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# Quantum Mechanical Study of the Structure and Spectroscopic (FT-IRand FT-Raman), Fukui Function Analysis and First-Order Hyperpolarizability of 2-Amino-1H-Purine-6(7H)-Thione by Density Functional method

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Abstract: The Fourier transform infrared (FTIR) and FT Raman spectra of 2-Amino-1Hpurine-6(7H)-thione in the solid phase were recorded in the region 4000–450 cm<sup>-1</sup> and 4000– 100 cm<sup>-1</sup> respectively. The molecular geometry, vibrational frequencies, infrared intensities, Raman activities and atomic charges were calculated using density functional theory calculation (B3LYP) with 6-311++G (d, p) basis set. Complete vibrational assignments and analysis of the fundamental modes of the compound were carried out using the observed FTIR and FT Raman data. Stability of the molecule arising from hyper-conjugative interactions, and charge delocalization has been analyzed using Natural Bond Orbital (NBO) analysis. Using the method B3LYP, the dipole moment ( $\mu$ ), polarizability ( $\alpha$ ) and the hyperpolarizability ( $\beta$ ) values of the investigated molecule has been computed. Potential Energy Distribution (PED) was computed for the assignment of unambiguous vibrational fundamental modes. The calculated HOMO and LUMO energies also confirm that charge transfer occurs within the molecule. Fukui functions were calculated to identify changes in the reactivity of the molecule. Molecular Electrostatic Potential of the title compound was also performed to study the attractive and repulsive nature of the atoms. Thermodynamic properties (heat capacity, entropy and enthalpy) of the title compound at different temperatures are calculated. Finally, Simulated FTIR and FT Raman spectra of 2-Amino-1Hpurine-6(7H)-thione showed good agreement with the observed spectra. Keywords: FTIR; FT-Raman; First order DFT; NBO; Fukui function.

# 1. Introduction

2-amino-1H-purine-6(7H)-thione is commonly called 6 thioguanine. It is commercially marketed as Lanvis, Thionine, and 6TG. The effects of 2-amino-1H-purine-6(7H)-thione in treatment of malignancies, rheumatic diseases, dermatologic conditions, inflammatory bowel disease, and solid organ transplant rejection,

its incorporation into the DNA to bring about the cytotoxic effect and its pharmacokinetics have been understood by several previously done studies[1].It is an Anti-Cancer drug, effective in treating childhood lymphoblastic leukemia [2]. It functions as efficient as a poly (ADP-ribose) polymerase (PARP) inhibitor in selectively killing BRCA2-defective tumors in a xenograft model [3]. The molecular formula of 2-amino-1Hpurine-6(7H)-thione is  $C_5H_5N_5S$ . An extensive work has been carried out on the title compound and its derivates in recent years [4]. Literature survey reveals that to the best of our knowledge no DFT wavenumber calculations, complete vibrational analysis and molecular properties of 2-Amino-1H-purine-6(7H)-thione have been reported so far. Hence, we have undertaken detailed theoretical and experimental investigation of vibrational spectra of this molecule completely and to identify the various normal modes with greater wavenumber accuracy. Density functional theory (DFT) calculations have been performed to support our wavenumber assignments. In addition, NBO analysis, NLO analysis, HOMO and LUMO analysis, Fukui function, Molecular Electrostatic Potential (MEP) and thermodynamic properties are calculated at the B3LYP/6-311++G (d, p) level.

## 2. Methodology

#### 2.1 Experimental details

High grade pure sample 2-Amino-1H-purine-6(7H)-thione was purchased from Sigma–Aldrich chemical company with a stated purity 97% and it was used without further purification. The FT-IR spectrum was recorded in the region 4000–450 cm<sup>-1</sup> with sample in the KBr pellet, using Perkin Elmer FTIR BX spectrometer. The resolution of the spectrum is 4 cm<sup>-1</sup>. The FT-Raman spectrum was obtained in the range 4000–100cm<sup>-1</sup> using Bruker RFS 100/S FT Raman spectrophotometer with a 1064 nm Nd: YAG laser source of 100 mW power. Liquid nitrogen cooled Ge-diode was used as a detector. Spectra were collected for samples with 1000 scan accumulated for over 30 min duration. The spectral resolution after apodization was 2 cm<sup>-1</sup>. A correction according to the fourth power scattering factor was performed, but no instrumental correction was done. The spectral measurements are carried out at Sophisticated Analytical Instruments Facility (SAIF), Indian Institute of Technology (IIT), Chennai.

## 2.2 Computational details

The entire calculations were performed at Density Functional (DFT) levels on a Pentium IV personal computer using Gaussian 03W [5] program package invoking gradient geometry optimization [6]. The harmonic vibrational frequencies were calculated at the same level of theory for the optimized structures and obtained frequencies were scaled by a factor of 0.961 [7]. The geometry was optimized at B3LYP/6-311++ G (d, p) level. The optimized structural parameters were used in the vibrational frequency calculation at DFT levels to characterize all stationary points as minima. We have used DFT/B3LYP approach for the computation of molecular structure, vibrational frequencies and energies of optimized structures in the present work using GAUSSVIEW program with symmetry considerations along with available related molecules, vibrational frequency assignments were made with a high degree of accuracy. Next the spectra were analyzed in terms of the Potential Energy Distribution (PED) contributions by using the Vibrational Energy Distribution Analysis program (VEDA) written by Michal H. Jamroz[8, 9]. The mean linear hyper polarizability and mean first hyperpolarizability properties of the title compound were obtained by molecular polarizabilities based on theoretical calculations. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes are used with full width at half maximum of 10cm<sup>-1</sup>. The natural bonding orbital (NBO) calculations [10] were performed using NBO 3.1 program as implemented in the Gaussian 03W package at the above said level in order to understand various second order interaction between the filled orbital of one subsystem and vacant orbital of another subsystem, which is measure of the intermolecular and intra molecular delocalization or hyper conjugation.

## 2.2.1. Prediction of Raman intensities

The Raman activities  $(S_i)$  calculated with the GAUSSIAN 03W program were subsequently converted to relative Raman intensities  $(I_i)$  using the following relationship derived from the theory of Raman scattering [11].

$$\mathbf{I}_{i} = \frac{\mathbf{f}(\mathbf{v}_{0} - \mathbf{v}_{i})^{4} \mathbf{S}_{i}}{\mathbf{v}_{i} \left[1 - \exp\left(\frac{\mathbf{h} \mathbf{c} \mathbf{v}_{i}}{\mathbf{K}_{b} T}\right)\right]}$$

Where  $v_0$  is the exciting frequency in cm<sup>-1</sup>  $v_i$  is the vibrating wavenumber of the i<sup>th</sup> normal mode *h*, c and k<sub>b</sub> are the fundamental constants and f is a normalization factor for all peak intensities.

# 3. Results and Discussions

# 3.1. Molecular geometry

Table 1 Geometrical parameters optimized in 2-Amino-1H-purine-6(7H)-thione Bond length Bond angle with 6-311++G (d, p) basis set.

Molecular	B3LYP/6-311++G(d,p)	Experimental <sup>a</sup>		
Parameters				
N1-C2	1.363	1.406		
$N_1-C_9$	1.375	1.266		
$N_1 - H_{12}$	1.010	1.050		
$C_2-N_3$	1.319	1.260		
C <sub>2</sub> -H <sub>13</sub>	1.080	1.100		
N <sub>3</sub> -C <sub>4</sub>	1.369	1.456		
$C_4-N_5$	1.359	1.450		
$C_4-C_9$	1.401	1.337		
$N_5-C_6$	1.305	1.260		
$C_6-N_7$	1.38	1.345		
C <sub>6</sub> -N <sub>11</sub>	1.376	1.266		
N <sub>7</sub> -C <sub>8</sub>	1.397	1.369		
N <sub>7</sub> -H <sub>14</sub>	1.013	1.012		
C <sub>8</sub> -C <sub>9</sub>	1.406	1.351		
$C_{8}-S_{10}$	1.672	1.576		
N <sub>11</sub> -H <sub>15</sub>	1.009	1.050		
N <sub>11</sub> -H <sub>16</sub>	1.010	1.050		
$C_2 - N_1 - C_9$	106.2	99.6		
$C_2 - N_1 - H_{12}$	128.4	130.1		
$N_1 - C_2 - N_3$	113.4	114.3		
N <sub>1</sub> -C <sub>2</sub> -H <sub>13</sub>	121.8	122.8		
C <sub>9</sub> -N <sub>1</sub> -H <sub>12</sub>	125.4	130.1		
$N_1 - C_9 - C_4$	105.4	111.1		
$N_1 - C_9 - C_8$	131.7	131.3		
N <sub>3</sub> -C <sub>2</sub> -H <sub>13</sub>	124.8	122.8		
$C_2-N_3-C_4$	104.7	104.0		
$N_3-C_4-N_5$	126.1	128.9		
N <sub>3</sub> -C <sub>4</sub> -C <sub>9</sub>	110.3	111.0		
$N_5-C_4-C_9$	123.6	120.0		
$C_4-N_5-C_6$	114.5	115.0		
$C_{4}-C_{9}-C_{8}$	122.9	117.6		
$N_5 - C_6 - N_7$	124.1	120.0		
N <sub>5</sub> -C <sub>6</sub> -N <sub>11</sub>	119.9	120.9		
$N_7 - C_6 - N_{11}$	116.0	120.0		
C <sub>6</sub> -N <sub>7</sub> -C <sub>8</sub>	125.1	119.0		
C <sub>6</sub> -N <sub>7</sub> -H <sub>14</sub>	119.9	120.4		
C <sub>6</sub> -N <sub>11</sub> -H <sub>15</sub>	118.3	120.0		

C <sub>6</sub> -N <sub>11</sub> -H <sub>16</sub>	113.2	120.0
C <sub>8</sub> -N <sub>7</sub> -H <sub>14</sub>	114.9	117.4
N <sub>7</sub> -C <sub>8</sub> -C <sub>9</sub>	109.8	112.7
$N_7 - C_8 - S_{10}$	122.1	123.6
$C_9-C_8-S_{10}$	128.1	123.6
H <sub>15</sub> -N <sub>11</sub> -H <sub>16</sub>	114.5	118.8

<sup>a</sup> – Takenfrom reference [12, 13]



Figure 1 Numbering system adopted in this study for 2-Amino-1H-purine-6(7H)-thione

The optimized geometric parameters (bond lengths and bond angles) of the title molecules are given in **Table 1** using DFT/ B3LYP with 6-311G++ (d, p) basis set. The atom numbering scheme adopted in this study is given in **Fig. 1**. **Table 1** compares the calculated bond length and bond angles for 2-Amino-1H-purine-6(7H)-thione with those of experimental data [12]. From the theoretical values, it is found that some of the calculated parameters are slightly deviated from experimental values, due to fact that the theoretical calculations belong to molecule in the gaseous phase and the experimental results belong to molecule in solid state. The molecule has one C-H bond lengths, two C-C bond lengths, nine C-N bond lengths, four N-H bond lengths and one C-S bond length. The C-C bond length value of the ring is found to be around 1.4 Å at DFT method with 6-311++G (d, p) basis set and agree well with experimental value of structurally related compound [12, 13]. The C-H bond length value calculated at B3LYP/6-311++G (d, p) level is found to be 1.1 Å and the N-H bond length value calculated at B3LYP/6-311++G (d, p) level is 1.67 Å and the experimental value is 1.576 Å is found to be high compared to other bond length values.

# 3.2. Vibrational assignments

Table 2 Vibrational assignments of fundamental modes of 2-amino-1H-purine-6(7H)-thionealong with calculated IR, Raman intensities and normal mode descriptions (characterized by PED) based on quantum mechanical force field calculations using B3LYP force fields.

				DFT/ B3LYP/ 6-311G++		1G++			
	Exper	rimental	Calculated		(d, p)				
Mode	Wave	number	Wave	Ι	R	Ra	man		
no	(c	<sup>m<sup>-1</sup></sup> )	number <sup>a</sup> (S	Inten	sities <sup>b</sup>	Acti	vity <sup>c</sup>	Vibrational Assignment (% PED)	
	FTIR	FT	$(am^{-1})$	Rel.	Abs.	Rel.	Abs.	-	
		Raman	(cm)						
1	-	-	3538	44	8	61	38	STRE NH (100)	
2	3335	-	3492	88	16	86	54	STRE NH (100)	
3	3287	3280	3440	63	12	158	100	STRE NH (100)	
4	-	-	3434	46	8	121	77	STRE NH (100)	
5	2850	2916	3100	3	1	134	85	STRE CH (99)	
6	1636	1661	1603	380	70	27	17	STRE NC (55) + BEND HNH (74)	
7	1582	1589	1570	253	47	2	1	STRE NC (70)+ BEND HNH (74)	
8	1541	1537	1539	539	100	62	39	BEND HNC (70) + BEND HNH (74) + BEND NCN(55)	
9	1481	1479	1490	113	21	64	41	STRE NC(70)	
10	1433	1440	1432	46	9	21	13	STRE NC (53)+ BEND CNC	
11	1272	1270	1202	1.7	2	0	6	(68)+BEND HCN (73)	
	13/3	1370	1393	15	3	8	5	BEND CNC(42)	
12	1339	-	1349	88	16	151	96	STRE NC(73)+BEND HNC(71)	
13	-	-	1329	75	14	17	10	STRE NC(70)+BEND HNC(70)	
14	-	1260	1326	68	13	98	62	STRE NC(62)+BEND HNC(70)+BEND CNC(42)	
15	1230	1229	1240	63	12	38	24	111111111111111111111111111111111111	
16	1166	1203	1161	9	2	32	20	STRE $NC(70)$ +BEND $HCN(73)$	
17	1140	1137	1146	129	24	10	6	STRE NC(60)+STRE	
								SC(64)+BEND HNC(70)	
18	1072	-	1097	28	5	5	3	STRE NC(62)+BEND HNC(55)	
19	-	1033	1064	21	4	8	5	STRE NC(62)+BEND HNC(55)	
20	975	973	989	51	9	3	2	STRE NC(35)+BEND	
21		022	044	52	10	6	2	HNC(55)+BEND CNC(42)	
21	-	922	944	21	10	15	3 10	STRE NC(70)+ STRE SC(64)	
22	-	-	918	<u> </u>	4	15	10	BEND CNC(68)+BEND NCN(53)	
23	837	839	831	11	2	1	0	TORS HCNC( 87)	
24	/90	//6	803	13	2	2	I	STRE NC(46)+BEND CNC(68)+BEND NCN(55)	
25	776	-	736	7	1	1	1	TORS CNCC(72)+TORS	
26			(0 <b>0</b>	•			0	CNCN(70)+OUT NCNC(85)	
26	-	-	692	20	4	1	0	TORS CNCN(70)+OUT NNNC(89)	
27	679	648	637	0	0	0	0	TORS CNCN(77)+OUT SNCC(78)	
28	-	-	630	21	4	1	1	BEND NCN(76)+TORS HNCC(90)	
29	599	-	600	45	8	2	2	TORS HNCC(90)	

30	-	564	560	26	5	1	1	TORS HNCC(90)+OUT SNCC(78)
31	558	-	545	120	22	21	13	STRE NC(62)+BEND
						_	-	CNC(36)+TORS HNCN(83)
32	-	525	534	165	31	5	3	BEND CNC(36)+TORS HNCN(83)
33	-	-	504	15	3	5	3	STRE NC(35)+BEND
								CNC(68)+BEND NCN(76)
34	476	478	499	54	10	1	1	TORS HNCC(88)
35	420	-	420	3	1	8	5	STRE SC(64)+ BEND
								CNC(41)+BEND NCN(55)
36	-	362	351	1	0	0	0	TORS CNCN(77)+TORS
								NCNC(79)+ OUT NNNC(89)+OUT
								NCNC(85)
37	-	-	311	44	8	3	2	BEND NCN(76)+TORS HNCN(71)
38	-	-	304	37	7	5	3	BEND NCN(76)+TORS HNCN(83)
39	-	234	197	7	1	6	4	BEND CNC(41)+BEND
								NCN(50)+BEND SCN(63)
40	-	216	187	3	1	0	0	TORS CNCC(72)+TORS
								CNCN(74)
41	-	134	139	12	2	0	0	TORS NCNC(79)+TORS
								CNCN(74)+OUT NNNC(89)+OUT
								NCNC(85)
42	-	-	121	10	2	0	0	TORS NCNC(79)+TORS
								CNCN(74)+OUT SNCC(78)

STRE, Stretching: BEND, Bending: TORS, Torsion: OUT, Out of plane bending.

<sup>a</sup> Scaling factor 0.961 for B3LYP/6-311++G (d,p)

<sup>b</sup>Relative absorption intensities normalized with highest peak absorption equal to 100.

<sup>c</sup>Relative Raman intensities normalized to 100 (R; Real, A; Absolute).



Figure 2 FTIR spectra of *2-Amino-1H-purine-6(7H)-thione* (Experimental and DFT/B3LYP/6-311++G (d, p))



Figure 3 FT Raman spectra of 2-Amino-1H-purine-6(7H)-thione (Experimental and DFT/B3LYP/6-311++G (d, p))

The vibrational spectrum is mainly determined by the modes of the free molecule observed at higher wavenumbers, together with the lattice (translational and vibrational) modes in the low wavenumber region. In our present study, we have performed a frequency calculation analysis to obtain the spectroscopic signature of 2-Amino-1H-purine-6(7H)-thione. The 12-Amino-1H-purine-6(7H)-thione molecule consists of 16 atoms therefore they have 42vibrational normal modes. All the frequencies are assigned in terms of fundamental, overtone and combination bands. Assignments have been made on the basis of Potential Energy Distribution (PED). The measured (FTIR and FT-Raman) wavenumbers and assigned wavenumbers of the some selected intense vibrational modes calculated at the B3LYP level with basis sets 6-311++G (d, p) along with their PED are given in **Table 2**. This reveals good correspondence between theory and experiment in main spectral features. The experimental and theoretical FTIR and FT-Raman spectra are shown in **Figs. 2 and 3**. Inclusion of IR and Raman spectra contain a number of bands at specific wavenumbers. On the whole, the predicted Vibrationalwavenumbers are in good agreement with the experimental results.

## **3.2.1.** C–H vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region3100- $2800 \text{cm}^{-1}$  which is the characteristic region for the ready identification of C-H stretching vibrations [14-16]. These vibrations are found to be affected due to the nature and position of the substituents. Accordingly, in the present study, the IR bandis observed at2850 cm<sup>-1</sup> and Raman band at 2916 cm<sup>-1</sup>. Theoretically computed C-H vibrations by B3LYP/6-311G++ (d, p) method of scaled values is approximately coincides with experimental value. As indicated by the PED, this mode (Mode no.5) involves99% of contribution suggesting that it is a pure stretching mode.

The C-H in plane bending vibrations normally occurred as a number of strong to weak intensity sharp bands in the region 1300-1000cm<sup>-1</sup>[17] and are very useful for characterization purposes. The bands identified at 1072, 1114, 1166, 1230cm<sup>-1</sup> in IR and bending vibrations identified at 1033, 1137, 1203, 1229, 1260 cm<sup>-1</sup> in Raman are assigned for C-H in plane bending.

## 3.2.2 N-H vibrations

It has been observed that the presence of N-H in various molecules may be correlated with a constant occurrence of absorption bands whose positions are slightly altered from one compound to another this is because of atomic group vibrates independently of the other groups in the molecule and has its own frequency. In all the hetero cyclic compounds the N-H stretching vibrations occur in the region 3500-3220cm<sup>-1</sup> [18-20]. The position of absorption in this region depends upon the degree of hydrogen bonding and physical state of the sample. In the present investigation the N-H stretching vibrations have been found at 3335 cm<sup>-1</sup> and 3287 cm<sup>-1</sup> in Raman spectrum with the 100% of PED contribution. Theoretically computed N-H vibrations by B3LYP method of scaled values approximately coincides with experimental value.

## 3.2.3 C=S vibrations

In general the assignment of the band due to the C=S stretching vibration is found over the region of 1275-1030 cm<sup>-1</sup>[21]. In the present work the band observed at 1140cm<sup>-1</sup> in FTIR and 1137cm<sup>-1</sup> in FT-Raman are assigned to C=S stretching vibration. Theoretically computed values are found to be in good agreement with experimental results with 64% PED contribution.

## 3.2.4 C=N and C-N vibrations

The stretching vibrations of C=N occurs at 1615-1575 cm<sup>-1</sup> and C-N occurs at 1200-1020 cm<sup>-1</sup>[22]. In this study, the bands are identified at 1582 cm<sup>-1</sup> in FTIR spectra and at 1589 cm<sup>-1</sup> in FT Raman spectra have been assigned to C=N stretching vibrations. For C-N stretching, the bands are identified at 1072, 1140, 1166 cm<sup>-1</sup> in FTIR spectra and at 1033, 1137, 1203 cm<sup>-1</sup> in FT Raman spectra. The theoretically scaled wave numbers at 1064, 1097, 1146, 1161 cm<sup>-1</sup> by B3LYP/6-311++ G(d,p) method corresponds to C-N stretching vibrations coincides with the experimental value with thePED of 62%, 62%, 60% and 70% respectively. For C=N stretching vibration, the theoretically scaled wave numbers at 1570 cm<sup>-1</sup> by B3LYP/6-311++ G (d, p) method coincides with the experimental value with 70% PED contribution. The remaining vibrations of fundamental modes are also assigned and listed in Table 2.

#### 4. Other molecular properties

#### 4.1 NBO analysis

NBO analysis provides the most accurate possible 'natural Lewis structure' picture of  $\varphi$ , because all the orbital details are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intra and intermolecular interactions. The second-order Fock matrix was carried out to evaluate the donor–acceptor interactions in NBO analysis [23]. The interactions result is the loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy E2 associated with the delocalization  $i \rightarrow j$  is estimated as

$$E_{\mathbf{2}} = \Delta E_{ij} = \frac{q_i (F_{ij})^2}{\varepsilon_j - \varepsilon_i}$$

Where  $q_i$  is the donor orbital occupancy,  $\varepsilon_i$  and  $\varepsilon_i$  are diagonal elements and  $F_{ij}$  is the off diagonal NBO Fock matrix element. Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second order micro disturbance theory are reported [24, 25]. The larger  $E_2$  value, more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non Lewis NBO orbitals correspond to a stabilizing donor acceptor interaction. NBO analysis has been performed on the molecule at the B3LYP/6-311++G (d, p) level in order to elucidate the conjugation, hyper-conjugation and delocalization of electron density within the molecule. The larger  $E_2$  value, the more intensive is the interaction between electron donors and acceptors, i.e., the more electrons donating tendency from electron donors to acceptors and the greater extent of conjugation of the whole system. The intra molecular interaction is formed by the orbital overlap between  $\sigma$  and  $\pi$  (C–C, C–H, C-S and C-N) and  $\sigma^*$  and  $\pi^*$  (C-C, C-H, C-S and C-N)) bond orbital which results intra molecular charge transfer (ICT) causing stabilization of the system. The strong inter-molecular hyper conjugative interaction of the  $\sigma$  and  $\pi$  electrons of C–C, C–N, C–H, and C-S to the anti C–C, C–N, C-S and C–H bond of the ring leads to stabilization of some part of the ring as evident from **Table 3**. For example the intra-molecular hyper conjugative interaction of  $\sigma$  (C<sub>4</sub>–C<sub>9</sub>) distribute to  $\sigma^*$  (N<sub>1</sub>–C<sub>9</sub>),  $\sigma^*$  (N<sub>1</sub>–H<sub>12</sub>),  $\sigma^*$  (C<sub>8</sub>–S<sub>10</sub>) leading to stabilization of 6.43 kJ/mol. This enhanced conjugation with bonding orbital of  $\pi$  (C<sub>2</sub>–N<sub>3</sub>) distribute to  $\pi^*$  (C<sub>4</sub>–C<sub>9</sub>) which leads to strong delocalization of 28.14 kJ/mol. The similar calculations have been performed for other interactions as shown in **Table 3**. The stabilization energy (E2) associated with hyper conjugative interaction LP (1) of N<sub>7</sub> to (N<sub>5</sub>-C<sub>6</sub>) is obtained as 2.22 kJ/mol as shown in **Table 3**, which quantify to extend the intermolecular hydrogen bonding. The most important interaction energy, related to the resonance in the molecule, is the electrons donating from bonding donator  $\pi$  (C<sub>2</sub>–N<sub>3</sub>) to the antibonding acceptor  $\pi^*$  (C<sub>4</sub>–C<sub>9</sub>) with large stabilization energy of 97.05 kJ/mol.

Donor (i)	Туре	ED/e	Acceptor	Туре	ED/e	$E(2)^{a}$	E(j)-E(i) <sup>b</sup>	F(i,j) <sup>c</sup>
			(j)			(KJ\mol)	(a.u.)	(a.u.)
$N_1 - C_2$	σ	1.9829	$N_1 - C_9$	σ*	0.0271	2.92	1.39	0.057
	σ	1.9829	C <sub>4</sub> - N <sub>5</sub>	$\sigma^*$	0.0363	0.89	1.45	0.032
	σ	1.9829	C4 - C9	σ*	0.0625	0.53	1.42	0.025
	σ	1.9829	C <sub>8</sub> - C <sub>9</sub>	σ*	0.0563	9.39	1.39	0.103
N <sub>1</sub> - C <sub>9</sub>	σ	1.97853	N <sub>1</sub> - C <sub>2</sub>	σ*	0.0488	2.05	1.29	0.046
	σ	1.97853	N <sub>1</sub> - H <sub>12</sub>	σ*	0.0227	1.19	1.23	0.034
	σ	1.97853	C <sub>4</sub> - C <sub>9</sub>	σ*	0.0625	3.86	1.55	0.07
	σ	1.97853	N <sub>7</sub> - C <sub>8</sub>	σ*	0.0743	1.05	1.34	0.034
	σ	1.97853	C <sub>8</sub> - C <sub>9</sub>	σ*	0.0563	8.32	1.51	0.101
N <sub>1</sub> - H <sub>12</sub>	σ	1.98879	N <sub>1</sub> - C <sub>9</sub>	σ*	0.0271	1.65	1.31	0.042
C <sub>2</sub> - N <sub>3</sub>	σ	1.98126	N <sub>1</sub> - H <sub>12</sub>	σ*	0.0227	1.7	1.2	0.04
	σ	1.98126	C <sub>2</sub> - H <sub>13</sub>	σ*	0.0255	1.05	1.26	0.033
	σ	1.98126	N <sub>3</sub> - C <sub>4</sub>	σ*	0.0369	2.18	1.54	0.052
	σ	1.98126	C <sub>4</sub> - N <sub>5</sub>	σ*	0.0363	9.86	1.56	0.111
C <sub>2</sub> - N <sub>3</sub>	π	1.83483	C <sub>4</sub> - C <sub>9</sub>	π*	0.4679	28.14	0.38	0.1
C <sub>2</sub> - H <sub>13</sub>	σ	1.98791	N <sub>1</sub> - C <sub>9</sub>	σ*	0.0271	1.37	1.16	0.036
	σ	1.98791	$C_2 - N_3$	σ*	0.0071	0.59	1.19	0.024
	σ	1.98791	N <sub>3</sub> - C <sub>4</sub>	σ*	0.0369	3.07	1.21	0.055
N <sub>3</sub> - C <sub>4</sub>	σ	1.97398	N <sub>1</sub> - C <sub>2</sub>	σ*	0.0488	0.87	1.26	0.03
	σ	1.97398	C4 - N5	σ*	0.0363	6.11	1.55	0.087
C <sub>4</sub> - N <sub>5</sub>	σ	1.97654	N <sub>1</sub> - C <sub>9</sub>	σ*	0.0271	1.31	1.5	0.04
	σ	1.97654	N <sub>3</sub> - C <sub>4</sub>	σ*	0.0369	4.97	1.54	0.078
	σ	1.97654	C <sub>4</sub> - C <sub>9</sub>	σ*	0.0625	3.96	1.52	0.07
	σ	1.97654	N <sub>5</sub> - C <sub>6</sub>	σ*	0.0341	2.38	1.53	0.054
	σ	1.97654	C <sub>6</sub> - N <sub>11</sub>	σ*	0.0353	4.46	1.47	0.073
C <sub>4</sub> - C <sub>9</sub>	σ	1.95129	N <sub>1</sub> - C <sub>9</sub>	σ*	0.0271	4.34	1.32	0.068
	σ	1.95129	$N_1 - H_{12}$	σ*	0.0227	6.43	1.02	0.073
	σ	1.95129	$C_8 - S_{10}$	σ*	0.0168	5.21	1.09	0.068
C <sub>4</sub> - C <sub>9</sub>	π	1.6054	C <sub>2</sub> - N <sub>3</sub>	π*	0.3689	17.9	0.28	0.064
	π	1.6054	N <sub>5</sub> - C <sub>6</sub>	π*	0.4513	7.28	0.28	0.041
	π	1.6054	$C_8 - S_{10}$	π*	0.4925	39.06	0.24	0.088
N <sub>5</sub> - C <sub>6</sub>	σ	1.97176	N <sub>3</sub> - C <sub>4</sub>	σ*	0.0369	5.29	1.55	0.081
N <sub>5</sub> - C <sub>6</sub>	π	1.78689	C <sub>4</sub> - C <sub>9</sub>	π*	0.4679	35.23	0.38	0.11

Table 3 Second order	perturbation theory	analysis of Fock	matrix in NBO	basis for 2-A	1mino-1H-purine-
6(7H)-thione.					

	π	1.78689	N <sub>5</sub> - C <sub>6</sub>	π*	0.4513	6.31	0.34	0.044
C <sub>6</sub> - N <sub>7</sub>	σ	1.97792	N <sub>5</sub> - C <sub>6</sub>	σ*	0.0341	2.39	1.54	0.054
C <sub>6</sub> - N11	σ	1.98635	C <sub>4</sub> - N <sub>5</sub>	σ*	0.0363	1.7	1.64	0.047
N <sub>7</sub> - C <sub>8</sub>	σ	1.98224	N <sub>1</sub> - C <sub>9</sub>	σ*	0.0271	3.61	1.47	0.065
	σ	1.98224	C <sub>6</sub> - N <sub>7</sub>	σ*	0.062	2.94	1.37	0.057
	σ	1.98224	C <sub>6</sub> - N <sub>11</sub>	σ*	0.0353	3.52	1.44	0.064
N <sub>7</sub> - H <sub>14</sub>	σ	1.98296	N <sub>5</sub> - C <sub>6</sub>	σ*	0.0341	3.11	1.34	0.058
	σ	1.98296	C <sub>6</sub> - N <sub>11</sub>	σ*	0.0353	0.57	1.29	0.024
	σ	1.98296	C <sub>8</sub> - C <sub>9</sub>	σ*	0.0563	2.04	1.3	0.046
C <sub>8</sub> - C <sub>9</sub>	σ	1.96229	N <sub>1</sub> - C <sub>2</sub>	σ*	0.0488	1.62	1.13	0.038
	σ	1.96229	C <sub>8</sub> - S <sub>10</sub>	σ*	0.0168	2.13	1.13	0.044
$C_8 - S_{10}$	σ	1.97918	C <sub>4</sub> - C <sub>9</sub>	σ*	0.0625	2.31	1.41	0.051
	σ	1.97918	C <sub>6</sub> - N <sub>7</sub>	σ*	0.062	2.6	1.29	0.052
	σ	1.97918	C <sub>8</sub> - C <sub>9</sub>	σ*	0.0563	4.33	1.38	0.07
C <sub>8</sub> - S <sub>10</sub>	π	1.96702	C <sub>4</sub> - C <sub>9</sub>	π*	0.4679	7.05	0.35	0.05
	π	1.96702	$C_8 - S_{10}$	π*	0.4925	2.61	0.27	0.027
N <sub>11</sub> - H <sub>15</sub>	σ	1.9862	N <sub>5</sub> - C <sub>6</sub>	σ*	0.0341	5.97	1.33	0.08
N <sub>11</sub> - H <sub>16</sub>	σ	1.98598	N 5-C6	σ*	0.0341	0.68	1.32	0.027
	σ	1.98598	C <sub>6</sub> - N <sub>7</sub>	σ*	0.062	6.33	1.2	0.079
C <sub>2</sub> - N <sub>3</sub>	π	0.36885	C <sub>4</sub> - C <sub>9</sub>	π*	0.4679	97.05	0.04	0.081
N <sub>5</sub> - C <sub>6</sub>	π	0.45131	C <sub>4</sub> - C <sub>9</sub>	π*	0.4679	69.12	0.04	0.069
C <sub>8</sub> - S <sub>10</sub>	π	0.49247	C <sub>4</sub> - C <sub>9</sub>	π*	0.4679	48.63	0.08	0.083
	π	0.49247	N <sub>5</sub> - C <sub>6</sub>	π*	0.4513	1.4	0.05	0.01
N <sub>1</sub>	LP (1)	1.57398	$C_2 - N_3$	σ*	0.0071	40.03	0.29	0.097
			C <sub>4</sub> - C <sub>9</sub>	σ*	0.0625	46.72	0.32	0.111
			$C_8 - S_{10}$	σ*	0.4925	1.08	0.24	0.015
N <sub>3</sub>	LP (1)	1.89762	N <sub>1</sub> - C <sub>2</sub>	σ*	0.0488	12.08	0.73	0.085
			C <sub>4</sub> - C <sub>9</sub>	σ*	0.4679	7.41	0.99	0.077
			C <sub>8</sub> - C <sub>9</sub>	σ*	0.0563	0.59	0.96	0.022
N <sub>5</sub>	LP (1)	1.86594	$N_1 - C_9$	σ*	0.0271	0.52	0.91	0.02
			N <sub>3</sub> -C <sub>4</sub>	σ*	0.0369	5.48	0.95	0.066
			C <sub>4</sub> - C <sub>9</sub>	σ*	0.4679	11.21	0.93	0.093
N <sub>7</sub>	LP (1)	1.63714	$N_5-C_6$	σ*	0.4513	2.22	0.93	0.044
S <sub>10</sub>	LP (1)	1.98556	N <sub>7</sub> -C <sub>8</sub>	σ*	0.0743	3.16	1.13	0.054
N <sub>11</sub>	LP (1)	1.7288	N <sub>5</sub> -C <sub>6</sub>	σ*	0.4513	0.59	0.94	0.022

<sup>a</sup>E(2)means energy of hyper conjugative interaction (stabilization energy).

<sup>b</sup>Energy difference donor and acceptor i and j NBO orbitals.

<sup>c</sup>F(i, j) is the Fork matrix element between i and j NBO orbitals.

# 4.2 Nonlinear Optical effects

The polarizability  $\alpha$  and the hyper polarizability  $\beta$  and the electric dipole moment  $\mu$  of title compound are calculated by finite field method using B3LYP/6-311++G (d, p) basis set available in DFT package. To calculate all the electric dipole moments and the first hyperpolarizabilities for the isolated molecule, the origin of the Cartesian coordinate system (x, y, z) = (0, 0, 0) was chosen at own center of mass of2-Amino-1H-purine-6(7H)-thione.

The first hyperpolarizabilities ( $\beta_0$ ) of this novel molecular system, and related properties ( $\beta$ ,  $\alpha_0$  and  $\alpha$ ) of 2-Amino-1H-purine-6(7H)-thione were calculated using 6-311++G (d, p) basis set, based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [26]. They determine not only the strength of molecular interactions (long-range inter induction, dispersion force, etc.) as well as the cross sections of different scattering and collision process but also the nonlinear optical properties (NLO) of the system [27, 28]. First hyperpolarizability is a third rank tensor that can be described by  $3\times3\times3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman Symmetry [29]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the  $3\times3\times3$  matrixes is a tetrahedral. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes

$$E = E^{0} - \mu_{\alpha}F_{\alpha} - \frac{1}{2}\alpha_{\alpha\beta}F_{\alpha}F_{\beta} - \frac{1}{6}\beta_{\alpha\beta\gamma}F_{\alpha}F_{\beta}F_{\gamma} + \cdots$$

Where  $E^0$  is the energy of the unperturbed molecules,  $F_{\alpha}$  the field at the origin  $\mu_{\alpha}$  and  $\alpha_{\alpha\beta}\beta_{\alpha\beta\gamma}$  are the components of dipole moments, polarizability and the first hyperpolarizabilities respectively. The total static dipole moments  $\mu$ , the mean polarizabilities  $\alpha_0$ , the anisotropy of the polarizabilities  $\alpha$  and the mean first hyperpolarizabilities  $\beta$ , using the x, y and z components they are defined as:

The total static dipole moment is

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$
  
The isotropic polarizability is  

$$\alpha_0 = \frac{(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3}$$
  
The polarizability anisotropy invariant is  
 $\alpha = 2^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \alpha_{xx}^2]^{1/2}$   
and the average hyperpolarizability is  
 $\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{\frac{1}{2}}$   
and  
 $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$   
 $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$   
 $\beta_z = \beta_{zzz} + \beta_{xyz} + \beta_{yyz}$ 

The total static dipole moment, polarizabilities and first hyper-polarizabilities of 2-Amino-1H-purine-6(7H)-thione were calculated. **Table 4** lists the values of the electric dipole moment (Debye) and dipole moment components, polarizabilities and hyperpolarizabilities of the 2-Amino-1H-purine-6(7H)-thione. In addition to the isotropic polarizabilities and polarizabilities anisotropy invariant were also calculated. In our present study, the calculated value of dipole moment was found to be 1.75588 (Debye) at 6-311++ (d, p) level. The polarizabilities and first hyperpolarizabilities of 2-Amino-1H-purine-6(7H)-thione are 242.657 a.u. and  $4.54\times10^{-30}$ esu, by B3LYP/6-311G++ (d, p) level, which are comparable with the reported values of similar derivatives. The magnitude of the molecular hyperpolarizability $\beta$ , is one of key factors in a NLO (non-linear optical) system. Total dipole moment of title molecule is approximately to those of urea and first order hyperpolarizability of title molecule is 12 times greater than those of urea ( $\beta$  of urea is 0.3728\times10^{-30} esu) [30]. The results indicate that the titlemolecule is good candidate of NLO material.

Table 4 The B3LYP/ 6-311++G (d, p) calculated electric dipole moments  $\mu$  (Debye), dipole moments compound, polarizability $\alpha$  (in a.u.),  $\beta$  components and  $\beta_{tot}$  (10<sup>-30</sup>esu) value of 2-Amino-1H-purine-6(7H)-thione

Parameters	B3LYP	Parameters	B3LYP
β <sub>xxx</sub>	-104.41	$\mu_x$	-0.7127
β <sub>xxy</sub>	158.037	$\mu_y$	-0.1246
β <sub>xyy</sub>	-62.415	$\mu_z$	1.59989
β <sub>yyy</sub>	255.371	μ	1.75588
β <sub>zxx</sub>	52.8923	$\alpha_{xx}$	133.89403
$\beta_{xyz}$	-11.677	$\alpha_{xy}$	-7.899663
β <sub>zyy</sub>	17.7826	$\alpha_{yy}$	155.63391
β <sub>xzz</sub>	14.937773	$\alpha_{xz}$	-15.61649
β <sub>yzz</sub>	88.8475	$\alpha_{yz}$	-15.9079
β <sub>zzz</sub>	-51.247	α <sub>zz</sub>	75.877583
$\beta_{tot}(a.u)$	525.07881	$\alpha_0$	121.80184
$\beta_{tot}$ (e.s.u)	4.54E-30	α	1.81E-23
		$\Delta \alpha$ (a.u)	242.65744
		$\Delta \alpha$ (e.s.u)	3.60E-23

#### 4.3 Fukui function

Fukui indices are, in short, reactivity indices; they give us information about which atoms in a molecule have a larger tendency to either loose or accept an electron, which we chemist interpret as which are more prone to undergo a nucleophilic or an electrophilic attack, respectively. The Fukui function is defined as [31]:

$$f(r) = \left(\frac{\delta\rho(r)}{\delta N}\right)r$$

Where q(r) is the electronic density, N is the number of electrons and r is the external potential exerted by the nuclease. The Fukui function is a local reactivity descriptor that indicates the preferred regions where a chemical species will change its density when the number of electrons is modified. Therefore, it indicates the pro- pensity of the electronic density to deform at a given position upon accepting or denoting electrons [32]. Also, it is possible to define the corresponding condensed or atomic Fukui functions on the jth atom site as

$$f_j^- = q_i(N) - q_j(N-1)$$
 (1)

$$f_j^+ = q_j(N+1) - q_j(N)$$
(2)

$$f_j^0 = \frac{1}{2} [q_j(N+1) - q_j(N-1)]$$
(3)

For an electrophilic  $f_j^-$  (r),nucleophilic or free radical attack  $f_j^+$  (r), on the reference molecule, respectively. In these equations, q is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.) at the j<sup>th</sup> atomic site is the neutral (N), anionic (N + 1) or cationic (N-1) chemical species. The Fukui function allows determining the pin point distribution of the active sites on a molecule, the value of this function is completely dependent of the kind of charges used. In **Table 5** it is reported the values of the Fukui function obtained from the Mulliken charges. From the values reported in **Table 5**, the reactivity order for the electrophilic case is  $H_{15} > H_{14} > H_{16} > S_{10} > N_{11} > C_8 > H_{13} > H_{12} > N_3$ . On the other hand, for nucleophilic attack we observe  $S_{10} > N_5 > C_9 > H_{13} > H_{12} > H_{14} > H_{16} > H_$ 

Table 5 Values of the	Fukui function of 2-Amino-1H-Purine-6(7H)-thioned	considering Mulliken charges
according with Eqns. (	(1)-(3).	

Atoms	$\mathbf{f}_{j}^{-}$	$\mathbf{f_j}^+$	$f_j^0$
N <sub>1</sub>	-0.0058	0.0346	0.014385
C <sub>2</sub>	-0.0093	0.0578	0.024258
N <sub>3</sub>	0.0110	0.0601	0.03556
C4	-0.8754	0.0182	-0.4286
N <sub>5</sub>	-0.0826	0.1363	0.02684
C <sub>6</sub>	-0.3371	-0.0218	-0.17944
N <sub>7</sub>	-0.0254	0.0251	-0.00013
C <sub>8</sub>	0.1811	-0.0764	0.052355
C <sub>9</sub>	-0.4304	0.1343	-0.14805
S <sub>10</sub>	0.2835	0.3213	0.302395
N <sub>11</sub>	0.2283	0.0484	0.138365
H <sub>12</sub>	0.0464	0.0520	0.049222
H <sub>13</sub>	0.0486	0.0750	0.06181
H <sub>14</sub>	0.5110	0.0503	0.280652
H <sub>15</sub>	1.0997	0.0455	0.572567
H <sub>16</sub>	0.3565	0.0391	0.197812

## 4.4 Thermodynamic properties

Table 6 Thermodynamic properties at different temperatures at the B3LYP/6-311++G (d, p) level for 2-Amino-1H-purine-6(7H)-thionemolecule.

T (K)	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
100	277.05	60.88	4.28
200	332.85	106.05	12.59
298.15	383.47	149.7	25.17
300	384.4	150.47	25.45
400	433.13	189.04	42.48
500	478.82	220.42	63.02
600	521.28	245.16	86.35
700	560.6	264.63	111.87
800	596.98	280.18	139.14
900	630.74	292.84	167.81
1000	662.15	303.34	197.64

On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity  $(C_{p,m}^{0})$ , entropy  $(S_{m}^{0})$ , and enthalpy changes  $(\Delta H_{m}^{0})$  for the title molecule are obtained from the theoretical harmonic frequencies and listed in **Table6**. From **Table 6**, it can be observed that these thermodynamic functions are increased with temperature ranging from 100 to 1000 K due to the fact that the molecular vibrational intensities increase with temperature[33]. The correlation equations between heat capacity, entropy, enthalpy changes and temperatures are fitted by quadratic formulas and the corresponding fitting factors (R<sup>2</sup>) for these thermodynamic properties are 0.99946, 0.9999 and 0.99935, respectively. The corresponding fitting equations are as follows and the correlation graphics of those shown in **Fig. 4**.

 $C_{p,m}^{\theta} = 9.1584 + 0.54562\text{T}-2.54291 \text{ x } 10^{-4}\text{T}^{2} (\text{R}^{2} = 0.99946)$   $S_{m}^{\theta} = 219.821 + 0.5937\text{T}-1.51804 \text{ x } 10^{-4}\text{T}^{2} (\text{R}^{2} = 0.9999)$  $H_{m}^{\theta} = -7.21744 + 0.07498\text{T} + 1.32134 \text{ x } 10^{-4}\text{T}^{2} (\text{R}^{2} = 0.99935)$  All the thermodynamic data supply helpful information for the further study on the 2-Amino-1H-purine-6(7H)-thione. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics in thermo chemical field [34]. Notice: all thermodynamic calculations are done in gas phase and they could not be used in solution.



Figure 4 Correlation graphs of thermodynamic properties at different temperature for 2-Amino-1Hpurine-6(7H) thione.

# 4.5 HOMO-LUMO energy



Figure 5 The atomic orbital compositions of the frontier molecular orbital of 2-Amino-1H-purine-6(7H)-thione

HOMO energy = -6.0023 eV LUMO energy = -1.926 eV HOMO-LUMO energy gap = -4.076 eV

Highest occupy molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) or very important parameters for quantum chemistry. We can determine the wave the molecule interacts with other species hence; they are called the frontier orbitals. HOMO, which can be thought the outer most orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand LUMO can be thought the inner most orbital containing free places to accept electrons [35]. 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 [36]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structure [37]. The atomic orbital compositions of the frontier molecular orbital are sketched in Fig. 5.

# 4.6 Molecular Electrostatic Potential



Figure 6 The Molecular Electrostatic Potential (MEP) of 2-Amino-1H-purine-6(7H)-thione

The 3D molecular electrostatic potential (MEP) of 2-Amino-1H-purine-6(7H)-thioneare illustrated in Fig.6. At any given point r(x, y, z) in the vicinity of a molecule, the molecular electrostatic potential, v(r) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r [38]. The MEPs is a plot of electrostatic potential mapped onto the constant electron density surface. The MEPs superimposed on top of the total energy density as a shell. The molecular electrostatic potential (MEP) is related to the electronic density which is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [39]. The different values of the electrostatic potential at the surface are represented by different colors. The color code of these maps in the range between -0.05 a.u. (deepest red) and +0.05 a.u. (white) in compound, where white indicates the strongest attraction (nucleophilic attack) and red indicates the strongest repulsion (electrophilic attack). The importance of MEPs lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color

grading and is very useful in research of molecular structure with its physicochemical property relationship [40]. As can be seen from the MEP of the title compound while region having the negative potential are over the electronegative atoms (Nitrogen and Sulfur), the region having the positive potential are over the hydrogen atoms. From this result, we can say that the hydrogen atom indicates the strongest attraction and nitrogen and sulfur atoms indicate the repulsion.



## 4.7Total, sum of alpha plus beta electrons DOS





Figure 8: The calculated TDOS diagram of 2-Amino-1H-Purine-6(7H)-Thione.

In the boundary region, neighboring orbitals may show quasi degenerate energy levels. In such cases consideration of only the HOMO and LUMO may not yield a realistic description of frontier orbitals. For this reason, the TDOS, sum of  $\alpha$  and  $\beta$  electron density of states [41,42], in terms of Mulliken population analysis were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 eV by using the Gauss Sum 2.2 program [43]. The TDOS,  $\alpha\beta$ DOS of 2-Amino-1H-purine-6(7H)-thione are plotted in Figs. 7 and 8. They provide a pictorial representation of MO (molecule orbital) compositions and their contributions to the chemical bonding. The most important application of the DOS plots is to demonstrate MO compositions and their contributions to the chemical bonding. The most important application of the positive and negative charges provide  $\alpha\beta$ DOS, TDOS diagrams. The  $\alpha\beta$ DOS

shows the bonding, sum of positive and negative electron with nature of the interaction of two orbitals, atoms or groups. In this case, the title molecule consists of 43  $\alpha$ -electrons and 43  $\beta$ -electrons, totally 86 electrons are occupied in density of states. The way designate a pictorial representation for cations and anions is essentially similar to that for neutral atoms in their ground state. Because of the short range of absorption, alphas are not, in general, dangerous to life unless the source is ingested or inhaled, in which case they become extremely dangerous [44]. A positive value of the  $\alpha\beta$ DOS indicates a bonding interaction, negative value means that there is an anti-bonding interaction and zero value indicates nonbonding interactions [45].

# 5. Conclusions

In the present work, the optimized molecular structure, thermodynamic and electronic properties, vibrational frequencies, intensity of vibrations of the title compound are calculated by DFT method using B3LYP/6-311++G (d, p) basis set. The optimized geometric parameters (bond lengths and bond angles) are theoretically determined by DFT theory and compared with the experimental data. The vibrational FT-IR and FT-Raman spectra of the 2-amino-1H-purine-6(7H)-thionemolecule are recorded and on the basis of agreement between the calculated and experimental results, the assignments of all the fundamental vibrational modes of the title compound are made unambiguously based on the results of the PED output obtained from normal coordinate analysis. The NBO analysis explained the intra molecular hydrogen bonding and the hyper conjugative interaction in the molecule. The charge delocalization on the molecule is different with different HOMO, LUMO energy levels. Low HOMO-LUMO energy gap value indicates the intramolecular charge transfer inside the molecule. Fukui function helps to identifying the electrophilic/nucleophilic nature of a specific site within a molecule. The MEP shows the negative potential sites are on Nitrogen and Sulfur atoms as well as the positive potential sites around the hydrogen atoms. Orbital energy interactions between selective functional groups are analyzed by density of energy states. The correlations between the statistical thermodynamical and temperature are also obtained. It was seen that the heat capacities, entropies and enthalpies increase with the increasing temperature owing to the intensities of the molecular vibrations increase with increasing temperature.

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