

Density Functional Theory investigation of bond length, bond angle and thermodynamic parameters in 1,2,3,4-tetrahydro-6- phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile

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ABSTRACT

Theoretical chemistry method has been adopted to correlate the structural and electronic properties such as bond length, bond angle, Mullikan's 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 parameters 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-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile.

Keywords: DFT, HOMO-LUMO, dipole moment, energy gap, thermodynamic 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 functional that is functions of another. Application of density functional theory to UV, IR and NMR spectroscopies gives clear interpretations λ_{\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 applications¹, biological uses²⁻⁸, herbicidal effects⁹, pesticidal impact¹⁰, synthetical applications¹¹, polymeric and material sciences.¹²

In the present work, we have correlated experimental and theoretical IR and NMR spectrum along with molecular structure of 1,2,3,4-tetrahydro-6- phenyl-4-oxo-2-thioxopyrimidine-5-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.

MATERIALS AND METHOD

Computational studies of dihydropyrimidine carbonitriles was performed on Intel ® Pentium Dual Core personal computer using the Gaussian 09 software package program. Geometries were optimized using DFT/B3LYP level at 6-311++G(d,p) basis set and applied in calculations for vibrational frequencies to confirm the stationary point as minima by utilizing Gauss View 5.0 visualization program.

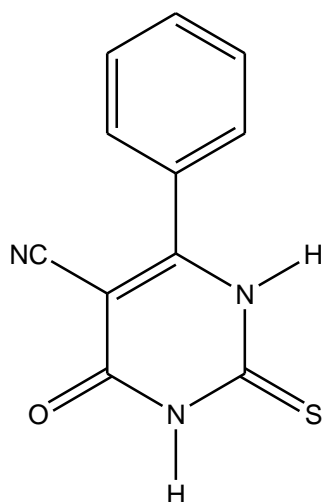
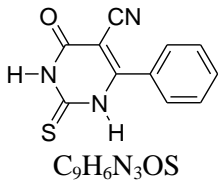


Figure 1: Structure of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile

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

Table 1: Experimental and theoretical spectral data of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile

 $C_9H_6N_3OS$	Experimental data	Theoretical data
IR data cm^{-1}	3371: -NH stretch. (2° amide) 3055 :Ar-H stretch. 2241 : -C≡N stretch. (nitrile) 1612 : -C=O stretch. (carbonyl) 1473 : Ar. C=C stretch. 1431 : -NH bending (2° amide) 1180 : C-N stretch. (amide) 1111 : C=S stretch.(thiol)	3472 : -NH stretch. (2° amide) 3456 : -NH stretch. (2° amide) 3089 :Ar-H stretch. 2247 : C≡N stretch. (nitrile) 1709 : -C=O stretch. (carbonyl) 1580 : Ar. C=C stretch. 1337 : -NH bending (2° amide) 1189 : C-N stretch. (amide) 1099 : C=S stretch.(thiol)

$^1\text{H-NMR } \delta$ (ppm) 400 MHz, DMSO	8.1 (1H, s, -N-H) 7.6-8.0 (5H, m, Ar-H)	H19 : 8.27 (-NH) H21 : 7.80 (-NH) H7 : 7.41 (Ar-H) H8 : 7.70 (Ar-H) H10 : 7.70 (Ar-H) H9 : 7.85 (Ar-H) H11 : 8.11 (Ar-H)
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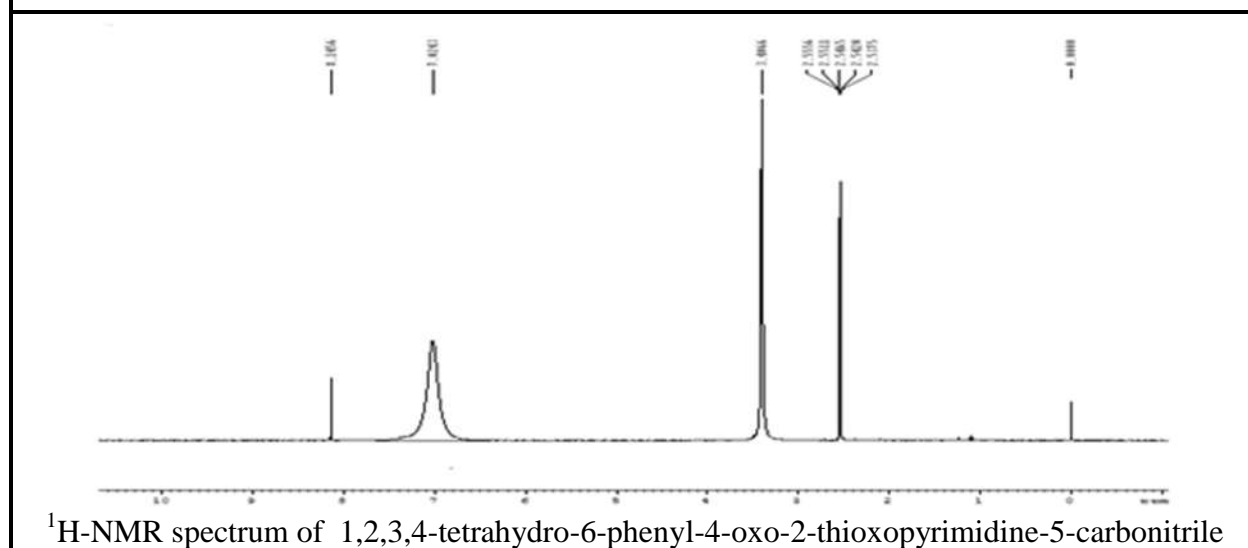
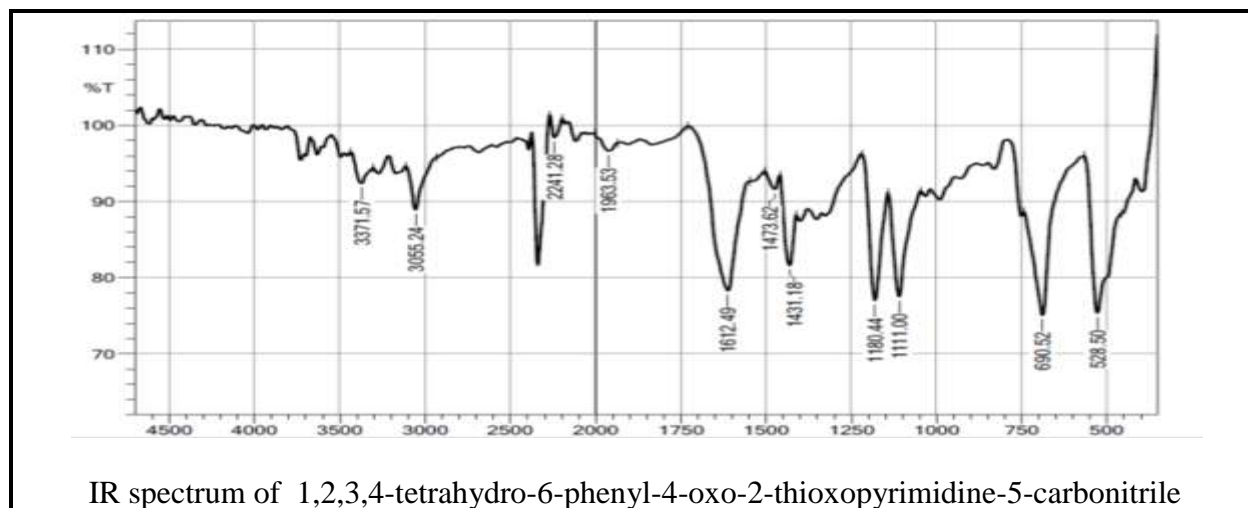


Figure 2: Experimental IR and $^1\text{H-NMR}$ spectrum of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile

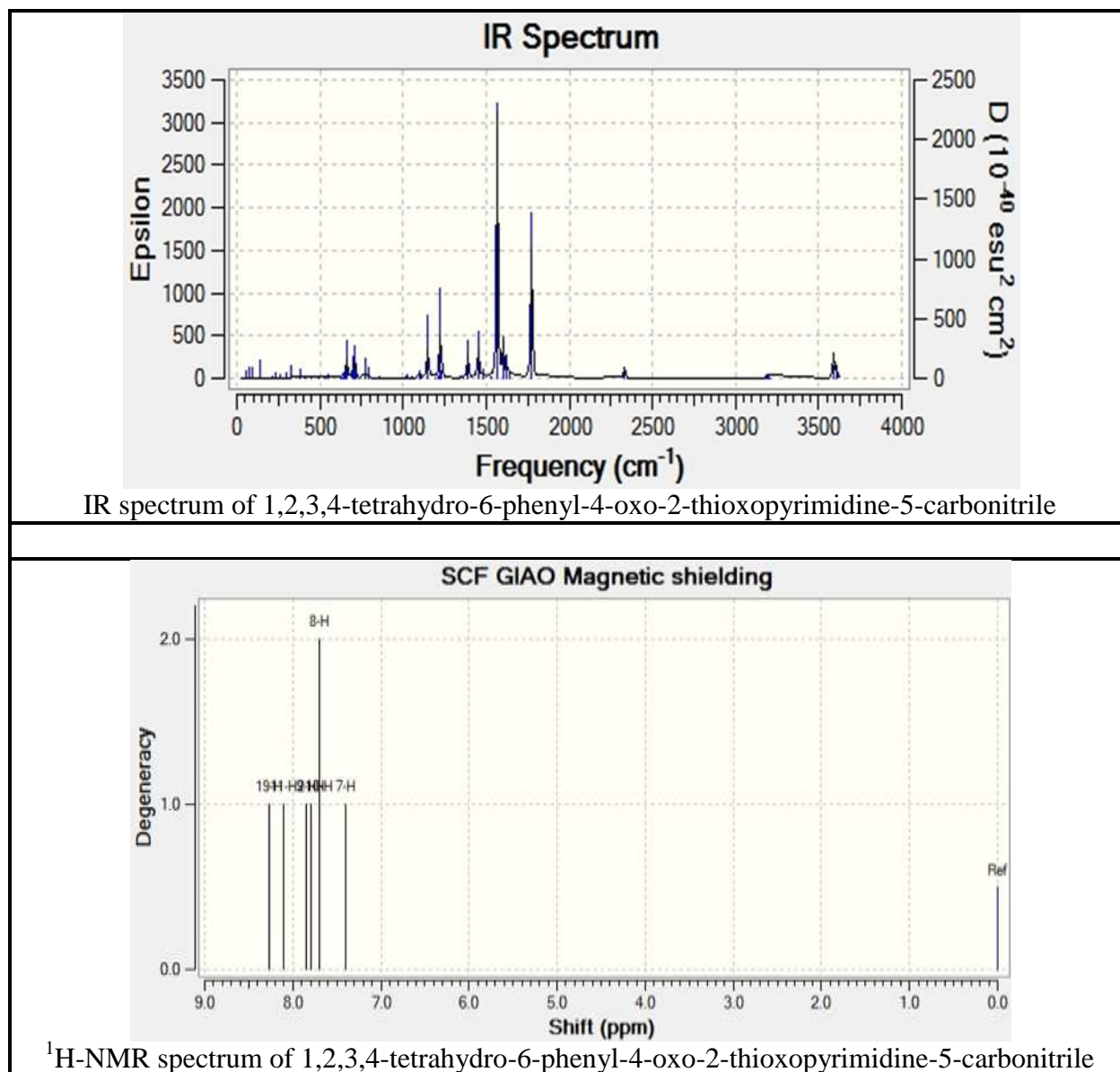


Figure3: Theoretical IR and ¹H-NMR spectrum of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile

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 possess 23 atoms hence there 63 normal modes of fundamental vibrations are expected. Slight variation has been observed in experimental and theoretical IR and ¹H-NMR data for the said compound. For better up gradation 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° 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 1709 cm^{-1} while experimental carbonyl of amide group absorption is observed at 1612 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 2247 cm^{-1} whereas experimentally it is seen at 2241 cm^{-1} .

Aromatic C=C stretching vibrations:

Aromatic C=C stretching is observed in range between 1585-1600 and 1400-1500 cm^{-1} . Experimental C=C stretching absorbs in the range 1473 cm^{-1} while theoretically aromatic C=C stretching absorption bands is seen at 1580 cm^{-1} .

N-H vibrations:

2° amides shows N-H stretching between 3300-3500 cm^{-1} . For compound it is observed theoretically at 3472 and 3456 cm^{-1} and experimentally it is observed at 3371. The 2° N-H bending is observed at 1431 cm^{-1} experimentally and theoretically it is seen at 1337 cm^{-1} .

Optimized Structure:

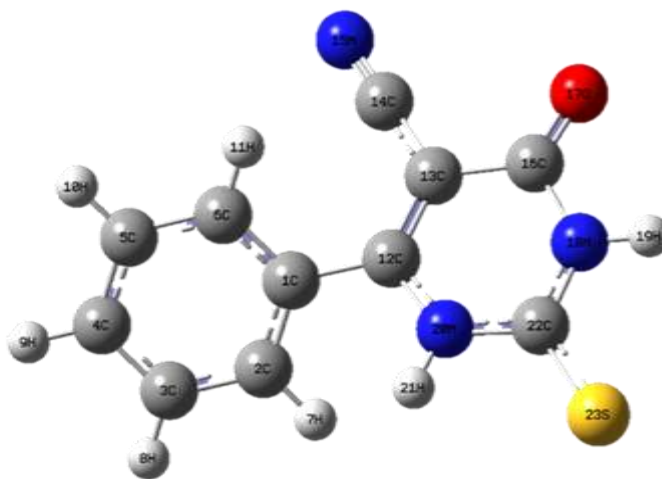


Figure 3: Optimized Structure of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile

Bond lengths:

Table 2: Optimized bond lengths (Å°) of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT method at B3LYP level using 6-311++G (d,p) basis sets

Atoms	Bond lengths ($^\circ\text{Å}$)
C1-C2	1.4039
C1-C6	1.4009
C1-C12	1.4787

C2-C3	1.3908
C2-H7	1.0847
C3-C4	1.3940
C3-H8	1.0836
C4-C5	1.3938
C4-H9	1.0838
C5-C6	1.3909
C5-H10	1.0835
C6-H11	1.0821
H11-C14	2.6883
C12-C13	1.3749
C12-N20	1.3735
C13-N14	1.4203
C13-C16	1.4715
C14-N15	1.1557
C16-O17	1.2096
C16-N18	1.4104
N18-H19	1.0130
C18-N22	1.3658
N20-H21	1.0109
N20-C22	1.3813
C22-S23	1.6575

Bond Angles:

Table3: Optimized bond angles of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT method at B3LYP level using 6-311++G (d, p) basis sets

Atoms	Bond Angles
C2-C1-C6	119.4
C2-C1-C12	119.7
C6-C1-C12	120.9
C1-C2-C3	120.2
C1-C2-H7	120.2
C3-C2-H7	119.5
C2-C3-C4	120.1
C2-H3-H8	119.7
C4-C3-H8	120.2
C3-C4-C5	119.9
C3-C4-H9	120.0
C5-C4-H9	120.0
C4-C5-C6	120.3
C4-C5-H10	120.2
C6-C5-H10	119.5
C1-C6-C5	120.0
C1-C6-H11	120.2
C5-C6-H11	119.8
C1-C12-C13	125.7

C1-C12-N20	115.3
C13-C12-N20	119.0
C13-C12-C14	122.7
C12-C13-C16	120.1
C14-C13-C16	117.1
C13-C16-O17	125.9
C13-C16-N18	113.8
O17-C16-N18	120.3
C16-C18-H19	115.5
C16-N18-C22	127.8
H19-N18-C22	116.6
C12-N20-H21	119.0
C12-N20-C22	126.0
H21-N20-C22	114.9
N18-C22-N20	113.3
N18-C22-S23	124.6
N20-C22-S23	122.1
C13-C14-N15	179.7
C2-C1-C6	119.4
C2-C1-C12	119.7
C6-C1-C12	120.9

Mullikens atomic charges:

Atomic charges depend 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 C13 (1.470) and C1 (1.356) while more negative charge is present on C6 (-0.892) and C2 (-0.610).

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

Table 4: Computed Mulliken Atomic Charges (a.u) by Natural Population Analysis (NPA) calculated by DFT at B3LYP/6-311++G (d, p) basis set

Atom	Charge
C1	1.356
C2	-0.610
C3	-0.085
C4	-0.454
C5	-0.148
C6	-0.892
H7	0.200
H8	0.183
H9	0.182
H10	0.187
H11	0.216
C12	-0.098

C13	1.470
C14	-1.428
N15	-0.158
C16	0.279
O17	-0.281
N18	-0.310
H19	0.374
N20	-0.042
H21	0.291
C22	0.357
S23	-0.591
C1	1.356
C2	-0.610

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. HOMO-LUMO energy gap can be used to predict the absorption maxima (λ_{\max}) of the molecules by the following formula¹³⁻¹⁴.

$$\text{Energy gap (eV)} = \text{Energy gap (Hartree or a.u.)} \times 27.2113834$$

$$\lambda_{\max} = 1240 / \text{Energy gap (eV)}$$

For the compound λ_{\max} was determined and found to be 312.107nm as shown in **Table5**.

Table5: HOMO, LUMO(a.u.), λ_{\max} , dipole moment(D) and SCF energy (a.u.) values of 1,2,3,4-tetrahydro-6-phenyl-4-oxo-2-thioxopyrimidine-5-carbonitrile by DFT method at B3LYP level using 6-311++G (d, p) basis set.

Basis set	E (RB+HF-LYP) (au)	HOMO (eV)	LUMO (eV)	Energy gap (eV)	Dipole moment (D)	λ_{\max} nm
6-311++G (d, p)	-1061.273	-6.912	-2.939	3.973	6.5141	312.107

Thermochemical parameters:

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

Parameter	4a
Total E (Thermal) Kcal mol⁻¹.	110.795
Translational	0.889
Rotational	0.889
Vibrational	109.018
Total (C_v)	49.561
Cal mol ⁻¹ Kelvin ⁻¹	
Translational	2.981
Rotational	2.981
Vibrational	43.600
Total Entropy (S)	115.349
Cal mol ⁻¹ Kelvin ⁻¹	

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

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 by 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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