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# EXPERIMENTAL AND DENSITY FUNCTIONAL THEORY INVESTIGATION OF BOND LENGTH, BOND ANGLE AND THERMODYNAMIC PARAMETERS IN DIHYDROPYRIMIDINE CARBONITRILE

**Jayraj S. Aher[1*], Manoj R. Gaware[2] & Dnyaneshwar D. Lokhande[3]**
*[1*]Department of Chemistry, K.T.H.M College, Nashik, (M.S), India.*
*[2]Department of Chemistry, Arts, Commerce and Science College, Nandgaon, Nashik, (M.S), India.*
*[3] KPG Arts, Commerce and Science College, Igatpuri, Nashik, (M.S), India.*

## Abstract

*Theoretical chemistry method has been adopted to correlate the structural and electronic properties such as bond length, bond angle, Mullikens charges, HOMO-LUMO energy values, energy gap, dipole moment (μ), electron affinity (A), ionization potential (I), electronegativity (χ), global hardness (η), softness(σ), electrophilicity index (ω) and thermodynamic paremeters using density functional theory (DFT) at the B3LYP/6-311 G ++ (d, p) basis set of dihydropyrimidine carbonitrile namely 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile.*

***Keywords**: DFT, HOMO-LUMO, dipole moment, energy gap, themodynamic parameters.*

**Introduction**: Density functional theory (DFT) is a quantum mechanical modelling method used to investigate the electronic structure in the ground state of many systems, particularly atoms, molecules and condensed phase. Using this theory many properties can be evaluated using functionals that is functions of another.

Application of density functional theory to UV, IR and NMR spectroscopies gives clear interpretations $\lambda_{max}$ values, modes of vibrations, vibrational frequencies, coupling constant etc. Pyrimidines are important heterocyclic moiety in many organic compounds and contributed due importance in pharmacological applications[1], biological uses[2-11], herbicidal effects[12], pesticidal impact[13], synthetical applications[14], polymeric and material sciences.[15-18]

In the present work, we have correlated experimental and theoretical IR and NMR spectrum along with molecular structure of dihydropyrimidine carbonitrile (Figure 1) investigated by determining the chemical indexes using density functional theory (DFT) at the B3LYP/6-311++G (d, p) level. To the best of our knowledge the structural and thermodynamic parameters of this compound has not been reported earlier in open literature.

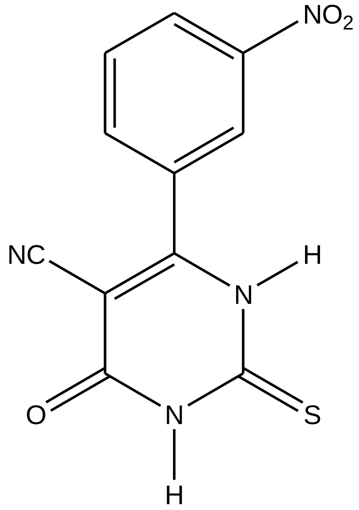


**FIGURE 1:** Structure of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

**Computational Details**: Computational calculations were performed on an Intel Core i3 personal computer using the Gaussian 09W program[19] package without any constraint on the geometry. Geometries of the compound was optimized by DFT/B3LYP at 6-311++G (d, p) basis set to confirm the structure as minima. Absence of imaginary frequency confirms the energy minima. The vibrational frequency assignments and other parameters were made using Gauss View 5.0 molecular visualization program.

**Spectral Data:** The spectral data of the compound is shown below. The experimental IR and $^1$H-NMR spectral data of the compound is listed in table 1 while experimental and theoretical IR and $^1$H-NMR spectrum are shown in figure 2 and figure 3.

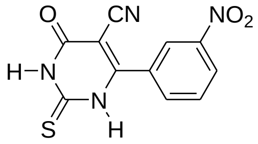
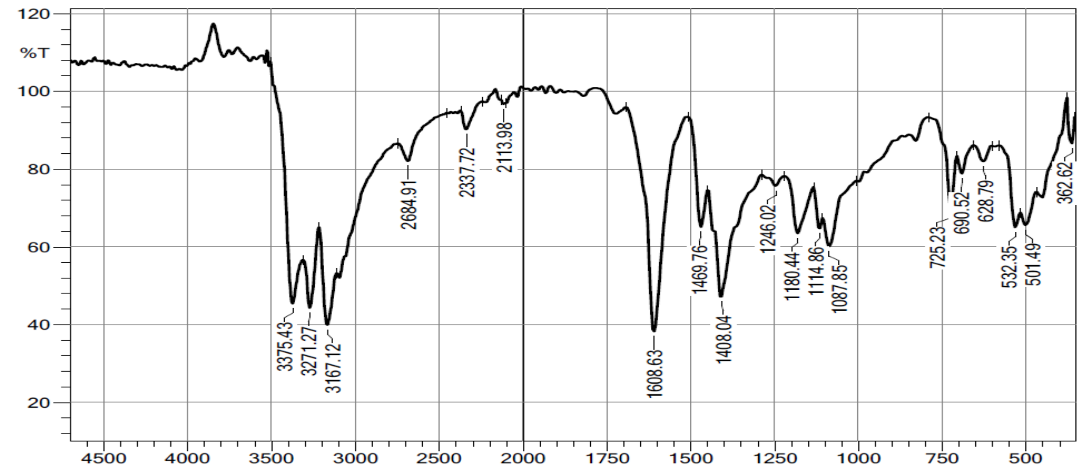
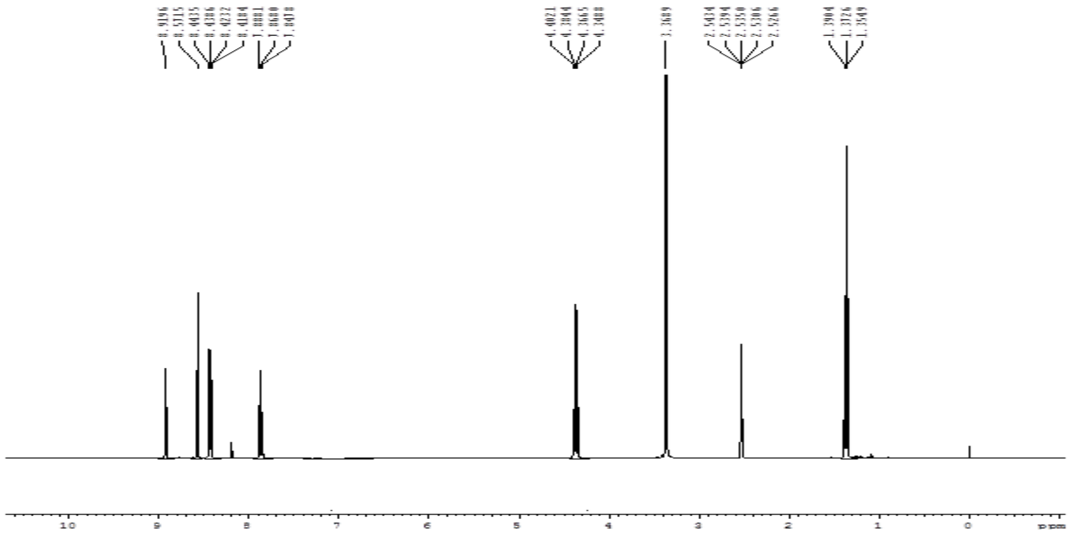
| <br>$C_9H_6N_4O_3S$ | Experimental data | Theoretical data |
|---|---|---|
| IR data cm$^{-1}$ | 3375 : -NH stretch. (2$^{o}$ amide)<br>3271 : -NH stretch. (2$^{o}$ amide)<br>3167 : Ar-H stretch.<br>2114 : -C≡N stretch. (nitrile)<br>1609 : -C=O stretch. (carbonyl)<br>1568 : -C=C (olefin)<br>1470 : -N-O stretch. (nitro)<br>1411 : Ar. C=C stretch.<br>1408 : -NH bending (2$^{o}$ amide)<br>1246 : Ar-N stretch. (nitro)<br>1180 : C-N stretch. (amide)<br>1088 : C=S stretch. (thiol) | 3468 : -NH stretch. (2$^{o}$ amide)<br>3453 : -NH stretch. (2$^{o}$ amide)<br>3105 : Ar-H stretch.<br>2248 : C≡N stretch. (nitrile)<br>1712 : -C=O stretch. (carbonyl)<br>1465 : -C=C (olefin)<br>1535 : -N-O stretch. (nitro)<br>1510 : Ar. C=C stretch.<br>1337 : -NH bending (2$^{o}$ amide)<br>1322 : Ar-N stretch. (nitro)<br>1192 : C-N stretch. (amide)<br>1117 : C=S stretch.(thiol) |
| $^{1}$H-NMR δ (ppm)<br>400 MHz, DMSO | 8.92 (1H, s, -N-H)<br>8.51 (1H, s, -N-H)<br>8.44 (1H, d, Ar-H)<br>8.42 (1H, d, Ar-H)<br>7.88 (1H, d, Ar-H)<br>7.84 (1H, d, Ar-H) | H19 : 7.66 (-NH)<br>H17 : 8.33 (-NH)<br>H7 : 8.52 (Ar-H)<br>H8 : 7.84 (Ar-H)<br>H9 : .33 (Ar-H)<br>H21 : 8.68 (Ar-H) |

**TABLE1:** Experimental and theoretical spectral data of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

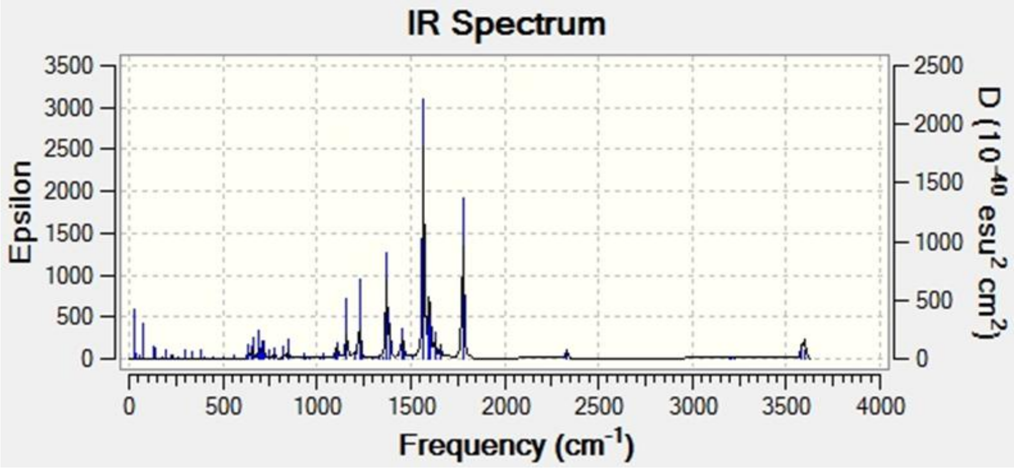


IR spectrum of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

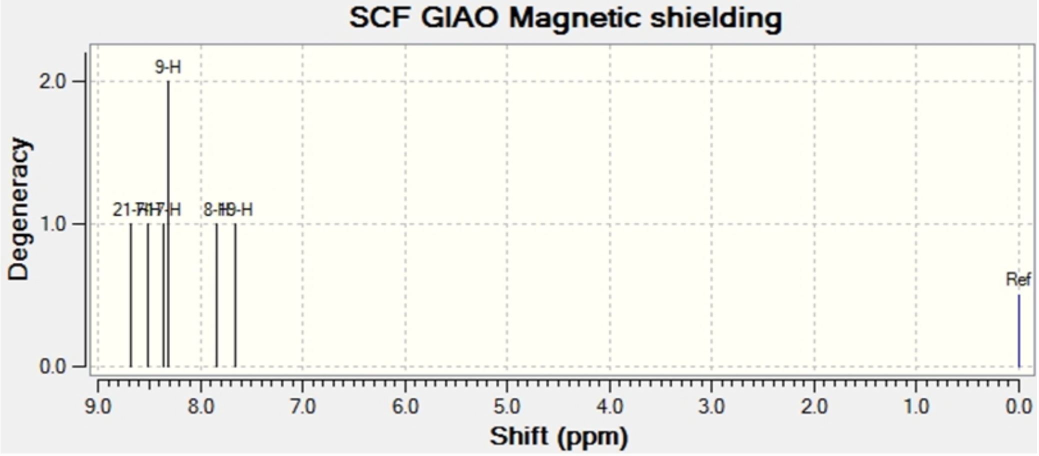


$^1$H-NMR spectrum of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

**FIGURE 2:** Experimental IR and $^1$H-NMR spectrum of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile



IR spectrum of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile



$^1$H-NMR spectrum of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

**FIGURE 3:** Theoretical IR and $^1$H-NMR spectrum of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

## RESULT AND DISCUSSION:

**Molecular geometry:** The optimized geometrical parameters such as bond length, bond angle are listed in table 2 and 3 respectively according to the numbering reported in optimized structure of the compound in figure 3. The point group symmetry of the planar structure of the compound is C1. The compound possess25 atoms hence there 69 normal modes of fundamental vibrations are expected. Slight variation has been observed in experimental and theoretical IR and $^1$H-NMR data for the said compound. For better upgradation across agreement between observed and calculated vibrational frequencies, calculated absorption frequencies were adjusted by multiplying with scaling factor 0.9631 for density functional theory resulting in computed absorption frequencies. The scaled vibrational frequencies are listed in table 1.

*C=O stretching vibrations:*

Open chain simple carbonyl from 2$^o$ amide group (NH-C=O) absorbs within the range 1640-1700 cm$^{-1}$. Computed stretching of carbonyl in amide group for the compound is at 1712 cm$^{-1}$ while experimental carbonyl of amide group absorption is observed at 1609 cm$^{-1}$.

*C≡N stretching vibrations:*

Stretching frequency of nitriles group occurs in the region 2220-2260 cm$^{-1}$. Theoretical C≡N stretching frequency was seen at 2248 cm$^{-1}$ whereas experimentally it is seen ranging between 2114 cm$^{-1}$.

*C=C stretching vibrations:*

Aromatic C=C stretching is observed in range between 1585-1600 and 1400-1500 cm$^{-1}$ while olefinic C=C stretching absorbs in the range 1640-1680 cm$^-$1 Theoretically aromatic C=C stretching absorption bands is seen at 1510 cm$^{-1}$ while olefinic C=C stretching bands is seen at 1568 cm$^{-1}$. Experimentally aromatic C=C stretching is observed at 1411 cm$^{-1}$ while that for olefinic C=C stretching is observed at 1465 cm$^{-1}$.

*N-H vibrations:*

2$^o$ amides shows N-H stretching between 3300-3500 cm$^{-1}$. For compound it is observed theoretically at 3468 and 3453 cm$^-$1 and experimentally it is observed at 3375 and

271 cm$^{-1}$ respectively. The 2$^{o}$ N-H bending is observed at 1337 cm$^{-1}$ experimentally and theoretically it is seen at 1408 cm$^{-1}$.

*C-N and N-O stretching vibrations:*

Aromatic nitro compounds have stretching vibration of N-O at 1500-1550 and 1290-1360 cm$^{-1}$ respectively. Theoretically, -N-O and C-N stretching vibrations of compound is seen at 1535and 1322 cm$^{-1}$ and experimentally it is seen at 1470 cm$^{-1}$ and 1246 cm$^{-1}$.

**Optimized Structure:**

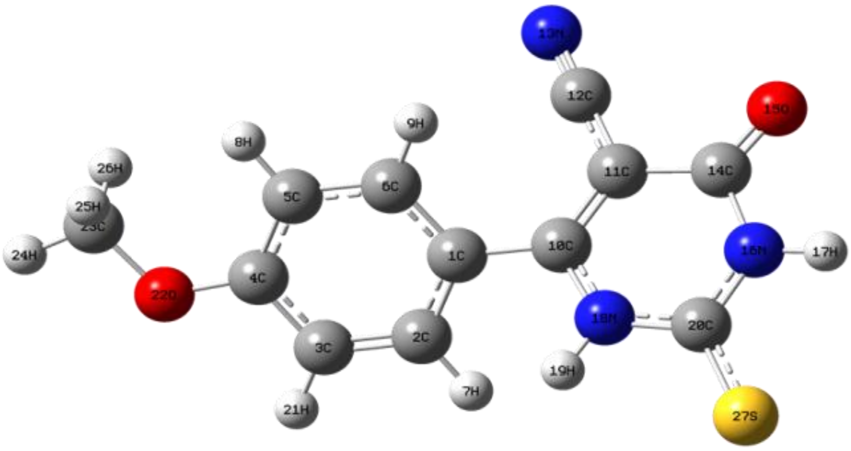


**FIGURE 3:** Optimized Structure of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile

**Bond lengths:**

| Atoms | Bond lengths ($^{o}$A) |
|---|---|
| C1-C2 | 1.3839 |
| C1-C6 | 1.4023 |
| C1-C10 | 1.4821 |
| C2-C3 | 1.3880 |
| C2-H7 | 1.0824 |
| C3-C4 | 1.3895 |
| C3-N22 | 1.4843 |
| C4-C5 | 1.3918 |
| C4-H21 | 1.0813 |
| C5-C6 | 1.3914 |
| C5-H8 | 1.0828 |
| C6-H9 | 1.0821 |
| C10-C11 | 1.3728 |
| C10-N18 | 1.3716 |
| C11-C12 | 1.4200 |
| C11-C14 | 1.4736 |
| C12-N13 | 1.1556 |

| | |
|---|---|
| C14-O15 | 1.2086 |
| C14-N16 | 1.4088 |
| N16-H17 | 1.0133 |
| N18-H19 | 1.0113 |
| N18-C20 | 1.3846 |
| C20-S25 | 1.6542 |
| N22-O23 | 1.2218 |
| N22-O24 | 1.2233 |

**TABLE 2:** Optimized bond lengths (A$^{o}$) of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT method at B3LYP level using 6-311++G (d, p) basis sets

**Bond Angles:**

| **Atoms** | **Bond Angles** |
|---|---|
| C2-C1-C6 | 119.5 |
| C2-C1-C10 | 119.5 |
| C6-C1-C10 | 121.0 |
| C1-C2-C3 | 118.8 |
| C1-C2-H7 | 122.2 |
| C3-C2-H7 | 119.0 |
| C2-C3-C4 | 122.4 |
| C2-C3-N22 | 118.5 |
| C4-C3-N22 | 119.1 |
| C3-C4-C5 | 118.4 |
| C3-C4-H21 | 119.7 |
| C5-C4-H21 | 121.9 |
| C4-C5-C6 | 120.5 |
| C4-C5-H8 | 119.8 |
| C6-C5-H8 | 119.7 |
| C1-C6-C5 | 120.4 |
| C1-C6-H9 | 120.0 |
| C5-C6-H9 | 119.6 |
| C1-C10-C11 | 125.0 |
| C1-C10-N18 | 115.6 |
| C11-C10-N18 | 119.3 |
| C10-C11-C12 | 122.5 |
| C10-C11-C14 | 120.0 |
| C12-C11-C14 | 117.4 |
| C11-C14-O15 | 125.7 |
| C11-C14-N16 | 113.7 |
| O15-C14-N16 | 120.6 |
| C14-N16-H17 | 115.5 |
| C14-N16-C20 | 128.0 |
| H17-N16-C20 | 116.5 |
| C10-N18-H19 | 119.4 |
| C10-N18-C20 | 125.8 |
| H19-N18-C20 | 114.7 |
| N16-C20-N18 | 113.2 |
| N16-C20-S25 | 124.7 |
| N19-C21-S25 | 122.1 |

| | |
|---|---|
| C3-N22-O23 | 117.4 |
| C3-N22-O24 | 117.4 |
| O23-N22-O24 | 125.2 |
| C11-H12-N13 | 180.0 |

**TABLE 3:** Optimized bond angles of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT method at B3LYP level using 6-311++G (d, p) basis sets

**Vibrational assignments:**

| **Selected normal mode** | **Calculated IR frequencies $cm^{-1}$ (Scaled)** | **IR intensities (km) mol** | **Assignments** |
|---|---|---|---|
| 69 | 3468 | 71.56 | N-H str. ($2^o$ amide) |
| 68 | 3453 | 98.41 | N-H str. ($2^o$ amide) |
| 67 | 3105 | 5.96 | Ar-H str. (sym) |
| 66 | 3092 | 0.49 | Ar-H str. (sym) |
| 65 | 3090 | 5.75 | Ar-H str. (asym) |
| 64 | 3077 | 2.12 | Ar-H str. (asym) |
| 63 | 2248 | 42.34 | C≡N str. (sym) |
| 62 | 1712 | 608.77 | C=O str. (amide) |
| 61 | 1597 | 47.00 | Ar. C=C str. |
| 60 | 1568 | 95.21 | C=C str. (olefin) |
| 59 | 1544 | 156.52 | C=C str. |
| 58 | 1535 | 167.52 | N-O str. (nitro) |
| 57 | 1510 | 871.82 | Ar. C=C str. |
| 56 | 1457 | 2.89 | Ar-H (ip) bending |
| 53 | 1337 | 103.15 | N-H bending |
| 52 | 1322 | 309.28 | Ar-N str. (nitro) |
| 48 | 1192 | 19.31 | C-N str.(sym) (amide) |
| 45 | 1117 | 148.26 | C=S str. |

**Table 4:** Experimental and computed (scaled) selected fundamental vibrations of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile.

**Mullikens atomic charges:**

Atomic charges depends on the arrangement of atom and how the atoms are defined. Natural Population Analysis (NPA) is used to generate information on the electron densities of the atom. Mullikens charges are obtained using NPA based on the DFT/ B3LYP/ 6-311 ++ G(d, p) basis set and are listed in table 5. More positive charge is present on C11 (1.344) and C1 (1.320) while more negative charge is present on C6 (-0.939) and C2 (-0.633).

**Computed Mulliken Atomic Charges (a.u) on 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile**.

| Atom | Charge |
|---|---|
| C1 | 1.320 |
| C2 | -0.633 |
| C3 | -0.372 |
| C4 | 0.396 |
| C5 | -0.415 |
| C6 | -0.939 |
| H7 | 0.281 |
| H8 | 0.214 |
| H9 | 0.206 |
| C10 | -0.041 |
| C11 | 1.344 |
| C12 | -1.455 |
| N13 | -0.147 |
| C14 | 0.277 |
| O15 | -0.277 |
| N16 | -0.281 |
| H17 | 0.367 |
| N18 | -0.034 |
| H19 | 0.308 |
| C20 | 0.345 |
| H21 | 0.253 |
| N22 | -0.162 |
| O23 | 0.009 |
| O24 | 0.007 |
| S25 | -0.571 |

**TABLE 5:** Computed Mulliken Atomic Charges (a.u) by Natural Population Analysis (NPA) calculated by DFT at B3LYP/6-311++G (d, p) basis set

**HOMO-LUMO energy and absorption maxima:**

The HOMO is a highest occupied molecular orbital that can act as an electron donor and the LUMO is lowest unoccupied molecular orbital that can accept electron. Figure shows the HOMO-LUMO plot for the compound which clearly indicates that electron cloud moves from aromatic ring to pyrimidine ring. The small energy difference (0.150 a.u. or 4.07 eV) between HOMO and LUMO indicates their closeness. HOMO-LUMO energy gap can be used to predict the absorption maxima (λmax) of the molecules by the following formula[20-21].

**Energy gap (eV)** = Energy gap (Hartree or a.u.) x 27.2113834

**λmax** =1240/Energy gap (eV)

For the compound $\lambda_{max}$ was determined and found to be 350.48 nm as shown in **Table 6.**

| Basis set | E (RB+HF-LYP) (au) | HOMO (eV) | LUMO (eV) | Energy gap (eV) | Dipole moment (D) | λmax eV |
|---|---|---|---|---|---|---|
| 6-311++G (d, p) | -1265.831 | -7.184 | -3.646 | 3.538 | 4.0093 | 350.480 |

.**TABLE 6:** HOMO, LUMO (a.u.), λmax, dipole moment (D) and SCF energy (a.u.) values of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT method at B3LYP level using 6-311++G (d, p) basis set.

**Thermochemical parameters:**

| **Parameter** | **4a** |
|---|---|
| **Total E (Thermal)** Kcal mol$^{-1}$. | 110.795 |
| Translational | 0.889 |
| Rotational | 0.889 |
| Vibrational | 109.018 |
| **Total ($C_v$)** Cal mol$^{-1}$ Kelvin$^{-1}$ | 49.561 |
| Translational | 2.981 |
| Rotational | 2.981 |
| Vibrational | 43.600 |
| **Total Entropy (S)** Cal mol$^{-1}$ Kelvin$^{-1}$ | 115.349 |
| Translational | 42.188 |
| Rotational | 32.925 |
| Vibrational | 40.235 |
| **Zero Point vibrational energy** (Kcal mol$^{-1}$) | 102.610 |
| Rotational constant (GHz) | 0.70042 |
| | 0.35651 |
| | 0.24608 |
| Dipole Moment (D) | 6.5141 |
| Molar Mass (amu) | 229.031 |

**TABLE 7:** Theoretically computed energy (a.u.), zero-point vibrational energy, (Kcal/mol), rotational constant (GHz), entropy (Cal/mole) of 1,2,3,4-tetrahydro-6-(3-nitrophenyl)-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT/B3LYP at 6-311++G (d, p) basis set.

## Conclusion:

The optimized geometries were computed by DFT/ B3LYP at 6-311++G (d, p) basis set using Gaussian 09W package and Gauss A-5.0. Vibrational assignments were examined DFT methods of computation and the values predicted by DFT/B3LYP at 6-31++G (d, p) were found to be nearly in good agreement with the experimental values of the compound. The absorption maxima of the synthesized molecule are obtained from HOMO-LUMO energy gap.

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