

Ab initio and DFT studies on structure, vibrational spectra of 4-tert-butyl-1,3-thiazol-2-amine (BTA)

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Theoretical studies have been carried out on 4-tert-butyl-1, 3-thiazol-2-amine (BTA) using both the B3LYP/6-311+G and HF/6-311+G methods. The geometrical parameters and vibrational spectra of BTA have been calculated and analyzed. The calculated IR wavenumbers have been compared with the observed FTIR wavenumbers. The complete assignments have been performed based on the potential energy distribution (PED) of the vibrational modes. The wavenumbers obtained from B3LYP method are in good agreement with the observed wavenumbers when compared to HF method. It has been found that there is an excellent correlation with 0.999 regression coefficient between the experiment and calculated vibrations. Thermal properties like rotational constants, zero point vibrational energies and nonlinear optical properties like dipole moment, hyperpolarizabilities, NBO analysis and the effect of temperature on various thermodynamic properties have been calculated and reported.

Keywords: Thiazole, FTIR spectra, DFT calculations, Hyperpolarizability, Thermodynamic properties

1 Introduction

Thiazoles that contain sulfur atom are the important class of heterocyclic compounds. These are present in many natural/synthetic products, which have a wide range of pharmacological activities^{1,2} and also find various applications in the other fields such as polymers³, liquid crystals⁴, photonucleases⁵, fluorescent dyes⁶, insecticides⁷ and antioxidant⁸. Some of the drugs that contain thiazole ring are anticonvulsant riluzole, antiparkinsonian talipexole, antischistosomal miridazole, antihelmintic tiabendazole, antiulcer alizatidine, vitamin B₁, antibacterial sulfathiazole, and antiviral ritonavir. In case of natural products thiazole is present as a subunit in a large number of terrestrial and marine compounds, possessing different biological activities which play a vital role in the drug industry. Due to its fascinating biological activity, it is very interesting to study the geometrical, vibrational, thermal and nonlinear optical properties of the title molecule. Density functional theory (DFT) has become more useful to experimentalists in computing the geometrical parameters and other properties like vibrational, thermal, nonlinear, optical etc. of polyatomic molecules⁹.

In the present study, the FTIR spectral investigations of BTA have been carried out theoretically using *ab initio* and DFT methods for the first time and the calculated vibrational wavenumbers are compared with the experiment. The title molecule considered for this study has been synthesized and reported by Kumar *et al.*¹⁰ The geometrical parameters (like bond lengths, bond angles and dihedral angles), non-linear optical properties (like dipole moment, first hyperpolarizability and total hyperpolarizability), thermodynamic parameters (like total energy (E_{tot})), zero-point vibrational energy ($ZPVE$), heat capacities (C_v), entropy (S), total thermal energy (ϵ_{tot}), rotational constants (r_c) and rotational temperatures (r_T) and HOMO-LUMO energy gap (ΔE_g) have been calculated and reported. The effect of temperature on some thermodynamic properties at various temperatures have been calculated and reported.

2 Computational Details

The geometry optimization of the molecule plays an important role in predicting the geometrical, thermal, spectral and NLO properties since these are controlled by the geometry of the molecule. Geometry optimizations of the title molecule, i.e., 4-tert-butyl-1,3-thiazol-2-amine (BTA) (Fig. 1) have been carried

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out with Gaussian 03W software¹¹ using HF/6-311+G and B3LYP/6-311+G methods. For selecting a suitable basis set for BTA, the calculations have been carried to evaluate the vibrational frequencies using different basis sets like 6-31G, 6-311G, 6-31G* and 6-311+G using both the HF and B3LYP methods^{12,13}. Among all these basis sets, it is observed that the calculated vibrational frequencies using the 6-311+G basis set are in good agreement with the experimentally observed ones¹⁰. Also, to check the suitability of the basis set to explore properties of the BTA, calculations have been carried to evaluate the mean absolute deviation (MAD) values for the vibrational frequencies^{12,13} using both HF and B3LYP methods. Here also it is observed that the MAD value calculated by 6-311+G basis set has shown less deviation when compared to the other basis sets. Hence, 6-311+G basis set has been chosen for further studies. During optimization, the atomic positions of the molecule have been fully relaxed and frequency calculations has been carried out to ensure that the optimized geometry that has all positive frequencies and thus is a minimum on the potential energy surface. In this study, it is observed that the vibrational wavenumbers calculated using the HF and B3LYP functional tend to overestimate the experimentally reported values; hence, wavenumbers of BTA are scaled to obtain correct values. In scaled quantum mechanical method, the systematic errors of the computed harmonic force field are corrected by a few scaling factors which are found to be well transferable between chemically related molecules¹⁴⁻¹⁷ and these scaling factors are recommended for general use. In the scaling of vibrational frequencies of BTA, 0.855 (HF) and 0.92 (B3LYP) factors have been used for NH₂ functional group vibrations and remaining are scaled with 0.905 (HF) and 0.963 (B3LYP). The assignments of the calculated wavenumbers have been made by considering PEDs. The PEDs are computed for the quantum chemically calculated

wavenumbers using VEDA 4 program¹⁸ and Gauss View 3.0 package¹⁹ have been used to get visual animation and also for the verification of the vibrational wavenumbers. The molecule belongs to Cs symmetry. The 60 vibrational modes of BTA are dispersed among the symmetry species as $\Gamma = 36A'$ (in-plane) + $24A''$ (out of plane). The calculated FTIR spectra of BTA using the B3LYP/6-311+G method is shown in Fig. 2 and for the sake of comparison the experimentally reported FTIR¹⁰ spectra is also shown. The correlation plot between the calculated and experimental IR frequencies is shown in Fig. 3. It can be seen from Fig. 3 that the IR frequencies calculated using the B3LYP method are in good agreement with the experiment, when compared to the HF method, hence the spectral analysis has been discussed based on B3LYP/6-311+G results only. The optimized geometry obtained from both the HF and B3LYP methods has been used for calculating the thermodynamic and NLO properties of the title molecule. The effect of temperature on some thermodynamic parameters has been calculated and reported.

3 Geometric Structural Analyses

Since the molecular parameters are controlled by the molecular geometry, the geometry optimization is a crucial step for the calculation of IR spectra of BTA. The optimized bond lengths, bond angles and dihedral angles of BTA are given in Table 1, using both the methods namely HF/6-311+G and B3LYP/6-311+G methods. All bond lengths in thiazole ring are in the range of 1.85-1.30 Å, which are in good agreement with the reported data for thiazole²⁰ and methyl substituted amino thiazole²¹. The calculated bond length of -C₁N₇- in both the B3LYP (1.36 Å) and HF (1.35 Å) methods (Table 1) is in good agreement with the reported value of 1.34 Å for the substituted amino thiazole²¹. The calculated bond lengths of -C₁=N₅- and -C₃=C₄- are 1.30 and 1.36 Å, respectively, in B3LYP method, and 1.28 and 1.34 Å, respectively, in HF method (Table 1) which are in good agreement with the reported values 1.31 and 1.34 Å, respectively, for the substituted amino thiazole²¹. The calculated bond angles of -S₂C₁N₅-, -S₂C₁N₇- and -N₅C₁N₇- are 114.1°, 120.7° and 125.1°, respectively, in B3LYP method and 114.1°, 121.1° and 124.7°, respectively, in HF method (Table 1), which are in good agreement with the reported values of 115.0°, 121.0° and 123.5°, respectively, for the substituted amino thiazole²¹.

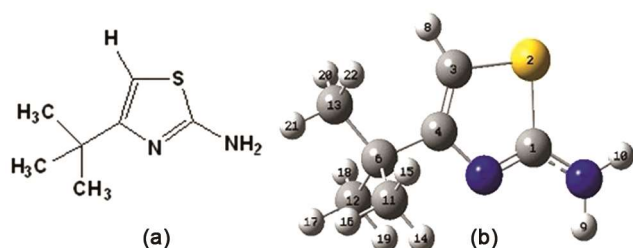


Fig. 1 — (a) Geometry of BTA and (b) optimized geometry of BTA with atom numbers

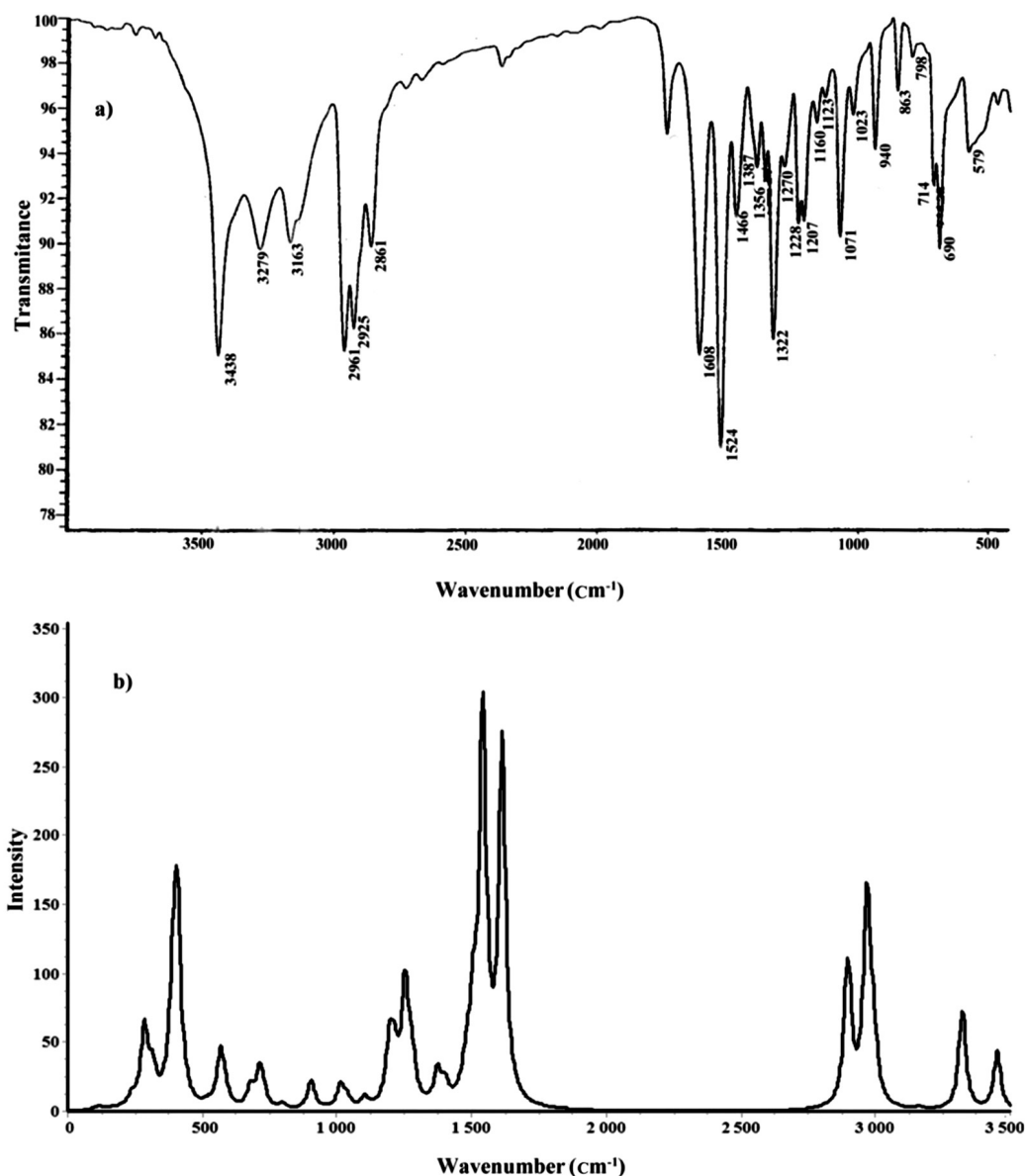


Fig. 2 — IR spectra of BTA (a) experimental FTIR spectra¹⁰ in KBr and (b) calculated spectra obtained from B3LYP/6-311+G level theory (scaled)

4 Infrared Spectra Analysis

4.1 NH₂ vibrations

The IR frequencies corresponding to the symmetric and asymmetric stretching modes of amine functional group are very important in the primary amines moieties^{21,22}. In all the primary aromatic amines, the ν -NH vibrational frequency^{22,23} occurs in the region 3300–3500 cm^{-1} . Singh *et al.*²⁴, reported the symmetric and asymmetric stretching frequencies for the amino thiazole occurs at 3270 cm^{-1} and 3400 cm^{-1} , respectively. As the title molecule contains a primary

amine group, the B3LYP calculated vibrational frequencies which occur at 3322 cm^{-1} and 3452 cm^{-1} have been assigned to the ν_s -NH and ν_{as} -NH vibrational frequencies, respectively (Fig. 2), which are in good agreement with the experimentally observed ν_s -NH (3279 cm^{-1}) and ν_{as} -NH (3438 cm^{-1}) frequencies, respectively¹⁰. As expected these two vibrational frequencies are pure stretching modes in nature and the respective PED contributions for symmetric and asymmetric stretching are 98% and 100%, respectively (mode numbers 1 and 2 in Table 2). Among the different vibrational modes of NH₂, the

scissoring mode has its own importance in IR spectrum while analyzing the spectrum of the molecule²³. According to literature, the s-NH₂ mode^{23,25} occurs in the region 1530-1650 cm⁻¹. In the case of amino thiazole, the s-NH₂ mode²⁴ is reported at 1620 cm⁻¹ and Rao *et al.*²⁶ reported this mode at 1615 cm⁻¹. In the case of the title molecule, the s-NH₂ mode is observed at 1608 cm⁻¹ and the calculated mode has been assigned at 1613 cm⁻¹ (Fig. 2), which is in good agreement with both the reported and observed values¹⁰. The respective PED contribution for this mode is 86% (mode number 13) as shown in Table 2.

4.2 CH vibrations (ring)

The CH stretching vibrational mode in thiazoles and in substituted thiazoles^{25,27} occurs in the region of 3190-3050 cm⁻¹. Sbrana *et al.*²⁸ reported this vibration at 3123 cm⁻¹ in substituted thiazole. In the case of BTA, the observed value of ν-CH mode occurs at 3163 cm⁻¹ and the calculated value has been assigned

as 3162 cm⁻¹ with its corresponding PED as 99% (mode number 3). In substituted amino thiazoles, the β-CH mode²⁵ occurs in the region of 1077-1140 cm⁻¹. In the case of BTA the calculated value for β-CH mode is 1102 cm⁻¹ which is in good agreement with both the observed (1123 cm⁻¹) and the reported values^{10,25,28} and the PED contribution for this mode is 63% (mode number 30) (Table 2).

According to literature the experimental γ-CH vibrational modes in substituted thiazoles²⁵ occur in the region 650-700 cm⁻¹ and this mode has been observed for BTA at 690 cm⁻¹, which is in good agreement with the calculated value of 677 cm⁻¹ and the PED contributions for this mode are 93% and 76% (mode number 41 and 40, respectively) (Table 2).

4.3 CH₃ vibrations

In case of stretching vibrations, which are characteristic for the CH₃ group and the two significant bands which arise due to the asymmetrical

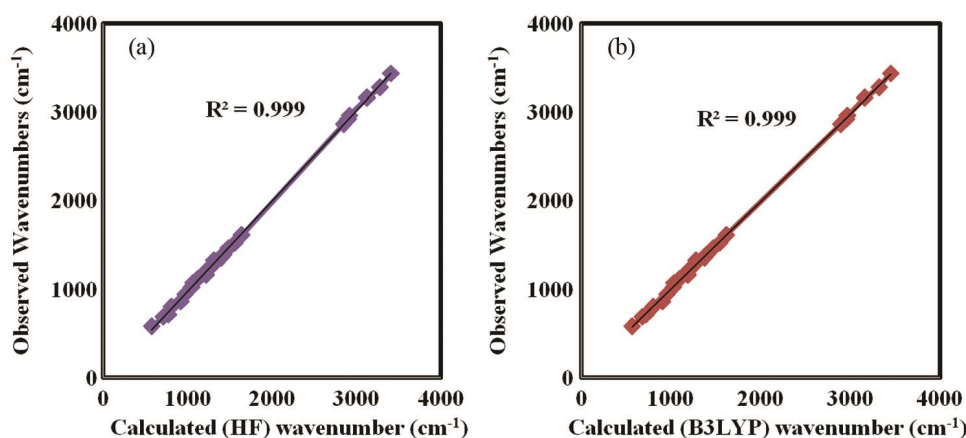


Fig. 3 — Correlation plot of IR frequencies between (a) HF/6-311+G Vs experimental frequencies ($Y_{HF} = 1.020X + 46.3$) and (b) B3LYP/6-311+G Vs experimental frequencies of BTA ($Y_{B3LYP} = 0.988X + 13.63$)

Table 1 — Calculated bond lengths, bond angles and dihedral angles for BTA at HF/6-311+G and B3LYP/6-311+G methods

| | Bond length (Å) | | Bond angle (°) | | Dihedral angle (°) | | | |
|--------------------------------|-----------------|-------|--|--------|--------------------|--|--------|--------|
| | HF | B3LYP | HF | B3LYP | HF | B3LYP | | |
| C ₁ S ₂ | 1.81 | 1.85 | C ₁ S ₂ C ₃ | 86.63 | 86.06 | N ₇ C ₁ S ₂ C ₃ | -180.0 | 180.0 |
| C ₁ N ₅ | 1.28 | 1.30 | C ₁ N ₅ C ₄ | 113.39 | 113.16 | N ₇ C ₁ N ₅ C ₄ | 180.0 | -180.0 |
| C ₁ N ₇ | 1.35 | 1.36 | C ₃ C ₄ N ₅ | 115.28 | 115.42 | S ₂ C ₃ C ₄ C ₆ | -180.0 | 179.9 |
| C ₃ S ₂ | 1.81 | 1.82 | C ₃ C ₄ C ₆ | 127.57 | 127.07 | C ₁ N ₅ C ₄ C ₆ | -180.0 | -180.0 |
| C ₃ C ₄ | 1.34 | 1.36 | N ₅ C ₄ C ₆ | 117.14 | 117.51 | C ₃ C ₄ C ₆ C ₁₁ | -120.4 | -120.4 |
| N ₅ C ₄ | 1.40 | 1.41 | C ₄ C ₆ C ₁₁ | 108.70 | 108.78 | C ₃ C ₄ C ₆ C ₁₂ | 120.4 | 120.5 |
| C ₄ C ₆ | 1.52 | 1.52 | C ₄ C ₆ C ₁₂ | 108.70 | 108.78 | N ₅ C ₄ C ₆ C ₁₁ | 59.6 | 59.5 |
| C ₆ C ₁₁ | 1.54 | 1.55 | C ₄ C ₆ C ₁₃ | 111.24 | 111.22 | N ₅ C ₄ C ₆ C ₁₂ | -59.6 | -59.5 |
| C ₆ C ₁₂ | 1.54 | 1.55 | C ₁₁ C ₆ C ₁₂ | 109.54 | 109.37 | N ₅ C ₄ C ₆ C ₁₃ | 180.0 | -179.9 |
| C ₆ C ₁₃ | 1.54 | 1.54 | C ₁₁ C ₆ C ₁₃ | 109.32 | 109.34 | | | |
| | | | C ₁₂ C ₆ C ₁₃ | 109.32 | 109.33 | | | |
| | | | S ₂ C ₁ N ₅ | 114.10 | 114.10 | | | |
| | | | S ₂ C ₁ N ₇ | 121.10 | 120.70 | | | |
| | | | N ₅ C ₁ N ₇ | 124.70 | 125.10 | | | |

Table 2 — Calculated and observed infrared wavenumbers (cm^{-1}) and assignments with potential energy distribution (PED) of BTA

| Mode No | Species | Calculated wavenumber | | | | Observed wavenumber | Assignment (%PED) |
|---------|---------|-----------------------|--------|---------------|--------|---------------------|--|
| | | HF/6-311+G | | B3LYP/6-311+G | | | |
| | | Unscaled | Scaled | Unscaled | Scaled | | |
| 1 | A' | 3991 | 3412 | 3753 | 3452 | 3438 | vasNH(100) |
| 2 | A' | 3841 | 3284 | 3611 | 3322 | 3279 | vsNH(98) |
| 3 | A' | 3457 | 3129 | 3284 | 3162 | 3163 | vC2H4(99) |
| 4 | A' | 3254 | 2945 | 3108 | 2992 | | vCH3-dia(93) |
| 5 | A'' | 3249 | 2940 | 3103 | 2988 | | vCH3-dia(93) |
| 6 | A' | 3223 | 2917 | 3084 | 2969 | 2961 | vCH3-dia(98) |
| 7 | A'' | 3220 | 2914 | 3081 | 2967 | | vCH3(96) |
| 8 | A' | 3211 | 2906 | 3075 | 2961 | | vCH3-dia(96) |
| 9 | A'' | 3207 | 2903 | 3073 | 2958 | 2925 | vCH3-dia(95) |
| 10 | A' | 3158 | 2858 | 3014 | 2902 | | vCH3-sym(96) |
| 11 | A' | 3148 | 2849 | 3006 | 2894 | | vCH3-sym(96) |
| 12 | A'' | 3148 | 2849 | 3006 | 2894 | 2861 | vCH3-sym(96) |
| 13 | A' | 1813 | 1641 | 1675 | 1613 | 1608 | s NH2(86)+vC1N20(12) |
| 14 | A' | 1722 | 1559 | 1601 | 1541 | | v NCN(84)+ s NH2(15) |
| 15 | A' | 1714 | 1551 | 1565 | 1506 | 1524 | δ CH3-dia(41)+ vC6C2(33) |
| 16 | A' | 1669 | 1510 | 1548 | 1490 | | δ CH3-dia(38)+ v C6C2(43) |
| 17 | A'' | 1655 | 1498 | 1542 | 1485 | | δ CH3-dia(60) |
| 18 | A' | 1648 | 1491 | 1533 | 1476 | | δ CH3-dia(83) |
| 19 | A'' | 1642 | 1486 | 1527 | 1470 | | δ CH3-dia(87) |
| 20 | A' | 1641 | 1486 | 1527 | 1470 | 1466 | δ CH3-dia(86) |
| 21 | A'' | 1627 | 1473 | 1512 | 1456 | | δ CH3-dia(90) |
| 22 | A' | 1576 | 1426 | 1455 | 1401 | 1387 | δ CH3-sym(79) |
| 23 | A' | 1548 | 1401 | 1429 | 1375 | | δ CH3-sym(86) |
| 24 | A'' | 1544 | 1398 | 1423 | 1370 | 1356 | δ CH3-sym(97) |
| 25 | A' | 1452 | 1314 | 1327 | 1277 | | vNC(34)+rCH3(25)+ rNH2(28) |
| 26 | A' | 1428 | 1292 | 1300 | 1252 | | rNH2(68)+vN20C1(13)+ β C2H4(14) |
| 27 | A' | 1372 | 1242 | 1260 | 1213 | | rCH3(52)+ β C2H4(35) |
| 28 | A' | 1352 | 1224 | 1241 | 1194 | | v C7C16(26) + rCH3(35) |
| 29 | A'' | 1348 | 1220 | 1237 | 1191 | | r CH3(73) |
| 30 | A' | 1244 | 1126 | 1145 | 1102 | 1123 | β C2H4(63)+rNH2(21) |
| 31 | A' | 1173 | 1062 | 1077 | 1036 | | rCH3(52)+ β C2H4(15) |
| 32 | A'' | 1159 | 1049 | 1067 | 1027 | | rCH3(62) |
| 33 | A' | 1144 | 1035 | 1052 | 1012 | | r CH3(35)+r NH2(11) |
| 34 | A'' | 1070 | 969 | 990 | 953 | | rCH3(68) |
| 35 | A' | 1027 | 929 | 952 | 916 | | r CH3(78) |
| 36 | A' | 1021 | 924 | 939 | 904 | | v C7C8(35)+r CH3(52) |
| 37 | A'' | 1015 | 919 | 938 | 903 | | β C2C6N5(30)+rCH3(21) |
| 38 | A' | 888 | 804 | 827 | 796 | | v C6C7(15)+rCH3(32) |
| 39 | A' | 855 | 774 | 750 | 722 | | v S3C2(75) |
| 40 | A'' | 801 | 725 | 738 | 710 | | γ C2H4(76) |

(Contd.)

Table 2 — Calculated and observed infrared wavenumbers (cm^{-1}) and assignments with potential energy distribution (PED) of BTA (*Contd.*—)

| Mode No | Species | Calculated wavenumber | | | | Observed wavenumber | Assignment (%PED) |
|---------|---------|-----------------------|--------|---------------|--------|---------------------|---|
| | | HF/6-311+G | | B3LYP/6-311+G | | | |
| | | Unscaled | Scaled | Unscaled | Scaled | | |
| 41 | A'' | 787 | 712 | 704 | 677 | 690 | γ C2H4(93) |
| 42 | A' | 682 | 618 | 609 | 586 | | ν S3C1(24)+ τ NH2(46) |
| 43 | A'' | 665 | 602 | 589 | 567 | | τ S3C1N5(61)+ ζ NH2(35) |
| 44 | A' | 635 | 575 | 585 | 563 | | δ CH3(30)+ ν S3N5(24)+ τ NH2(46) |
| 45 | A' | 582 | 526 | 539 | 519 | | ν C6C7(32)+ γ C1S3C2(15) |
| 46 | A' | 501 | 453 | 463 | 446 | | s C12C8(35)+ s C6C16(23) |
| 47 | A'' | 486 | 440 | 424 | 407 | | ω NH2(81) |
| 48 | A'' | 439 | 398 | 407 | 392 | | ω NH2(50)+ τ CH3(48) |
| 49 | A' | 401 | 363 | 370 | 356 | | bendNH2(45)+ bend CH3(35) |
| 50 | A'' | 371 | 336 | 327 | 314 | | bendCH3(30)+ γ N20H22(70) |
| 51 | A' | 347 | 314 | 313 | 301 | | bendNH2(11)+ bendCH3 (27) |
| 52 | A' | 336 | 304 | 307 | 295 | | δ CCC(46) |
| 53 | A'' | 329 | 298 | 297 | 285 | | τ CH3(78) |
| 54 | A'' | 321 | 291 | 295 | 283 | | τ NH2(70) |
| 55 | A' | 293 | 265 | 267 | 257 | | τ CH3(63) |
| 56 | A'' | 269 | 244 | 245 | 236 | | τ C2C6N5(30)+ τ N5C1N20(60) |
| 57 | A'' | 247 | 224 | 225 | 216 | | τ CH3(81) |
| 58 | A' | 191 | 173 | 176 | 169 | | β CH3(35)+ β NH2(61) |
| 59 | A'' | 131 | 119 | 119 | 114 | | β CH3(30)+ γ C6N5(63) |
| 60 | A'' | 59 | 54 | 49 | 47 | | δ CH3(50)+ ζ^* (45) |

and symmetrical stretching vibrations occurs in the region of $3000\text{-}2850\text{ cm}^{-1}$, respectively^{12,13,22}. The reported values for these vibrational modes are 2960 cm^{-1} , 2935 cm^{-1} (asymmetrical) and 2860 cm^{-1} (symmetrical)²⁸. In the title molecule, the calculated values for the above mentioned vibrations appears at 2894 cm^{-1} (symmetric) and 2969 and 2958 cm^{-1} (asymmetric), which are in good agreement with the observed values, i.e., 2861 cm^{-1} (symmetric) and 2961 and 2925 cm^{-1} (asymmetric)¹⁰. The PED contribution for these vibrations is $\sim 96\%$ (mode numbers 6, 9 and 12) (Table 2).

In case of methyl substituted amino thiazoles, the methyl deformation vibrations occur in the region of $1350\text{-}1475\text{ cm}^{-1}$. The reported values for the symmetric and asymmetric deformation vibrations are 1460 cm^{-1} and 1375 cm^{-1} , respectively²⁵. In case of BTA, the calculated values for the methyl deformation vibrations appear at 1470 cm^{-1} (asymmetric) and 1401 cm^{-1} and 1370 cm^{-1} (symmetric), which are in good agreement with the observed vibrations that occurs at 1466 cm^{-1} for asymmetric and 1387 cm^{-1} and 1356 cm^{-1} for symmetrical modes¹⁰. The PED contributions of these modes have been mentioned in Table 2 (mode numbers 15 to 24).

4.4 C=N, C-N, S-C vibrations (ring)

In general, the -C=N- ring stretching vibrational mode^{23,25} occurs in the range $1550\text{-}1505\text{ cm}^{-1}$. In case of BTA, the calculated value of 1541 cm^{-1} for this vibration mode is in good agreement with both the observed (1524 cm^{-1}) and the reported values. In thiazole ring, the reported values for the -C=N- ring stretching vibrations^{24,28} are 1322 cm^{-1} and 1315 cm^{-1} . In case of BTA, the calculated -C=N- vibration occurs at 1277 cm^{-1} , which is in good agreement with the observed (1322 cm^{-1}) and reported values. In amino thiazole, the reported value for -S-C- vibrational mode²³ is 690 cm^{-1} . In case of BTA, the calculated -S-C- vibration occurs at 722 cm^{-1} , which is in good agreement with both the observed (714 cm^{-1}) and the reported values²³. The corresponding PEDs have been mentioned in Table 2 (mode 25 to 39).

5 Natural Bond Orbital (NBO) Analyses

NBO analysis provides an efficient method for studying the intra and intermolecular bonding and the interaction among bonds and also useful for investigating the charge transfer or conjugative interaction in molecular systems²⁹. This can be done by considering all possible interactions between filled

donor and empty acceptor NBOs and estimating their energy by second order perturbation theory. For each donor NBO (*i*) and acceptor NBO (*j*) the stabilization energy $E(2)$ associated with electron delocalization between donor and acceptor is estimated as:

$$E(2) = \Delta E_{ij} = q_i \left(\frac{F(i,j)^2}{E_j - E_i} \right) \quad \dots (1)$$

where q_i is the orbital occupancy, E_j and E_i are diagonal elements and $F(i, j)$ is the off-diagonal NBO Fock matrix element. The larger $E(2)$ value indicates the more intensive interaction between electron donors and electron acceptors, i.e., more donating tendency from electron donors to electron acceptors and greater is the extent of conjugation in the whole system.

In the present study, NBO analysis has been performed on the title molecule at the DFT/B3LYP/6-311+G level and the results of the second order perturbation theory analysis of Fock matrix are shown in Table 3. The strong intra-molecular hyper conjugative interaction of the σ and π electrons of (C–C), (C–N) and (C–S) to the anti σ and π electrons of (C–C), (C–N) and (C–S) bonds leads to stabilization of the ring system. The interaction of σ (C₁-N₅) to σ^* (C₆-C₇) leads to stabilization of ~ 3.0 kcal/mole and the interactions between σ (C₂-S₃) to σ^* (C₁-N₂₀) and σ^* (C₆-C₇) result in the stabilization of 3.9 and 6.3 kcal/mole, respectively. The interaction of σ (N₅-C₆) to σ^* (C₁-N₂₀) and σ (C₇-C₁₆) to σ^* (N₅-C₆) leads to stabilization of approximately 6.7 and 3.8 kcal/mole, respectively. The most important interactions related to the resonance in the molecule are electron donation from the lone pairs of S₃, N₅ and N₂₀ to the bonding and antibonding orbitals. The interactions between the LP(2) S₃ of the ring hetero atom to the anti bonding orbitals namely π^* (C₁-N₅) and π^* (C₂-C₆) result in the stabilization of 20.32 and 12.86 kcal/mole, respectively. The interactions between the LP(1) N₅ of the ring hetero atom to the anti bonding orbitals namely π^* (C₁-N₅) and π^* (C₂-C₆) results having the stabilization of 20.32 and 12.86 kcal/mole, respectively, which indicates the delocalization. The interaction between the π^* (C₁-N₅) to π^* (C₂-C₆) results in the stabilization of ~ 42 kcal/mol. The interaction between LP(1) N₂₀ with the π^* (C₁-N₅) results in the stabilization of ~ 50 kcal/mol denotes larger delocalization within the ring.

Table 3 — Second order perturbation energy ($E(2)$, kcal/mol) between donor and acceptor orbitals of BTA calculated at B3LYP/6-311+G method

| Donor (<i>i</i>) | Acceptor (<i>j</i>) | $E(2)^a$ | $E(j)-E(i)^b$ (au) | $F(i,j)^c$ (au) |
|---|--|----------|-----------------------|--------------------|
| σ (C ₁ -S ₃) | σ^* (C ₂ - H ₄) | 2.01 | 2.01 | 0.042 |
| | σ^* (N ₂₀ -H ₂₁) | 2.55 | 1.07 | 0.047 |
| σ (C ₁ - N ₅) | σ^* (C ₆ - C ₇) | 2.69 | 1.29 | 0.053 |
| π (C ₁ - N ₅) | π^* (C ₂ - C ₆) | 18.67 | 0.35 | 0.075 |
| σ (C ₂ - S ₃) | σ^* (C ₁ - N ₂₀) | 3.88 | 1.05 | 0.057 |
| | σ^* (C ₆ - C ₇) | 6.24 | 1.01 | 0.071 |
| σ (C ₂ - H ₄) | σ^* (C ₂ - C ₆) | 2.82 | 1.17 | 0.051 |
| | σ^* (N ₅ - C ₆) | 4.47 | 1.00 | 0.060 |
| σ (C ₂ - C ₆) | σ^* (C ₂ - H ₄) | 2.07 | 1.25 | 0.045 |
| | σ^* (C ₆ - C ₇) | 3.14 | 1.16 | 0.054 |
| π (C ₂ - C ₆) | π^* (C ₁ - N ₅) | 7.55 | 0.27 | 0.044 |
| | π^* (C ₇ - C ₈) | 2.16 | 0.64 | 0.034 |
| | π^* (C ₇ - C ₁₂) | 2.16 | 0.64 | 0.034 |
| σ (N ₅ - C ₆) | σ^* (C ₁ - N ₂₀) | 6.56 | 1.21 | 0.080 |
| | σ^* (C ₂ - H ₄) | 2.32 | 1.25 | 0.048 |
| σ (C ₆ - C ₇) | σ^* (C ₂ - S ₃) | 2.79 | 0.77 | 0.042 |
| σ (C ₇ - C ₈) | π^* (C ₂ - C ₆) | 2.49 | 0.61 | 0.037 |
| σ (C ₇ - C ₁₂) | σ^* (C ₂ - C ₆) | 2.49 | 0.61 | 0.037 |
| σ (C ₇ - C ₁₆) | σ^* (N ₅ - C ₆) | 3.75 | 1.03 | 0.055 |
| σ (C ₈ - H ₉) | σ^* (C ₇ - C ₁₆) | 2.92 | 0.86 | 0.045 |
| σ (C ₈ - H ₁₀) | σ^* (C ₇ - C ₁₂) | 2.87 | 0.85 | 0.044 |
| σ (C ₈ - H ₁₁) | σ^* (C ₆ - C ₇) | 2.78 | 0.90 | 0.045 |
| σ (C ₁₂ - H ₁₃) | σ^* (C ₆ - C ₇) | 2.79 | 0.90 | 0.045 |
| σ (C ₁₂ - H ₁₄) | σ^* (C ₇ - C ₈) | 2.87 | 0.85 | 0.044 |
| σ (C ₁₂ - H ₁₅) | σ^* (C ₇ - C ₁₆) | 2.92 | 0.86 | 0.045 |
| σ (C ₁₂ - H ₁₇) | σ^* (C ₇ - C ₈) | 2.91 | 0.86 | 0.045 |
| σ (C ₁₂ - H ₁₈) | σ^* (C ₆ - C ₇) | 3.10 | 0.91 | 0.048 |
| σ (C ₁₂ - H ₁₉) | σ^* (C ₇ - C ₁₂) | 2.91 | 0.86 | 0.045 |
| σ (N ₂₀ - H ₂₁) | σ^* (C ₁ - S ₃) | 5.14 | 0.81 | 0.059 |
| | σ^* (C ₁ - N ₅) | 4.85 | 1.27 | 0.070 |
| LP(1)S ₃ | σ^* (C ₁ - N ₅) | 2.35 | 1.25 | 0.048 |
| LP(2)S ₃ | π^* (C ₁ - N ₅) | 20.32 | 0.25 | 0.066 |
| | π^* (C ₂ - C ₆) | 12.86 | 0.29 | 0.054 |
| LP(1)N ₅ | σ^* (C ₁ - S ₃) | 18.92 | 0.47 | 0.085 |
| | σ^* (C ₁ - N ₂₀) | 2.47 | 0.81 | 0.041 |
| | σ^* (C ₂ - C ₆) | 5.94 | 0.97 | 0.069 |
| LP(1) N ₂₀ | π^* (C ₁ - N ₅) | 49.81 | 0.27 | 0.109 |
| π^* (C ₁ -S ₃) | π^* (C ₁ - S ₃) | 41.92 | 0.04 | 0.063 |

For numbering of atoms of BTA refer Fig. 1; ^a Energy of hyper conjugative interactions; ^b Energy difference between donor and acceptor *i* and *j* NBO orbitals; ^c Fock matrix element between *i* and *j* NBO orbitals

6 Thermodynamic Properties

The study of thermodynamic properties of organic molecules has its own importance in the research area. The thermodynamic properties like total energy (E_{tot}), zero-point vibrational energy (ZPVE), heat capacities (C_v), entropy (S), total thermal energy (E_{tot}), rotational constants (r_c) and rotational temperatures (r_T) of BTA have been calculated at constant pressure using the B3LYP/6-311+G and HF/6-311+G optimized geometries and the results are given in Table 4. It can

be seen from the Table 4, that the variation in E_{tot} and ZPVEs obtained for the title molecule using both the B3LYP/6-311+G and HF/6-311+G methods are significant. The E_{tot} values obtained for BTA using B3LYP/6-311+G and HF/6-311+G methods are -781.65 and -953.81 au, respectively. The ZPVEs values obtained for BTA using B3LYP/6-311+G and HF/6-311+G methods are 115.34 and 123.418 kcal/mol, respectively. The rotational constant values are observed to be nearly same in both the methods. Dipole moment reflects the molecular charge distribution in the molecule and is given as a vector in three dimensions. Therefore, it can be used to depict the charge movement across the molecule. The dipole moment values calculated using both the methods differ slightly.

Table 4 — Thermodynamic parameters of BTA

| | HF/6-311+G | B3LYP/6-311+G |
|-------------------------------------|------------|------------------|
| Thermal parameters | | |
| E_{tot} | -953.81 | -781.65 hartrees |
| ZPVE | 123.418 | 115.34 Kcal/mol |
| r_c | 2.12050 | 2.08048 GHz |
| | 0.76354 | 0.75169 |
| | 0.64047 | 0.62931 |
| r_T | 0.10177 | 0.09985 Kelvin |
| | 0.03664 | 0.03608 |
| | 0.03074 | 0.03020 |
| Thermal energy (E) (Kcal/mol) | | |
| E_{trans} | 0.889 | 0.889 |
| E_{rot} | 0.889 | 0.889 |
| E_{vib} | 128.101 | 120.556 |
| E_{tot} | 129.878 | 122.334 |
| Specific heat (C_v) (Cal/mol-K) | | |
| C_{trans} | 2.981 | 2.981 |
| C_{rot} | 2.981 | 2.981 |
| C_{vib} | 33.818 | 36.895 |
| C_{tot} | 39.780 | 42.857 |
| Entropy (S) (Cal/mol-K) | | |
| S_{trans} | 41.045 | 41.045 |
| S_{rot} | 30.117 | 30.169 |
| S_{vib} | 26.600 | 30.120 |
| S_{tot} | 97.762 | 101.334 |

Table 5 — Thermodynamic properties of BTA at different temperatures at

| B3LYP/6-311+G level | | | | |
|---------------------|--------------------------------|----------------------|--------------------|-------------------|
| T (Kelvin) | E_{tot} (Kcal/mol) | C_v (cal/mol-K) | S (Cal/mol-K) | H (Kcal/mol) |
| 293 | 122.1 | 42.3 | 100.6 | 237.9 |
| 303 | 122.5 | 43.4 | 102.1 | 238.4 |
| 313 | 122.9 | 44.6 | 103.5 | 238.9 |
| 323 | 123.4 | 45.7 | 105.0 | 239.4 |
| 333 | 123.9 | 46.8 | 106.5 | 239.9 |
| 343 | 124.4 | 47.9 | 107.9 | 240.4 |
| 353 | 124.8 | 49.1 | 109.4 | 240.9 |
| 363 | 125.4 | 50.2 | 110.9 | 241.4 |
| 373 | 125.9 | 51.2 | 112.3 | 241.9 |

The variation in thermodynamic properties at different temperatures has been studied using the B3LYP/6-311+G optimized geometry and it is observed that the thermodynamic function value increases with increase of the temperature (Table 5).

Hence, the variation in thermodynamic properties with temperature can be attributed to the fact that as the temperature increases, the intensities of molecular vibration also increase^{13,30}. The correlations between these thermodynamic properties and temperature are shown in Fig. 4. The empirical correlations between the thermodynamic properties and temperature are deduced as follows:

$$\begin{aligned}
 H &= 0.05 T + 223.2 \\
 C_v &= -4 \times 10^{-5} T^2 + 0.137 T + 5.21 \\
 E_{\text{tot}} &= 8 \times 10^{-5} T^2 - 0.003 T + 116.4 \\
 S &= -3 \times 10^{-6} T^2 + 0.148 T + 57.32 \quad \dots (2)
 \end{aligned}$$

All the above mentioned thermodynamic data is helpful for the further studies on BTA. As all these thermodynamic calculations have been done in gas phase and can be used to compute the other thermodynamic energies according to the relationship of thermodynamic functions and estimate chemical reaction directions according to the second law of thermodynamics in thermochemistry³¹.

7 Non-Linear Optical Properties

The optical properties like total dipole moment (μ_{tot}), mean polarizability (α_m), molecular first hyperpolarizability (β_μ), and total hyperpolarizability (β_{tot}) have been calculated by using B3LYP/6-311+G and HF/6-311+G optimized geometries. The values of all these properties have been calculated using standard equations available in literature^{13,32-35}.

The total dipole moment can be calculated using the following equation:

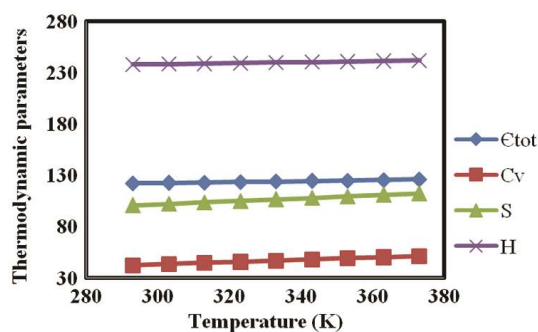


Fig. 4 — Correlation graph between temperature (in Kelvin) and thermodynamic properties like enthalpy (H), Entropy (S), specific heat (C_v) and total energy (E_{tot}) of BTA

$$\mu_{\text{tot}} = [(\mu_x^2 + \mu_y^2 + \mu_z^2)]^{1/2} \quad \dots(3)$$

The mean linear polarizability is defined as:

$$\alpha_m = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad \dots(4)$$

The first hyperpolarizability along the dipole moment direction can be given as:

$$\beta_\mu = (3/5) [(\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z) / |\mu|] \quad \dots (5)$$

Considering Kleinman symmetry³⁵ in the static limit, the β_x , β_y and β_z can be given as:

$$\begin{aligned} \beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yxx} + \beta_{yyy} + \beta_{yzz} \\ \beta_z &= \beta_{zxx} + \beta_{zyy} + \beta_{zzz} \end{aligned} \quad \dots (6)$$

The total hyperpolarizability is defined as:

$$\beta_{\text{tot}} = [(\beta_x^2 + \beta_y^2 + \beta_z^2)]^{1/2} \quad \dots (7)$$

The calculated values for the above mentioned parameters in Eqs (3-7) are obtained by a frequency job output from Gaussian software¹¹ and are shown in Table 6. The calculated dipole moment, polarizability and total hyperpolarizability values of BTA (0.55 Debye, 17.13×10^{-24} esu, 1.17×10^{-30} esu and 2.87×10^{-30} esu, respectively, in B3LYP method and 0.41 Debye, 15.43×10^{-24} esu, and 2.1×10^{-30} esu, respectively, in HF method) are listed in Table 6. Urea is a standard prototypical molecule which is used for the comparison of the NLO properties of molecular systems. And the β -value of the urea molecule was used frequently as a threshold value for the purpose of comparison. Here also the calculated β_{tot} value of

Table 6 — The dipole moment (in Debye), polarizability (in esu), hyperpolarizabilities (in esu) tensors computed with the B3LYP/6-311+G and HF/6-311+G methods

| | B3LYP/ 6-311+G | HF/6-311+G | B3LYP/6-311+G | HF/6-311+G | |
|--------------------|--------------------------|-------------------------|----------------------|------------------------|------------------------|
| μ_x | 0.2770 | 0.20 | β_{xxx} | 97.572 | 32.35 |
| μ_y | -0.0003 | -0.00003 | β_{xyy} | -0.004 | -0.008 |
| μ_z | -0.4750 | -0.3500 | β_{xyy} | 39.8 | 53.46 |
| μ_{tot} | 0.55 | 0.41 | β_{yyy} | -0.006 | 0.050 |
| | | | β_{xzz} | 49.6 | 15.3 |
| α_{xx} | 134.1 | 121.3 | β_{xyx} | -0.003 | -0.018 |
| α_{xy} | 0.001 | 0.006 | β_{yyz} | 18.12 | 19.58 |
| α_{yy} | 84.7 | 77.9 | β_{xzz} | -40.82 | -40.14 |
| α_{xz} | -10.26 | -8.41 | β_{vzz} | 0.003 | 0.011 |
| α_{yz} | 0.0007 | 0.0050 | β_{zzz} | 250.25 | 201.7 |
| α_{zz} | 127.97 | 113.12 | β_μ | 1.17×10^{-30} | 0.95×10^{-30} |
| α_m | 17.132×10^{-24} | 15.43×10^{-24} | β_{tot} | 2.87×10^{-30} | 2.1×10^{-30} |

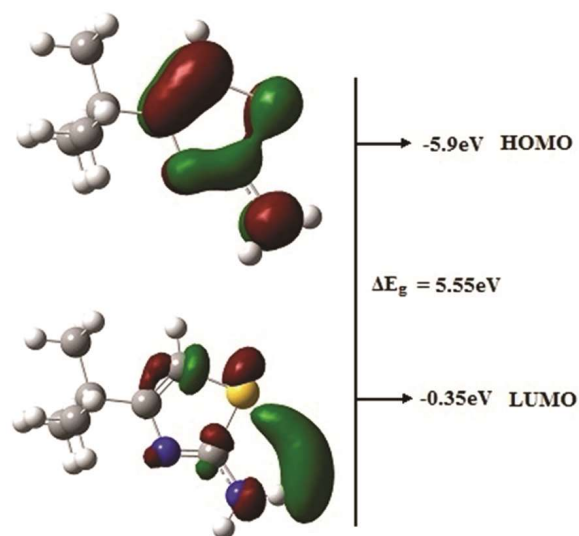


Fig. 5 — Frontier molecular orbitals (HOMO and LUMO) and the energy gap (ΔE_g) of BTA

BTA is compared with urea, and found to be 9.6 (B3LYP)/7.1(HF) times more than that of urea³⁶ (0.2991×10^{-30} esu).

8 HOMO-LUMO Energy Gap

The study of the frontier molecular orbitals, i.e., highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and the HOMO–LUMO energy gap (ΔE_g) energies of an organic molecule are significant in determining the way in which the molecule interacts with other species and also the chemical activity of the molecule³⁷⁻⁴⁰. The HOMO represents the ability to donate an electron whereas the LUMO represents the ability to obtain an electron. According to the Koopman's theory, the energy of HOMO is related to the ionization potential and LUMO is related to the electron affinity of molecule³⁹. The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by the excitation of one electron from the HOMO to LUMO. The HOMO, LUMO and ΔE_g energies of the title molecule have been calculated using B3LYP/6-311+G method and the results are shown in Fig. 5. The ΔE_g for BTA has been calculated as 5.55 eV, which is a critical parameter in determining the molecular charge transport property, there by measuring the conductivity of the molecule.

9 Conclusions

In the present study, the structural geometrical parameters, vibrational frequencies, thermodynamic

and nonlinear optical properties of BTA have been studied using both the B3LYP and HF methods with 6-311+G basis set. The structural parameters like bond length and angles obtained are in good agreement with reported values of thiazoles. It can be seen that the calculated vibrational frequencies of BTA computed using DFT/B3LYP/6-311+G method are in good agreement with the experiment. The spectral frequencies have been calculated using both the above mentioned methods and are compared with the observed spectra. The complete vibrational assignments of wavenumbers have been made on the basis of potential energy distribution and found to be in good agreement with the experiment. The differences between the calculated and observed frequencies of N-H vibrations are higher when compared to C-H, C-C, C-N and C-O frequencies. The values of asymmetric and symmetric stretching vibrations of methyl are in good agreement with the experimental values. The thermodynamic properties have been calculated for the title molecule using both the B3LYP and HF method using 6-311+G basis set and may be helpful in the estimation of chemical reaction directions. Using the B3LYP/6-311+G optimized geometry, the thermodynamic properties are calculated at constant pressure by varying the temperature and the correlation between them is found to be linear. The polarizability, first hyperpolarizability, and total hyperpolarizability imply that the title molecule may be useful as a NLO material. Furthermore, from the molecular orbital analysis, it can be seen that there is a possibility of intermolecular charge transfer within the molecule. From these studies, it can be concluded that the theoretical methods are very useful in predicting the geometrical, vibrational, optical, thermodynamic and charge transfer properties for the new molecule in advance.

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