115.16        | 114.99        | C2-N3-N4 | 112.81        | 113.02        |
| N2-C3-S7 | 121.13        | 121.39        | N3-N4-C5 | 113.47        | 113.82        |
| N4-C3-S7 | 123.72        | 123.63        | S1-C5-N4 | 114.30        | 113.85        |
| C3-N4-C5 | 102.74        | 102.85        | S1-C5-H9 | 121.65        | 121.68        |
| N1-C5-N4 | 109.99        | 109.60        | N4-C5-H9 | 124.05        | 124.47        |
| N1-C5-H9 | 123.76        | 123.95        | C2-N6-H7 | 113.52        | 114.51        |
| N4-C5-H9 | 126.26        | 126.45        | C2-N6-H8 | 117.65        | 119.60        |
| C3-S7-H8 | 93.52         | 91.93         | H7-N6-H8 | 114.33        | 116.57        |

# Table 5. Optimized geometrical parameters (bond lengths and bond angles) of 1h-1,2,4-triazole-3-thiol and 2-amino-1,3,4-thiadiazole

Table 6. The observed(FTIR and FT-Raman) and calculated (Unscaled and Scaled) frequencies using B3LYP and LSDA/6-311++G (d,p) and B3LYP/6-311++G (d, p) along with their probable assignments and potential energy distribution of 1h-1,2,4triazole-3-thiol

|      |             | Observ              | /ed   | Calculated | Calculated frequencies (cm <sup>-1</sup> ) |           |           |           |          |           |           | Assignments along       |
|------|-------------|---------------------|-------|------------|--|-----------|-----------|-----------|----------|-----------|-----------|-------------------------|
| S.No | Symmspecies | Freque              | ncy   | B3LYP/6-   | 311++G(d                                   | l,p)      |           | LSDA/ 6-3 | 311++G(d | ,p)       |           | with PED (%)            |
|      |             | (cm <sup>-1</sup> ) |       |            |  |           |           |           |          |           |           |                         |
|      |             | FT-                 | FT-   | Unscaled   | Scaled                                     | IR        | Raman     | Unscaled  | Scaled   | IR        | Raman     |                         |
|      |             | IR                  | Raman |            |  | Intensity | Intensity |           |          | Intensity | Intensity |                         |
| 1    | A'          | 3329                | -     | 3654       | 3340                                       | 9.54      | 848.33    | 3553      | 3333     | 7.90      | 738.46    | NH(100)                 |
| 2    | A'          | 3100                | 3081  | 3251       | 3106                                       | 27.61     | 119.12    | 3180      | 3109     | 32.11     | 95.63     | CH(100)                 |
| 3    | A'          | 2688                | -     | 2689       | 2688                                       | 8.60      | 503.35    | 2631      | 2680     | 9.03      | 592.35    | SH(99)                  |
| 4    | A'          | 1562                | -     | 1527       | 1565                                       | 0.20      | 1142.52   | 1507      | 1553     | 0.15      | 981.74    | NN(96)                  |
| 5    | A'          | 1481                | -     | 1471       | 1484                                       | 82.71     | 79.58     | 1445      | 1479     | 77.05     | 91.90     | CN(94)                  |
| 6    | A'          | 1414                | -     | 1401       | 1416                                       | 13.65     | 8.95      | 1401      | 1415     | 13.68     | 11.46     | CN(94)                  |
| 7    | A'          | 1324                | -     | 1311       | 1326                                       | 7.43      | 9.97      | 1332      | 1329     | 7.06      | 19.85     | CN(94)                  |
| 8    | A'          | 1261                | 1281  | 1262       | 1264                                       | 16.49     | 2.89      | 1256      | 1260     | 18.82     | 2.30      | CN(94)                  |
| 9    | A'          | 1176                | 1180  | 1162       | 1178                                       | 23.13     | 253.53    | 1173      | 1174     | 25.07     | 324.26    | CS(91)                  |
| 10   | A'          | -                   | 1096  | 1090       | 1094                                       | 4.23      | 256.98    | 1095      | 1099     | 8.61      | 142.89    | Rbend 1(80),            |
|      |             |                     |       |            |  |           |           |           |          |           |           | bCH(17)                 |
| 11   | A'          | 1038                | -     | 997        | 1028                                       | 13.48     | 71.47     | 985       | 1033     | 8.70      | 119.05    | bNH(78),                |
|      |             |                     |       |            |  |           |           |           |          |           |           | Rbend2(15)              |
| 12   | A'          |                     | 1001  | 983        | 996  | 28.72     | 179.47    | 967       | 991      | 19.31     | 241.76    | bCH(75), CN(21)         |
| 13   | A'          | 949                 | -     | 929        | 941  | 5.74      | 133.83    | 885       | 939      | 20.52     | 83.08     | Rbend2(73),             |
|      |             |                     |       |            |  |           |           |           |          |           |           | bNH(19)                 |
| 14   | Α″          | 848                 | -     | 849        | 848  | 49.32     | 361.84    | 797       | 832      | 19.32     | 385.50    | ωNH(69),ωCS(21)         |
| 15   | A'          | -                   | 742   | 732        | 740  | 71.03     | 337.71    | 724       | 737      | 92.47     | 224.47    | bCS(63), SH(23)         |
| 16   | A'          | 671                 | -     | 664        | 668  | 46.83     | 544.18    | 659       | 661      | 46.15     | 672.44    | bSH(61),                |
|      |             |                     |       |            |  |           |           |           |          |           |           | Rbend(17)               |
| 17   | Α″          | 581                 | -     | 521        | 572  | 22.98     | 147.98    | 559       | 594      | 11.71     | 135.92    | $\tau$ R torsion 1(59), |
|      |             |                     |       |            |  |           |           |           |          |           |           | ωCH(10)                 |
| 18   | Α″          | -                   | 464   | 486        | 469  | 88.72     | 52.42     | 498       | 459      | 100.52    | 82.19     | ωCH(57), ωNH(25)        |
| 19   | Α″          | -                   | 291   | 293        | 294  | 0.53      | 323.71    | 284       | 287      | 4.26      | 347.86    | ωCS(59), ωCH(27)        |
| 20   | A″          | -                   | 261   | 256        | 259  | 1.32      | 190.61    | 253       | 258      | 2.60      | 225.50    | $\tau$ R torsion 2(57)  |
| 21   | Α"          | -                   | 183   | 174        | 178  | 103.65    | 150.49    | 186       | 180      | 106.40    | 193.88    | ωSH(55), τ R            |
|      |             |                     |       |            |  |           |           |           |          |           |           | torsion 1(23)           |

B3LYP/6-311++G (d, p) along with their probable assignments and potential energy distribution of 1h-1,2,4-triazole-3-thiol.

|      |             | Obsei               | ved   | Calculate | d fre quen | cies (cm <sup>-1</sup> ) |           |           |          |           |           |                       |
|------|-------------|---------------------|-------|-----------|------------|--------------------------|-----------|-----------|----------|-----------|-----------|-----------------------|
| S.No | Symmspecies | Frequ               | ency  | B3LYP/6-  | 311++G(d   | l,p)                     |           | LSDA/ 6-3 | 311++G(d | ,p)       |           | Assignments           |
|      |             | (cm <sup>-1</sup> ) | -     |           |            |                          |           |           |          |           |           | along                 |
|      |             | FT-                 | FT-   | Unscaled  | Scaled     | IR                       | Raman     | Unscaled  | Scaled   | IR        | Raman     | with PED (%)          |
|      |             | IR                  | Raman |           |            | Intensity                | Intensity |           |          | Intensity | Intensity |                       |
| 1    | A'          | 3319                | 3320  | 3675      | 3322       | 9.64                     | 466.34    | 3626      | 3317     | 9.05      | 474.92    | NH2ass(100)           |
| 2    | A'          | 3112                | -     | 3566      | 3116       | 41.45                    | 78.54     | 3501      | 3113     | 68.05     | 153.57    | NH2ss(10)             |
| 3    | A'          | 3099                | -     | 3233      | 3099       | 1.67                     | 1401.21   | 3169      | 3095     | 1.98      | 1617.64   | CH(100)               |
| 4    | A'          | 1620                | 1613  | 1643      | 1624       | 160.59                   | 243.19    | 1599      | 1617     | 196.19    | 136.69    | NH2sciss(98)          |
| 5    | A'          | 1518                | -     | 1534      | 1526       | 6.94                     | 303.42    | 1509      | 1514     | 5.12      | 62.00     | NN(96)                |
| 6    | A'          | -                   | 1499  | 1486      | 1496       | 32.06                    | 406.10    | 1476      | 1491     | 3.22      | 714.92    | CN(94)                |
| 7    | A'          | 1338                | 1345  | 1333      | 1340       | 81.97                    | 75.24     | 1312      | 1333     | 20.27     | 30.26     | CN(94)                |
| 8    | A'          | 1219                | -     | 1243      | 1222       | 7.08                     | 958.00    | 1232      | 1225     | 11.13     | 927.46    | Rbend 1(80),          |
|      |             |                     |       |           |            |                          |           |           |          |           |           | CN(17)                |
| 9    | A'          | 1146                | -     | 1136      | 1140       | 16.19                    | 1734.42   | 1132      | 1138     | 26.68     | 1673.03   | CN(93)                |
| 10   | A'          | 1023                | -     | 1030      | 1025       | 24.55                    | 28.03     | 1017      | 1021     | 18.35     | 20.62     | NH2rock(76)           |
| 11   | A″          | 898                 | 909   | 888       | 890        | 27.02                    | 216.70    | 871       | 886      | 26.60     | 196.01    | NH2wag(70)            |
| 12   | A'          | 786                 | -     | 776       | 784        | 36.14                    | 56.23     | 751       | 780      | 22.11     | 94.52     | R bend 2(67),         |
|      |             |                     |       |           |            |                          |           |           |          |           |           | ch(21)                |
| 13   | A'          | 768                 | -     | 741       | 762        | 1.40                     | 296.74    | 725       | 760      | 14.86     | 91.58     | bCH(63), R bend       |
|      |             |                     |       |           |            |                          |           |           |          |           |           | 2(23)                 |
| 14   | A'          | -                   | 654   | 646       | 650        | 3.55                     | 367.91    | 648       | 649      | 4.54      | 455.08    | CS(85)                |
| 15   | Α'          | 616                 | -     | 631       | 613        | 92.62                    | 105.56    | 611       | 612      | 75.27     | 141.57    | CS(83)                |
| 16   | A'          | -                   | 593   | 586       | 590        | 20.26                    | 363.22    | 575       | 586      | 22.05     | 434.33    | bCH(61), R bend       |
|      |             |                     |       |           |            |                          |           |           |          |           |           | 2(23)                 |
| 17   | Α"          | 580                 | -     | 573       | 582        | 168.34                   | 366.22    | 570       | 579      | 13.99     | 97.72     | ωCH(59)               |
| 18   | A″          | 519                 | -     | 515       | 517        | 153.00                   | 152.22    | 434       | 522      | 352.55    | 304.34    | $\tau$ Rtorsion1(57), |
|      |             |                     |       |           |            |                          |           |           |          |           |           | ωCN(12)               |
| 19   | A″          | -                   | 380   | 365       | 361        | 0.48                     | 206.73    | 356       | 359      | 3.87      | 231.25    | ωCN(57)               |
| 20   | A″          | -                   | 304   | 294       | 290        | 51.24                    | 217.61    | 286       | 289      | 77.05     | 270.66    | τRtorsion 2(55),      |
|      |             |                     |       |           |            |                          |           |           |          |           |           | ωCH(19)               |
| 21   | A″          | -                   | 195   | 261       | 202        | 43.18                    | 58.52     | 257       | 220      | 65.07     | 60.09     | NH2twist(60)          |

| Table 7. The observed(FTIR  | and FT-Raman)     | and calculated (Unse  | caled and Scaled) | frequencies  | using B3LYP and    | LSDA/6-    |
|-----------------------------|-------------------|-----------------------|-------------------|--------------|--------------------|------------|
| 311++G (d,p) and B3LYP/6-31 | 1++G (d, p) along | g with their probable | assignments and   | potential er | nergy distribution | of 2-amino |
|                             |                   | 1,3,4-thiadia         | zole              |              |                    |            |





The Fig. 7-9 depicts the correlation of heat capacity at constant pressure (Cp), entropy (S) and enthalpy change ( $\Delta$ H<sup>o</sup>-T) with temperature along with the correlation equations. From, Table 9, one can find that the entropies, heat capacities and enthalpy changes are increasing with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature. The thermodynamic parameters increase steadily with temperature, for the both title compounds.

The corresponding relations between entropy, heat capacity and enthalpy with temperature are given below.For HTZT,the corresponding equations are

**B3LYP**  $S^0_m$  $=-2.49031 + 0.084926 T + 51.084125 x 10^{-5}T^{2} (R^{2} =$ 0.99964)  $C^{0}_{\ p,m}=$  -2.78153 + 0.063453 T + 4.113404 x 10^{-5}T^{2} (R^{2}=0.99930)  $\Delta H_m^0 = 1.65022 + 0.0111735 \text{ T} - 0.698028 \text{ x} 10^{-5} \text{T}^2 (\text{R}^2 = 1.65022 \text{ m}^2)$ 0.99953) LSDA  $S_{m}^{0}$  = -2.48257 + 0.085053 T + 50.93828564 x 10<sup>-5</sup>T<sup>2</sup> (R<sup>2</sup> = 0.99968) $C^{0}_{\ p,m}$  = -2.83361 + 0.064214 T + 4.0069752 x 10  $^{5}T^{2}$  (R² = 0.99951)  $\Delta H_m^0 = 1.65022 + 0.0111735 \text{ T} - 0.698028 \text{ x} 10^{-5} \text{T}^2 (\text{R}^2 = 1.65022 \text{ } \text{ m}^2)$ 0.99953) For ATDZ, the corresponding equations are **B3LYP**  $S_{m}^{0} = -2.5560 + 0.086679 T + 49.9867724 x 10^{-5}T^{2} (R^{2} = -2.5560 + 0.086679 T + 49.9867724 x 10^{-5}T^{2})$ 0.99988) $C^{0}_{\ p,m}$  = -3.40702 + 0.0702103 T + 3.132124 x 10^{-5}T^{2} (R^{2} = 0.099880)  $\Delta H^0_{\ m} = \ 1.61721 \ + \ 0.01202766 \ T \ - \ 0.9033524 \ x \ 10^{-5} T^2 \ (R^2 =$ 0.99935) LSDA  $S^0_{\ m}$  = -2.67677 + 0.088796 T + 49.8391457 x 10^{-5}T^2 (R^2 = 0.99985)  $C_{p,m}^{0}$  = -3.46843 + 0.070708 T + 3.402276 x 10<sup>-5</sup>T<sup>2</sup> (R<sup>2</sup> = 0.99857)  $\Delta H_{m}^{0} = 1.60281 + 0.0125074 T - 0.949993 x 10^{-5}T^{2} (R^{2} =$ 0.99935)







• Fig 9. Correlation graphic of enthalpy and temperature for 1h-1,2,4-triazole-3-thiol and 2-amino-1,3,4-thiadiazole



Fig 10. The Mulliken charge distribution of (a) 1h-1,2,4triazole-3-thiol and (b) 2-amino-1,3,4-thiadiazole

#### Mulliken atomic charges

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system. Since the charge distribution on the molecule has an important influence on the vibrational spectra, the net charge distribution. The total atomic charges of HTZT and ATDZ obtained by Mulliken population analysis with different DFT methods B3LYP and LSDA with 6-311++G(d,p) basis set were listed in Table 10. The magnitudes of the carbon atomic charges are found to be either positive or negative. These magnitude are changing between -0.09442 to 0.169045 for HTZT where as carbon atomic charges of ATDZ are negative. The negative value on carbon atoms in the aromatic ring leads to a redistribution of electron density. The nitrogen atoms N1, N2 and N4 in HTZT and N3, N4 and N6 in ATDZ exhibit their electro negative nature as expected. The better representative graphical form of the results has been done in Fig. 10. The corresponding plot of Mulliken atomic charges obtained by B3LYP and LSDA methods with 6-311++G(d,p) basis set is shown in Fiug.10.





Fig 11. <sup>-</sup>H NMR experimental spectrum of (a) 1h-1,2,4triazole-3-thiol and (b)2-amino-1,3,4- thiadiazole

NMR spectroscopy is currently used for structure and functional determination of biological macromolecules. Chemical shifts are recognised as an imperative part of the information contained in NMR spectra. They are valuable for structural interpretation due to their sensitivity to conformational variations. The experimental <sup>1</sup>H and <sup>13</sup>C NMR spectra of HTZT and ATDZ are shown in Figs. 11 and 12.



Fig 12. <sup>13</sup>C NMR experimental spectrum of 1h-1,2,4-triazole-3-thiol and2-amino-1,3,4-thiadiazole

Vibrational

Total

Total

 $\mu_x$ 

 $\mu_y$ 

 $\mu_z$ 

 $\mu_{total}$ 

(calmol<sup>-1</sup>Kelvin<sup>-1</sup>)

Translational

Rotational

Vibrational

**Translational** 

Rotational

Vibrational

Molar capacity at constant volume

Entropy (calmol<sup>-1</sup>Kelvin<sup>-1</sup>)

Dipole moment (Debye)

| Parameter                              | 1h-1,2,4-triazole-3-thiol 2-amino-1,3,4-thiadiazole |            |              |            |  |  |
|--|---|------------|--------------|------------|--|--|
|  | <b>B3LYP</b>  | LSDA       | <b>B3LYP</b> | LSDA       |  |  |
| SCF energy (Hartrees)                  | -640.53522  | -638.19556 | -640.52495   | -638.18626 |  |  |
| Zero-point vibrational Energy (kJ/mol) | 36.74278  | 36.26688   | 37.39145     | 36.67804   |  |  |
|  | 9.54308   | 9.61903    | 5.38000      | 5.44772    |  |  |
| Rotational constants (GHz)             | 2.17866   | 2.22190    | 3.44810      | 3.51233    |  |  |
|  | 1.77372   | 1.80497    | 2.10498      | 2.13794    |  |  |
| Thermal energy (kJ/mol)                |   |            |              |            |  |  |
| Total                                  | 40.063  | 39.583     | 40.681       | 40.050     |  |  |
| Translational                          | 0.889   | 0.889      | 0.889        | 0.889      |  |  |
| Rotational                             | 0.889   | 0.889      | 0.889        | 0.889      |  |  |

37.806

18.418

2.981

2.981

12.456

74.360

39.748

26.524

3.2959

0.3792

-0.0002

3.3177

8.088

38.285

18.328

2.981

2.981

12.366

74.480

39.748

26.569

8.163

3.3452

0.3851

-0.0016

3.3673

38.272

19.697

2.981

2.981

13.735

74.106

39.748

26.466

7.892

2.2310

-3.2585

0.7162

4.0135

38.904

19.263

2.981

2.981

13.301

73.698

39.748

26.512

7.438

1.8748

-3.2930

0.8772

3.8895

Table 8. Theoretically computed thermodynamic parameters of 1h-1,2,4-triazole-3-thiol and 2-amino-1,3,4-thiadiazole calculated at B3LYP and LSDA with the basic set 6-311++G(d,p) method

 Table 9. Thermodynamic properties at different temperatures at the DFT/B3LYP and LSDA with the basic set 6-311++G(d,p) level for1h-1,2,4-triazole-3-thiol and2-amino-1,3,4-thiadiazole

|        | 1h-1,2,4-tı            | iazole-3-th   | iol            |  |           |   | 2-amino-1,3,4-thiadiazole |                               |          |  |               |          |          |  |
|--------|------------------------|---|----------------|--|-----------|---|---------------------------|-------------------------------|----------|--|---------------|----------|----------|--|
| T (K)  | ) Entropy              |   | Entropy Heat ( |  | Heat Capa | Capacity Enthalpy                         |                           |                               | Entropy  |  | Heat Capacity |          | Enthalpy |  |
|        | S (J.mol <sup>-1</sup> | (J.mol <sup>-1</sup> .K <sup>-1</sup> ) Cp (J.mol–1.K <sup>-1</sup> ) |                | $\Delta H_0 \rightarrow T (kJ.mol^{-1})$ |           | S (J.mol <sup>-1</sup> .K <sup>-1</sup> ) |                           | Cp (J.mol-1.K <sup>-1</sup> ) |          | $\Delta H_0 \rightarrow T (kJ.mol^{-1})$ |               |          |          |  |
|        | B3LYP                  | LSDA  | B3LYP          | LSDA                                     | B3LYP     | LSDA                                      | B3LYP                     | LSDA                          | B3LYP    | LSDA                                     | B3LYP         | LSDA     |          |  |
| 100    | 58.69264               | 58.59226  | 10.57839       | 10.5282                                  | 0.872371  | 0.869981                                  | 58.07122                  | 58.07839                      | 9.636711 | 9.815966                                 | 0.83174       | 0.83652  |          |  |
| 200    | 67.46415               | 67.33031  | 15.31549       | 15.30115                                 | 2.165392  | 2.158222                                  | 66.44598                  | 66.67782                      | 15.45172 | 15.88432                                 | 2.07457       | 2.112811 |          |  |
| 298.15 | 74.50765               | 74.38576  | 20.31549       | 20.40631                                 | 3.912524  | 3.907744                                  | 73.72371                  | 74.13241                      | 21.25    | 21.68499                                 | 3.881453      | 3.965105 |          |  |
| 300    | 74.63193               | 74.51243  | 20.4087        | 20.50191                                 | 3.950765  | 3.945985                                  | 73.85516                  | 74.26625                      | 21.35038 | 21.78298                                 | 3.922084      | 4.003346 |          |  |
| 400    | 81.1783                | 81.09226  | 25.22228       | 25.35612                                 | 6.23805   | 6.24522                                   | 80.69073                  | 81.21893                      | 26.20459 | 26.58939                                 | 6.309751      | 6.431644 |          |  |
| 500    | 87.25382               | 87.19885  | 29.22562       | 29.36663                                 | 8.967495  | 8.989006                                  | 86.96224                  | 87.5717                       | 29.99283 | 30.33222                                 | 9.127629      | 9.287763 |          |  |
| 600    | 92.87285               | 92.84417  | 32.39245       | 32.53585                                 | 12.05545  | 12.0913                                   | 92.70076                  | 93.36759                      | 32.91587 | 33.21463                                 | 12.27772      | 12.46893 |          |  |
| 700    | 98.06166               | 98.05449  | 34.89484       | 35.03824                                 | 15.42304  | 15.47323                                  | 97.95172                  | 98.66396                      | 35.20076 | 35.46606                                 | 15.68834      | 15.90822 |          |  |
| 800    | 102.8561               | 102.8705  | 36.89771       | 37.0435                                  | 19.01769  | 19.08222                                  | 102.7772                  | 103.5229                      | 37.02916 | 37.27055                                 | 19.30449      | 19.54828 |          |  |
| 900    | 107.2992               | 107.3303  | 38.53011       | 38.6783                                  | 22.79159  | 22.87046                                  | 107.2275                  | 107.9995                      | 38.52772 | 38.75239                                 | 23.08317      | 23.35086 |          |  |
| 1000   | 111.4316               | 111.4771  | 39.88289       | 40.03107                                 | 26.71367  | 26.80688                                  | 111.3528                  | 112.1487                      | 39.78489 | 39.99044                                 | 27.00048      | 27.28967 |          |  |

Table 10. The charge distribution calculated by Mulliken methods for 1h-1,2,4-triazole-3-thiol and2-amino-1,3,4-thiadiazole

|            | 1h-1,2,4-tria | zole-3-thiol |       | Atoms 2-amino-1,3,4-thiadiazole<br>6-311++G(d,p) |          |  |  |
|------------|---------------|--------------|-------|--|----------|--|--|
|            | 6-311++G(0    | l,p)         | Atoms |  |          |  |  |
| Atoms      | B3LYP         | LSDA         |       | B3LYP  | LSDA     |  |  |
| N1         | -0.22687      | -0.23359     | S1    | 0.153646   | 0.170177 |  |  |
| N2         | -0.03486      | -0.01031     | C2    | -0.21228   | -0.29861 |  |  |
| C3         | -0.09442      | -0.14407     | N3    | -0.0698  | -0.04023 |  |  |
| N4         | -0.12648      | -0.07424     | N4    | -0.13959   | -0.13901 |  |  |
| C5         | 0.169045      | 0.088291     | C5    | -0.29381   | -0.38467 |  |  |
| H6         | 0.333486      | 0.371595     | N6    | -0.19242   | -0.16189 |  |  |
| <b>S</b> 7 | -0.28747      | -0.34906     | H7    | 0.272751   | 0.295085 |  |  |
| H8         | 0.075633      | 0.110622     | H8    | 0.247821   | 0.276769 |  |  |
| H9         | 0.191929      | 0.240754     | H9    | 0.233691   | 0.282369 |  |  |

| and SC TWIK spectra (u ppin) |   |                   |            |                          |                           |                    |       |  |  |  |  |
|------------------------------|---|-------------------|------------|--------------------------|---------------------------|--------------------|-------|--|--|--|--|
|                              |   | 1h-1,2,4-triazole | -3-thiol   |                          | 2-amino-1,3,4-thiadiazole |                    |       |  |  |  |  |
| Assignment                   | Expt (d <sub>iso</sub> )         6-311++G(d,p)         Chemical shift (d) |                   | Assignment | Expt (d <sub>iso</sub> ) | 6-311++G(d,p)             | Chemical shift (d) |       |  |  |  |  |
| <sup>13</sup> C              |   |                   |            |                          |                           |                    |       |  |  |  |  |
| C3                           | 8.27  | -1.68             | 6.59       | C2                       | 7.34                      | -2.02              | 5.32  |  |  |  |  |
| C5                           | 2.34  | -0.62             | 1.72       | C5                       | 10.49                     | 12.74              | -2.25 |  |  |  |  |
| <sup>1</sup> H               |   |                   |            |                          |                           |                    |       |  |  |  |  |
| H6                           | 23.86   | 25.54             | -1.68      | H7                       | 27.65                     | 29.47              | -1.82 |  |  |  |  |
| H8                           | 13.53   | 27.40             | -13.87     | H8                       | 26.05                     | 28.79              | -2.74 |  |  |  |  |
| H9                           | 18.30   | 22.93             | -4.63      | H9                       | 18.46                     | 22.58              | -4.12 |  |  |  |  |

 Table 11. Experimental and theoretical chemical shifts of 1h-1,2,4-triazole-3-thiol and 2-amino-1,3,4-thiadiazole in 1H and13C NMR spectra (d ppm)

The recorded and calculated <sup>1</sup>H and <sup>13</sup>C chemical shifts in  $CDCl_3$  solution solvent are collected in Table 11, the atom states were numbered according to Figs. 1 and 2.

It is recognized that accurate prediction of molecules geometries are essential for reliable calculation of magnetic properties. Therefore full geometry optimization of HTZT and ATDZ was performed by using B3LYP/6-311++G(d,p) method in CDCl3 solvent. Then Gauge-Including Atomic Orbital (GIAO) <sup>1</sup>H and <sup>13</sup>C chemical shift calculation of the compound have been made by same method. Application of the GIAO approach [50] to molecular system was significantly improved by an efficient application of the method to the *ab initio* SCF calculation, by using techniques borrowed from analytic derivative methodologies. The isotropic shielding values were used to calculate the isotropic chemical shifts with respect to *Tetramethylsilane* (TMS). It is clear from Table 11 that the agreement with experimental data is good

## HOMO and LUMO analysis



#### Fig 13. Surfaces of FMOs for 1h-1,2,4-triazole-3-thiol and 2amino-1,3,4-thiadiazole (Orbital numbers are extracted from the output results of the B3LYP calculation)

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for physicists and chemists. These orbital's are a pair of orbital's in the compound, which allows them to interact most strongly. These orbital's are sometimes called the frontier orbital's, because lie at the outer most boundaries of the electrons of compound. Both the HOMO-LUMO, orbital's are the main orbital takes part in chemical reactivity. Owing to the interaction between HOMO and LUMO orbital of a structure transition state transition of  $\pi - \pi^*$  type is observed with regard to the molecular orbital theory [54]. The energy of the HOMO is directly related to the ionization potential while the LUMO energy is directly related to the electron affinity. It also explains several types of reactions in the conjugated systems. The HOMO-LUMO analysis for the title compound has been carried out using B3LYP/6-311++G(d,p) method. The energy difference between HOMO and LUMO orbital which is called as energy gap is a critical parameter in determining molecular electrical transport properties because it is a measure electron conductivity calculated -0.19009eV and -0.2289 eV for HTZT and ATDZ, respectively. The 3D plots of molecular orbitals (HOMO and LUMO) are shown in Fig. 13. The calculated energies of HTZT and ATDZ at B3LYP method with 6-311++G(d,p) basis set are presented in Table 12.

Table 12. Calculated energies of 1h-1,2,4-4riazole-3-thiol and2-amino-1,3,4-thiadiazoleusing DFT/B3LYP/6-311++G(d,p)method

| nictilou                          |                      |                |  |  |  |  |  |  |  |
|-----------------------------------|----------------------|----------------|--|--|--|--|--|--|--|
| Parameters                        | 1h-1,2,4-4riazole-3- | 2-amino-1,3,4- |  |  |  |  |  |  |  |
|                                   | thiol                | thiadiazole    |  |  |  |  |  |  |  |
| E <sub>HOMO</sub> (eV)            | -0.34264             | -0.35077       |  |  |  |  |  |  |  |
| E <sub>LUMO</sub> (eV)            | 0.15255              | 0.12187        |  |  |  |  |  |  |  |
| E <sub>HOMO-LUMO</sub><br>gap(eV) | -0.19009             | -0.2289        |  |  |  |  |  |  |  |

#### Global and Local Reactivity Descriptors

Based on density functional descriptors global chemical reactivity descriptors of compounds such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined [28–32]. Pauling introduced the concept of electronegativity as the power of an atom in a compound to attract electrons to it. Hardness (η), chemical potential ( $\mu$ ) and electronegativity ( $\chi$ ) and softness are defined follows.

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_{v(r)}$$
$$\mu = \left( \frac{\partial E}{\partial N} \right)_{v(r)}$$
$$\chi = -\mu = -\left( \frac{\partial E}{\partial N} \right)_{v(r)}$$

where E and v(r) are electronic energy and external potential of anN-electron system respectively. Softness is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness.

Using Koopman's theorem for closed-shell compounds,  $\eta$ ,  $\mu$  and  $\chi$  can be defined as

$$\eta = \frac{(1-A)}{2} \\ \mu = \frac{-(1+A)}{2} \\ \chi = \frac{(1+A)}{2}$$

where A and I are the ionization potential and electron affinity of the compounds respectively. Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor. However, in many kinds of bonding viz covalent hydrogen bonding, partial charge transfer takes place. Recently Parr et al. [28] have defined a new descriptor toquantify the global electrophilic power of the compound as electrophilicityindex ( $\omega$ ), which defines a quantitative classification of the global electrophilic nature of a compound. Parr et al. [28] haveproposed electrophilicity index ( $\omega$ ) as a measure of energy loweringdue to maximal electron flow between donor and acceptor. They defined electrophilicity index ( $\omega$ ) as follows

 $\omega = \frac{\mu^2}{2\eta}$ 

The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [33–35]. The calculated value of electrophilicity index describes the biological activity of HTZT and ATDZ. All the calculated values of hardness, potential, softness and electrophilicity index are shown in Table 13.

#### Molecular polarizabilities

Organic material can present nonlinear optical (NLO) properties. NLO is at the forefront of current research because it provides the key functions of frequency shifting, optical memory for the emerging technologies in areas such as single telecommunications, processing and optical interconnections [60, 61]. In discussing nonlinear optical properties, the polarization of the molecule by an external radiation field is often approximated as the creation of an induced dipole moment by an external electric field.

$$S = \frac{1}{2}$$

The methods to predict and interact the molecular properties, the polarizabilities and hperpolarizabilities, which are more advanced and can often, achieve good agreement with experiment [62].

The molecular static polarizability tensors of HTZT and ATDZ were evaluated by employing the B3LYP and LSDA methods. To obtain reliable results, the standard 6-311++G(d,p)basis set were employed on both methods. All elements of static molecular polarizability and hyperpolarizability of HTZT and ATDZ were presented in Table 14. The polarizabilities and hperpolarizabilities are directly related to the macroscopic susceptibilities. The static polarizabilities and hperpolarizabilities determined by DFT method reveals that the title molecule has more polarization effect. Thus studied title molecule might some as a prospective building block for NLO materials.

### **NBO** analysis

The concept of natural atomic orbital (NAO) and natural bond orbital (NBO) analysis, which is very useful for distributing electrons into atomic and molecular orbitals, is used for the one electron density matrix to define the shape of the atomic orbitals in the molecular environment and then to derive molecular bonds from electron density from atoms. The NAOs resemble the pure atomic orbitals and are divided into a "natural minimal basis" corresponding to the occupied atomic orbitals for the isolated atom and a remaining set of natural "Rydberg" orbitals based on the magnitude of the occupation numbers. The minimal set of NAOs will normally be strongly occupied, while the Rydberg NAO will be weakly occupied. There are as many NAOs as the size of the atomic basis set, and the number of Rydberg NAOs increases as the basis set is enlarged [63].

Table 15 and 16 shows calculated natural orbital occupancy (number of electron (or) "natural population" of the orbital) of HTZT and ATDZ. For HTZT, it is noted that the maximum occupancies 1.99516, 1.99422, 1.98700, 1.98694, 1.98439 are obtained for BD(N2-C3), BD(N1-C5), BD(S7-H8), BD(N4-C5),

BD(C3-S7) respectively, and corresponding sp composition are also tabulated in Table 15. Therefore, the results suggest that the N2-C3, N1-C5 bond lengths of this compound are essentially controlled by the *p* character of these hybrid orbitals and also by the nature the N2-C3. For ATDZ, it is also noted that the maximum occupancies 1.99294, 1.99292, 1.98978, 1.98570, 1.98265 are obtained for BD(N4-C5), BD(C2-N3), BD(C2-N6), BD(N6-H7), BD(S1-C2) respectively, and corresponding sp composition are also tabulated in Table 16. Therefore, the results suggest that the N4-C5, C2-N3 bond lengths of this compound are essentially controlled by the *p* character of these hybrid orbitals and also by the nature the N4-C5. Delocalization of the electron density between occupied Lewis type (bond (or) lone pair) NBO orbital's and formally unoccupied (anti-bond (or) Rydberg) non Lewis NBO orbital's corresponding to a stabilizing donor- acceptor interaction have been performed atB3LYP/6-31+G(d,p) basis set. The energy of these interactions can estimated by the second order perturbation theory [30]. In Table 17, the perturbation energies of significant donor-acceptor interactions are comparatively presented for HTZT and ATDZ.

NBO theory allows the assignment of the hybridization of atomic lone pairs and of the atoms involved in bond orbitals. Interaction between atomic orbitals can be interpreted using NBO theory. NBO also gives the accurate natural Lewis structure picture of HTZT and ATDZ since it gives the maximum percentage of electron density. The second order Fock matrix was carried out to evaluate donor (i) and acceptor (j). The stabilization energy  $E^{(2)}$  associated with a delocalization  $i \rightarrow j$  is estimated as follows:

$$E(2) = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\varepsilon_i \varepsilon_j}$$

where  $q_i$  is the donor orbital occupancy,  $\varepsilon_j$  and  $\varepsilon_i$  are diagonal elements and F(i,j) is the off-diagonal NBO Fock matrix element [64]. Hyper conjugation is an important effect in which an occupied Lewis-type NBO is stabilized by overlapping with a non-Lewis typeorbital. This electron delocalization can be described as a charge transfer from a Lewis valence orbital with a decrease in its occupancy, to a non-Lewis. Several other types of valuable data, such as directionality, hybridization, and partial charges, have been analysed from the NBO results [65,66].

In Table 17, the perturbation energies of significant donoracceptor interactions are comparatively presented for HTZT and ATDZ. The larger the  $E^{(2)}$  value, the intense is the interaction between electron donors and electron acceptors. The interactions initiated by BD (1) N1-N2, BD (2) N2-N3, BD (1) C3-N4 and BD (2) N4-C5 donor NBOs of HTZTof the title compound are giving stabilization to their respective structures. Similarly, in ATDZ, the interactions initiated by BD (1) S1-C5, BD(2) C2-N3, BD(1) N3-N4, B(2) N4-C5 and BD(1) N6-H7 donor NBOs of ATDZof the title compound are giving stabilization to their respective structures. In HTZT, the interactions due to lone pair parent NBOs like LP (1) N2  $\rightarrow$  BD\* (2) N4-C5, LP (1) N2  $\rightarrow$ BD\* (1) C3-N4 and LP (2) S7  $\rightarrow$  BD\* (2) N2-N3 are giving reasonable amount of stabilization because of higher  $E^{(2)}$  value. Similarly, in ATDZ, the interaction due to lone pair of LP (2) S1  $\rightarrow$  BD\* (2) C2-N3. LP (1) N3  $\rightarrow$  BD\* (1) S1-C2. LP (1) N4  $\rightarrow$ BD\* (1) S1-C5 and LP (1) N6  $\rightarrow$  BD\* (1) S1-C2 are giving reasonable amount of stabilization because of higher  $E^{(2)}$  value. Above all the interaction among antibonding NBOs BD\* (2) N2-C3 and BD\* (2) C1 - C6 is giving the most possible stabilization to HTZT, since it has the most E<sup>(2)</sup> value around 74.39 kcal/mol.

| 1h-1,2,4-tri | azole-3-thiol   | 2-amino-1,3,4-thiadiazole<br>6-311++G(d,p)   |   |  |  |  |  |  |  |  |
|--------------|---|--|---|--|--|--|--|--|--|--|
| 6-311+-      | +G( <b>d</b> , <b>p</b> )   |  |   |  |  |  |  |  |  |  |
| B3LYP        | LSDA  | B3LYP  | LSDA  |  |  |  |  |  |  |  |
| -0.2476      | -0.0796   | -0.23632   | -0.07534  |  |  |  |  |  |  |  |
|              |   |  |   |  |  |  |  |  |  |  |
| -0.09505     | -0.15005  | -0.11445   | -0.16105  |  |  |  |  |  |  |  |
|              |   |  |   |  |  |  |  |  |  |  |
| -4.03885     | -12.5628  | -4.23155   | -13.2732  |  |  |  |  |  |  |  |
|              |   |  |   |  |  |  |  |  |  |  |
| 0.095045     | 0.15005   | 0.11445  | 0.16105   |  |  |  |  |  |  |  |
|              |   |  |   |  |  |  |  |  |  |  |
| -0.01824     | -0.14143  | -0.02771   | -0.17213  |  |  |  |  |  |  |  |
|              | 1,2,4-tris           6-311+           B3LYP           -0.2476           -0.09505           -4.03885           0.095045           -0.01824 | 1,5,7 initialization           1h-1,2,4-triazole-3-thiol           6-311++G(d,p)           B3LYP         LSDA           -0.2476         -0.0796           -0.09505         -0.15005           -4.03885         -12.5628           0.095045         0.15005           -0.01824         -0.14143 | 1,b,1         initialization           1h-1,2,4-triazole-3-thiol         2-amino-1,3           6-311++G(d,p)         6-311+           B3LYP         LSDA         B3LYP           -0.2476         -0.0796         -0.23632           -0.09505         -0.15005         -0.11445           -4.03885         -12.5628         -4.23155           0.095045         0.15005         0.11445           -0.01824         -0.14143         -0.02771 |  |  |  |  |  |  |  |

Table 13. Global and local reactivity descriptors and related molecular properties of 1h-1,2,4-triazole-3-thiol and 2-amino-1,3,4-thiadiazole

Table 14. Tensor components of the polarisabilities and its mean value  $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$  as well as the hyperpolarisabilities of 1h-1,2,4-triazole-3-thiol and 2-amino-1,3,4-thiadiazole calculated at B3LYP and LSDA methods

| using $6-311++G(d,p)$ basis set                                  |               |                           |               |               |  |  |  |  |  |  |  |
|--|---------------|---------------------------|---------------|---------------|--|--|--|--|--|--|--|
|  | 1h-1,2,4-tria | zole-3-thiol              | 2-amino-1,3   | 4-thiadiazole |  |  |  |  |  |  |  |
| Parameters   | 6-311+-       | +G( <b>d</b> , <b>p</b> ) | 6-311++G(d,p) |               |  |  |  |  |  |  |  |
|  | B3LYP         | LSDA                      | B3LYP         | LSDA          |  |  |  |  |  |  |  |
|  | Polari        | zability (α)              |               |               |  |  |  |  |  |  |  |
| α <sub>xx</sub>  | -29.0615      | -28.906                   | -32.0858      | -31.2195      |  |  |  |  |  |  |  |
| $\alpha_{yy}$  | -44.7725      | -44.464                   | -47.2623      | -46.8428      |  |  |  |  |  |  |  |
| $\alpha_{zz}$  | -44.5477      | -44.5512                  | -43.994       | -44.0892      |  |  |  |  |  |  |  |
| $\alpha_{xy}$  | -3.9024       | -4.0876                   | 2.9905        | 2.7239        |  |  |  |  |  |  |  |
| $\alpha_{xz}$  | -0.0083       | -0.003                    | 2.6191        | 2.1314        |  |  |  |  |  |  |  |
| α <sub>yz</sub>  | 0.0073        | 0.0034                    | -0.5345       | -0.4465       |  |  |  |  |  |  |  |
| $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$           | -39.460567    | -39.307067                | -41.114033    | -40.717167    |  |  |  |  |  |  |  |
|  | Anisot        | ropic tensor              |               |               |  |  |  |  |  |  |  |
| А  | 486.708446    | 486.831251                | 382.813164    | 417.298994    |  |  |  |  |  |  |  |
| В  | 15.2288479    | 16.7084943                | 16.0884653    | 12.1618594    |  |  |  |  |  |  |  |
| С  | 289.040767    | 293.541108                | 239.671978    | 245.135075    |  |  |  |  |  |  |  |
|  | Hyperpol      | larisability (β)          |               |               |  |  |  |  |  |  |  |
| $\beta_{xxx}$  | 33.1968       | 32.7936                   | 16.3964       | 19.3389       |  |  |  |  |  |  |  |
| β <sub>yyy</sub>   | -2.0554       | -1.7044                   | -13.9904      | -13.7702      |  |  |  |  |  |  |  |
| β <sub>zzz</sub>   | 0.0002        | 0.0004                    | 0.5805        | 0.3991        |  |  |  |  |  |  |  |
| $\beta_{xyy}$  | 4.4801        | 4.4154                    | 9.5954        | 10.0408       |  |  |  |  |  |  |  |
| β <sub>yxx</sub>   | 2.0751        | 1.6402                    | -6.2915       | -6.5629       |  |  |  |  |  |  |  |
| $\beta_{zxx}$  | -0.0143       | -0.0021                   | 7.2553        | 5.984         |  |  |  |  |  |  |  |
| $\beta_{xzz}$  | 3.0462        | 2.6981                    | 0.4863        | 0.4174        |  |  |  |  |  |  |  |
| β <sub>yzz</sub>   | -0.2464       | -0.3848                   | 0.0227        | -0.151        |  |  |  |  |  |  |  |
| β <sub>zyy</sub>   | -0.0056       | -0.0015                   | 0.4293        | 0.4032        |  |  |  |  |  |  |  |
| β <sub>x</sub>   | 40.7231       | 39.9071                   | 26.4781       | 29.7971       |  |  |  |  |  |  |  |
| β <sub>y</sub>   | -0.2267       | -0.449                    | -20.2592      | -20.4841      |  |  |  |  |  |  |  |
| β <sub>z</sub>   | -0.0197       | -0.0032                   | 8.2651        | 6.7863        |  |  |  |  |  |  |  |
| $\beta_{\text{Total}} \ge 10^{-30} \text{ cm}^3 \text{esu}^{-1}$ | 1.429         | 1.372                     | 1.016         | 1.166         |  |  |  |  |  |  |  |

| S.No | Bond Orbital | Occupancy | Atom       | Contribution from parent NBO (%) | Atomic hybrid       |
|------|--------------|-----------|------------|----------------------------------|---------------------|
|      |              |           |            | _                                | Contributions (%)   |
| 1    | BD(N1-N2)    | 1.97688   | N1         | 51.86                            | s(25.43) + p(74.45) |
|      |              |           | N2         | 48.14                            | s(22.19) + p(77.65) |
| 2    | BD(N1-C5)    | 1.99422   | N1         | 60.97                            | s(27.82) + p(72.11) |
|      |              |           | C5         | 39.03                            | s(28.68) + p(71.19) |
| 3    | BD(N1-H6)    | 1.94334   | N1         | 70.38                            | s(22.49) + p(77.43) |
|      |              |           | H6         | 29.62                            | s(99.92) + p(0.08)  |
| 4    | BD(N2-C3)    | 1.99516   | N2         | 59.60                            | s(40.70) + p(59.20) |
|      |              |           | C3         | 40.40                            | s(35.40) + p(64.49) |
| 5    | BD*(N2-C3)   | 1.94030   | N2         | 57.67                            | s(0.04) + p(99.78)  |
|      |              |           | C3         | 42.33                            | s(0.15) + p(99.65)  |
| 6    | BD(C3-N4)    | 1.97750   | C3         | 41.46                            | s(31.22) + p(68.68) |
|      |              |           | N4         | 58.54                            | s(26.64) + p(73.27) |
| 7    | BD(C3-S7)    | 1.98439   | C3         | 54.43                            | s(33.23) + p(66.63) |
|      |              |           | S7         | 45.57                            | s(18.27) + p(81.07) |
| 8    | BD(N4-C5)    | 1.98694   | N4         | 59.41                            | s(38.06) + p(61.84) |
|      |              |           | C5         | 40.59                            | s(34.81) + p(65.09) |
| 9    | BD*(N4-C5)   | 1.90404   | N4         | 60.34                            | s(0.07) + p(99.75)  |
|      |              |           | C5         | 39.66                            | s(0.02) + p(99.73)  |
| 10   | BD(C5-H9)    | 1.98277   | C5         | 61.02                            | s(36.65) + p(63.31) |
|      |              |           | H9         | 38.98                            | s(99.94) + p(0.06)  |
| 11   | BD(S7-H8)    | 1.98700   | <b>S</b> 7 | 57.99                            | s(16.37) + p(83.10) |
|      |              |           | H8         | 42.01                            | s(99.62) + p(0.38)  |

Table 15. Bond orbital analysis of 1h-1,2,4-triazole-3-thiolby B3LYP/6-311++G(d,p)

Table 16. Bond orbital analysis of 2-amino-1,3,4-thiadiazole by B3LYP/6-311++G(d,p)

| S.No | Bond Orbital | Occupancy | Atom | Contribution from parent NBO (%) | Atomic hybrid       |
|------|--------------|-----------|------|----------------------------------|---------------------|
|      |              |           |      | _                                | Contributions (%)   |
| 1    | BD(S1-C2)    | 1.98265   | S1   | 48.89                            | s(25.43) + p(82.13) |
|      |              |           | C2   | 51.11                            | s(28.84) + p(70.96) |
| 2    | BD(S1-C5)    | 1.98132   | S1   | 49.86                            | s(17.23)+ p(82.18)  |
|      |              |           | C5   | 50.14                            | s(27.68) + p(72.12) |
| 3    | BD(C2-N3)    | 1.99292   | C2   | 41.21                            | s(36.34)+ p(63.56)  |
|      |              |           | N3   | 58.79                            | s(38.45) + p(61.46) |
| 4    | BD*(C2-N3)   | 1.91522   | C2   | 42.81                            | s(0.02)+ p(99.80)   |
|      |              |           | N3   | 57.19                            | s(0.00) + p(99.83)  |
| 5    | BD(C2-N6)    | 1.98978   | C2   | 42.49                            | s(34.71)+ p(65.22)  |
|      |              |           | N6   | 57.51                            | s(29.75) + p(70.17) |
| 6    | BD(N3-N4)    | 1.97308   | N3   | 50.20                            | s(22.62)+ p(77.22)  |
|      |              |           | N4   | 49.80                            | s(22.60) + p(77.24) |
| 7    | BD(N4-C5)    | 1.99294   | N4   | 58.59                            | s(38.07)+ p(61.83)  |
|      |              |           | C5   | 41.41                            | s(34.69) + p(65.22) |
| 8    | BD*(N4-C5)   | 1.93534   | N4   | 56.14                            | s(0.00)+ p(99.84)   |
|      |              |           | C5   | 43.86                            | s(0.01) + p(99.81)  |
| 9    | BD(C5-H9)    | 1.98219   | C5   | 61.94                            | s(37.70)+ p(62.26)  |
|      |              |           | H9   | 38.06                            | s(99.94) + p(0.06)  |
| 10   | BD(N6-H7)    | 1.97396   | N6   | 69.44                            | s(25.52)+ p(74.39)  |
|      |              |           | H7   | 30.56                            | s(99.94) + p(0.06)  |
| 11   | BD(N6-H7)    | 1.98570   | N6   | 69.02                            | s(25.71)+ p(74.20)  |
|      |              |           | H7   | 30.98                            | s(99.93) + p(0.07)  |

| Donor             |                  | 1h 1 2  | 1 triozolo 3 | thial   |                                 | ,<br>  | 2-amino-134-thiadiazola      |          |        |  |  |
|-------------------|------------------|---|--------------|---------|---------------------------------|--|------------------------------|----------|--------|--|--|
| Donor             |                  | 111-1,2,4   | +-triazore-5 | -11101  | -                               |  | 2-ammo-1,:                   | 5,4-unau | lazore |  |  |
| (i)               | NBO (i)          | Acceptor<br>NBO (i) $E^{(2)a}_{(kcal/mol)}$ $E_j - E_i^b$ $F(i,j)^c$ Donor NBO (i)(a.u)(a.u)(a.u) |              | NBO (i) | E <sup>(2)a</sup><br>(kcal/mol) | E <sub>j</sub> –<br>E <sub>i</sub> <sup>b</sup><br>(a.u) | F(i,j) <sup>c</sup><br>(a.u) |          |        |  |  |
| BD (1)<br>N1 - N2 | BD*(1)C3<br>- S7 | 6.76  | 0.97         | 0.072   | BD (1) S1 - C5                  | BD*(1) C2 -<br>N6  | 5.14                         | 0.98     | 0.063  |  |  |
| BD (1)<br>N1 - H6 | BD*(2)N4<br>- C5 | 4.51  | 0.65         | 0.05    | BD (2) C2 - N3                  | BD*(2) N4 -<br>C5  | 10.14                        | 0.32     | 0.053  |  |  |
| BD (2)<br>N2 - C3 | BD*(1)N1<br>- H6 | 3.27  | 0.77         | 0.045   | BD (2) C2 - N3                  | BD*(1) N6 -<br>H7  | 4.9                          | 0.79     | 0.035  |  |  |
| BD (2)<br>N2 - C3 | BD*(2)N4<br>- C5 | 5.56  | 0.34         | 0.04    | BD (1) N3 - N4                  | BD*(1) C2 -<br>N6  | 5.93                         | 1.07     | 0.071  |  |  |
| BD (1)<br>C3 - N4 | BD*(1)C5<br>- H9 | 5.13  | 1.15         | 0.069   | BD (1) N3 - N4                  | BD*(1) C5 -<br>H9  | 6.9                          | 1.19     | 0.053  |  |  |
| BD (1)<br>N4 - C5 | BD*(1)C3<br>- S7 | 4.34  | 1.06         | 0.061   | BD (2) N4 - C5                  | BD*(2) C2 -<br>N3  | 8.79                         | 0.32     | 0.051  |  |  |
| BD (2)<br>N4 - C5 | BD*(2)N2<br>- C3 | 16.94   | 0.33         | 0.07    | BD (1) C5 - H9                  | BD*(1) N3 -<br>N4  | 4.96                         | 0.89     | 0.059  |  |  |
| BD (1)<br>C5 - H9 | BD*(1)C3<br>- N4 | 4.39  | 0.91         | 0.057   | BD (1) N6 - H7                  | BD*(2) C2 -<br>N3  | 5.03                         | 0.63     | 0.054  |  |  |
| LP (1)<br>N1      | BD*(2)N4<br>- C5 | 8.41  | 0.37         | 0.05    | LP (2) S1                       | BD*(2) C2 -<br>N3  | 26.09                        | 0.25     | 0.073  |  |  |
| LP (1)<br>N2      | BD*(1)C3<br>- N4 | 8.15  | 0.74         | 0.069   | LP (1) N3                       | BD*(1) S1 -<br>C2  | 12.09                        | 0.58     | 0.075  |  |  |
| LP (1)<br>N4      | BD*(1)N2<br>- C3 | 4.24  | 0.96         | 0.057   | LP (1) N4                       | BD*(1) S1 -<br>C5  | 10.76                        | 0.59     | 0.071  |  |  |
| LP (2)<br>S7      | BD*(2)N2<br>- C3 | 17.73   | 0.25         | 0.063   | LP (1) N6                       | BD*(1) S1 -<br>C2  | 11.26                        | 0.51     | 0.068  |  |  |
| BD*(2)<br>N2 - C3 | BD*(2)N4<br>- C5 | 74.39   | 0.01         | 0.052   |                                 |  |                              |          |        |  |  |

 Table 17. Significant donor-acceptor interactions in 1h-1,2,4-triazole-3-thiol /2-amino-1,3,4-thiadiazole and their second order perturbation energies

 ${}^{a}E^{(2)}$  means energy of hyperconjucative interactions. Energy difference between donor and acceptor i and j NBO orbitals. F(i,j) is the Fock matrix element between i and j NBO orbitals.

#### Conclusion

DFT calculations on the structure, vibrational, electronic and NMR spectra of the title compound have been discussed. The calculated results showed that the predicted geometry can well reproduce the structural parameters. The FT-IR and FT-Raman spectral measurements have been made for the 1h-1,2,4triazole-3-thiol and 2-amino-1,3,4-thiadiazole. B3LYP/6-311++G(d,p) and LSDA/6-311++G(d,p) method can generate reliable geometry and related properties of the title compounds. Thermodynamic properties in the range from 100 to 1000K are obtained. The NBO analysis reveals hyper conjugative interaction; Natural bond orbital analysis of the molecule confirms that the intramolecular charge transfer caused by pelectron cloud movement from donor to acceptor must be responsible for the non-linear optical properties of the title compound. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intramolecular charge transfer and bioactivity of the molecule. NMR chemical shifts have been calculated and compared with the experimental values.

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