Experimental and Density Functional Theory of 4-Amino-2-Mercapto-6-Phenylpyrimidine-5-Carboxamide

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ABSTRACT: The theoretical description of charge distribution, and related properties, such as chemical reactivity, bond length, bond angle, Mullikan atomic charges, HOMO-LUMO energy values, energy gap, dipole moment, electron affinity, ionisation potential, electronegativity, global hardness, softness, electrophilicity index and thermodynamic parameters are using Density Functional Theory (DFT) at the B3LYP/6-311 G ++ (d, p) basis set of 4-Amino-2-Mercapto-6-Phenylpyrimidine-5-Carboxamide.

Keywords: Computational Study; chemical reactivity; 4-Amino-2-Mercapto-6-Phenylpyrimidine-5-Carboxamide.

INTRODUCTION: The recent impact of Density Functional Theory (DFT) in the development of quantum chemistry is considerable and can be linked to achievement of so-called ''chemical accuracy'' at the end of the 1980s when gradient-corrected and hybrid functional methods were introduced. Based on the well-known Hohenberg Kohn theorems, DFT accepted tool for analysing structure, bonding and reactivity focuses on the electron density, itself as the carrier of all information in the molecular or atomic ground state.

Many researchers have reported the ab initio Hartree-Fock calculations and DFT study of different heterocyclic compounds[1-9] and reported FT-IR, HOMO-LUMO energy and other thermodynamic properties at B3LYP level using 6-31+G (d), 6-31++ G (d, p), 6-311G (d, p), 6-311++G (d, p) basis sets.

Pyrimidines and fused pyrimidines, being an integral part of DNA and RNA, play an essential role in several biological processes and have considerable chemical and pharmacological importance. Particularly, the pyrimidine ring can be found in the nucleoside antibiotics, antibacterial, antitumor, cardiovascular as well as agrochemical and veterinary products[10-15].

Literature survey reveals that, optimization and vibrational frequencies for 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide have not reported so far. Therefore, the 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide wassynthesize. The optimized geometries and vibrational frequencies of the title compound was carried out by Density Functional Theory method at B3LYP level is using 6-311++G (d, p) basis set. These frequencies are analysed and compared with the experimental data. HOMO and LUMO energy haveused to calculate absorption maxima of the molecule.

MATERIALS AND METHODS:

Computational Details: All computational calculations have performed on lenovo, Core i3 personal computer using the Gaussian 09W program[16] package without any constraint on the geometry. Geometries of the titled compound has optimized by DFT/B3LYP at 6-311++G (d, p), as basis sets in gas phase. Optimized geometry parameters have used in vibrational frequency calculations by DFT/B3LYP level at 6-311++G (d, p) to confirm the structure as minima. Absence of imaginary frequency confirms the energy minima. The vibrational frequency assignments and other parameters have made by using Gauss View 5.0 molecular visualization program.

Spectral Data: The spectral data of synthesized compound is as follow. The experimental and theoretical H[1]NMR and IR spectral data of the title compound in

table-1.The Theoretical and experimental IR and H¹NMRspectrum of titled compound islisted in table-2and table 3 respectively.
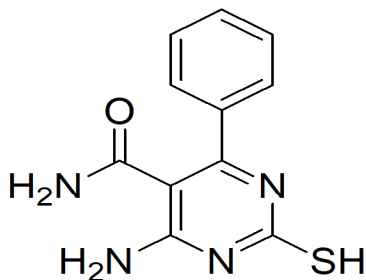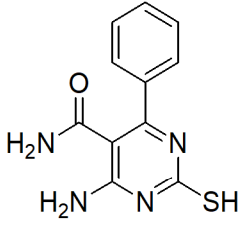

Figure 1: Structure of 4-Amino-2-Mercapto-6-Phenylpyrimidine-5-Carboxamide.

Table 1: Experimental and theoretical spectral data of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide.

(Mol. Formula $C_{11}H_{10}N_4OS$)	Experimental data	Theoretical data
H¹ NMR data δ(ppm)	(500 MHz, CDCl₃) 7.95 (2H , S,-NH₂) 8.19 (1H, S, -SH) 7.79 (2 H, S, CO-NH₂) 7.60-7.55 (5H, m, Ar-H)	H9-8.21, H8-4.81 (C-NH₂) H26-7.61, H24-7.60, H22-7.58,H25-7.51(Ar-H) H14-4.48, H15-4.36 (CO-NH₂) H12-4.42 (S-H)
IR data cm⁻¹	3396 N-H str. (1⁰ amide) 3315 N-H str. (1⁰ amine) 3159 Ar-H str. (sym) 2787 S-H str. 1689 C=O str. 1630 Ar C=C str. (asym) 1595 C=N str. 1205 C-N str. (1⁰ amine)	3583, 3523 N-H str. 3198 Ar-H str. 2686 S-H str. 1701 C=O str. 1616 Ar C=C 1560 C=N str. 1444 C-N str.

RESULTS AND DISCUSSION:

Molecular Geometry: Theoretical calculations related to geometry optimization haveperformed by DFT method with the B3LYP level at 6-311G++ (d, p) basis set in the ground state. According to the numbering reported in optimized structure **(figure-2)** of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide. The optimized geometry parameters such as bond lengths and bond angles have listed in **table 4** and **5** respectively. Comparison of experimental and the computational data shows good agreement for peak with high relative intensities.C1 point group symmetry shows the planar structure of the titled compound. Depending upon geometry of molecule fundamental mode of vibration calculated for linear and non-linear molecule using the formula 3N-5 and 3N-6. The titled compound is non-linear geometry and they contain 27 atoms therefore they shows 75 fundamental modes of vibrations.

The ab initio HF and DFT potentials systematically overestimate the vibrational wave numbers. These discrepancies have corrected either by computing a harmonic correction explicitly or by introducing a scaled field or directly scaling the calculated wave numbers with the proper factor. The scaling factor of 0.9631 has used for B3LYP method. Selected scaled fundamental modes of vibrations and FT-IR spectrum (experimental and theoretical) for titled compound have given in Table 2.

Vibration of Amide C=O Group: An amide carbonyl group absorbs strongly in the 1630-1690 cm⁻¹ region. For amide carbonyl, experimental vibration is reported at 1689 cm⁻¹. While computed C=O stretching frequency is obtained at 1616 cm⁻¹ by DFT method.

C=C Stretching Vibration: The region of C=C stretching vibrations have given in literature in the range of 1660-1580 cm⁻¹. Theoretically the vibrations have predicted at 1640-1616 cm⁻¹ by DFT method for aromatic olefin C=C. The experimental values has assigned at 1630 cm⁻¹.Computational vibrational frequencies haveobtained by DFT are in good agreement with the experimental values.

N-H Stretching Vibration: 1⁰amides shows N-H stretching observed in the range between 3300- 3500 cm⁻¹. The computed stretching frequency has observed at 3580, 3523 cm⁻¹.While experimental stretching frequency has observed at 3396 cm⁻¹.

S-H Stretching Vibration: The region of S-H starching vibration has given in literature in the range of 2400- 2550 cm⁻¹.The computed stretching frequency has observed at 2686 cm⁻¹.While the experimental stretching frequency has observed at 2787 cm⁻¹.

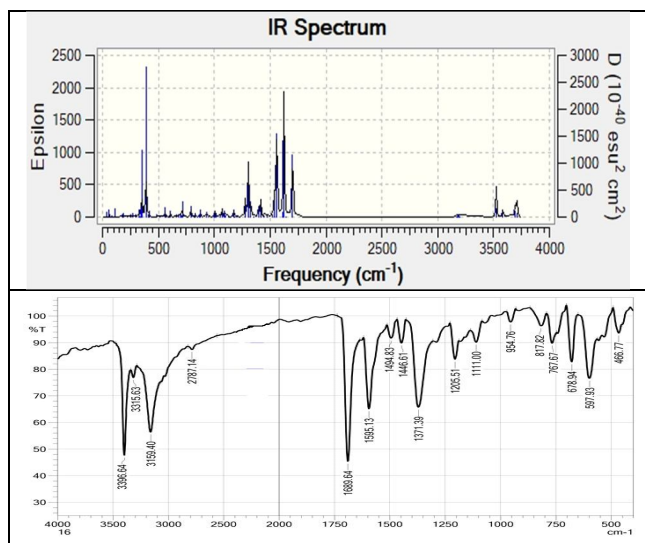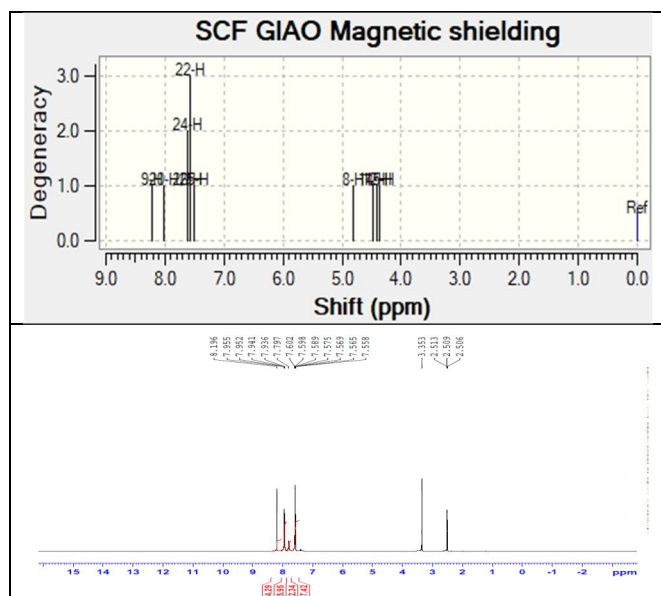## Table 2: Theoretical and experimental IR spectrum of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide.

Table 3: Theoretical and experimental H^{1}NMR spectrum of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide.

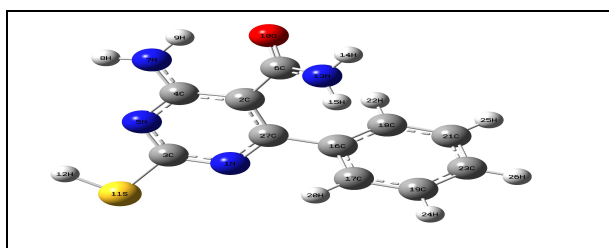### Optimised Structure:

Figure 2: Optimized structure of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide.

Bond Lengths:

Table 4: Optimized geometrical parameter, bond lengths (A^0) of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Atoms	Bond Lengths	Atoms	Bond Lengths	Atoms	Bond Lengths
N1-C3	1.3321	N13-H15	1.0066	C6-O10	1.2331
N1-C27	1.3429	N13-C18	3.1685	C6-N13	1.3611
C2-C4	1.4339	N13-H22	3.1455	N7-H8	1.0067
C2-C6	1.4948	C16-C17	1.4009	N7-H9	1.0124
C2-C27	1.4051	C16-C18	1.4012	S11-H12	1.3479
C3-N5	1.3243	C16-C27	1.4911	N13-H14	1.0086
C3-S11	1.7765	C17-C19	1.3924	C18-H22	1.084
C4-N5	1.3464	C17-H20	1.0831	C19-C23	1.3945
C4-N7	1.3449	C18-C21	1.392	C19-H24	1.0841
C21-C23	1.3946	C21-H25	1.0841	C23-H26	1.0842

Bond Angles:

Table 5: Optimized bond angles of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Atoms	Angles	Atoms	Angles
C3-N1-C27	116.5009	C17-C16-C27	119.6422
C4-C2-C6	118.3146	C18-C16-C27	121.1224
C4-C2-C27	115.3348	C16-C17-C19	120.3565
C6-C2-C27	126.3021	C16-C17-H20	119.0535
N1-C3-N5	127.4276	C19-C17-H20	120.588
N1-C3-S11	114.0547	N13-C18-C16	72.2551
N5-C3-S11	118.5015	N13-C18-C21	120.7155
C2-C4-N5	121.301	C16-C18-C21	120.3806
C2-C4-N7	122.412	C16-C18-H22	119.732
N5-C4-N7	116.2714	C21-C18-H22	119.8766
C3-N5-C4	116.6316	C17-C19-C23	120.1412
C2-C6-O10	121.7413	C17-C19-H24	119.7557
C2-C6-N13	117.7573	C23-C19-H24	120.099
O10-C6-N13	120.3203	C18-C21-C23	120.1331
C4-N7-H8	117.7676	C18-C21-H25	119.734
C4-N7-H9	118.7997	C23-C21-H25	120.1318
H8-N7-H9	122.4264	C19-C23-C21	119.8284
C3-S11-H12	94.7784	C19-C23-H26	120.1074
C6-N13-H14	116.8662	C21-C23-H26	120.0612
C6-N13-H15	122.2469	N1-C27-C2	122.1424
C6-N13-C18	82.1923	N1-C27-C16	113.9361
C6-N13-H22	67.7099	C2-C27-C16	123.8809
H14-N13-H15	118.5161	H15-N13-C18	59.1558
H14-N13-C18	117.1497	H15-N13-H22	78.8915
H14-N13-H22	110.5454	C17-C16-C18	119.1365

Vibrational Assignments:

Table 6: Experimental and computed (scaled) selected fundamental vibration of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide at B3LYP level using 6-311++G (d, p) as basis sets.

Selected normal mode	Calculated frequencies (scaled)	IR intensities (km) mol	Assignments
73	3583	48.89	N-H str. (1^0 amide)
72	3523	137.91	N-H str. (1^0 amine)
71	3198	4.97	Ar-H str. (sym)
70	3191	12.82	Ar-H str. (asym)
69	3182	14.97	Ar-H str. (asym)
68	3174	4.16	Ar-H str.(asym)
66	2686	0.10	S-H str.
65	1701	487.79	C=O str.
64	1640	0.47	Ar C=C str.(sym)
63	1624	641.00	N-H ben(1^0 amine)
62	1619	77.50	N-H ben. (1^0amide)
61	1616	39.47	Ar C=C str. (asym)
60	1560	601.38	C=N str.
56	1444	10.42	C-N str. (1^0 amine)
54	1394	69.01	C-N str. (1^0 amide)
43	1070	42.05	Ar-S str

Mulliken Atomic Charges: Atomic charges depends on the arrangements of atoms and how the atoms have defined. Natural Population Analysis (NPA) is use to generate information on the electron densities of the atoms. Mullikan charges are obtained using NPA based on the DFT/ B3LYP / 6-311 ++ G (d, p) basis set and are listed in table 7.More positive charge is present on C16 (0.747884) and more negative is present on C18 (-0.692134).

Table 7: Computed Mullikan Atomic Charges (a. u) by NPA calculated by DFT at B3LYP / 6-311++G (d, p) as basis set.

Atoms	Charges	Atoms	Charges	Atoms	Charges
N1	0.153201	O10	-0.353608	C19	-0.307928
C2	0.438597	S11	-0.311877	H20	0.204709
C3	0.177957	H12	0.068969	C21	-0.322820
C4	-0.017739	N13	-0.365660	H 22	0.194255
N5	-0.083895	H14	0.311776	C23	-0.253445
C6	-0.379526	H15	0.285056	H24	0.181906
N7	-0.353953	C16	0.747884	H25	0.186921
H8	0.298390	C17	0.047027	H26	0.156628
H9	0.314996	C18	-0.692134	C27	-0.325685

HOMO-LUMO Energya Absorption Maxima: The Highest Occupied Molecular Orbital (HOMO) that can acts as an electron donor and the Lowest Unoccupied Molecular Orbital (LUMO) that can accept electron. HOMO-LUMO energy gap can be used to predict the absorption maxima (λmax) of the molecule[17] by using following equations[18].Energy gap (eV) = Energy gap (Hartree or a.u.) x 27.2113834

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

For the compound HOMO - LUMO energy and λmax are calculated and has found at 256.641 nm as shown in table 8.

Table 8: HOMO-LUMO energy gap, λmax and chemical reactivity indices of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Basis set	E (RB+DFT-LYP) (a.u.)	HOMO (eV)	LUMO (eV)	Energy gap (eV)	λmax (nm)	Dipole moment (D)
6-311++G (d, p)	-1117.881	-6.581	-1.978	4.602	269.401	2.4680

THERMOCHEMICAL PARAMETERS:

Table 9: Theoretically computed energy (a.u.), zero-point vibrational energy, (kcal/ mole), rotational constant (GHz), entropy (cal /mole) dipole moment (D) and molar mass (a.m.u.) of 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide by DFT method at B3LYP level using 6-311++G (d, p) as basis sets.

Parameter	Values
Total E (Thermal)Kcal mol^{-1}	134.896
Translational	0.889
Rotational	0.889
Vibrational	133.119
Total (C_v)Cal mol^{-1}kelvin^{-1}	57.996
Translational	2.981
Rotational	2.981
Vibrational	52.034
Total entropy (S)Cal mol^{-1} kelvin^{-1}	123.645
Translational	42.402
Rotational	33.232
Vibrational	48.011
Zero point vibrational energy (Kcalmol^{-1})	125.489
Rotational constant (GHz)	0.56557 0.34757 0.22949
Dipole moment (D)	2.4680
Molar mass (amu)	246.057

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CONCLUSION: The 4-amino-2-mercapto-6-phenylpyrimidine-5-carboxamide has synthesized and characterised by FT-IR and H[1]NMR spectroscopy. The optimised geometries have computed by DFT / B3LYP at 6-311 ++G (d,P) as a basis set using Gaussian 09W package and Gauss A-5.0. Vibrational assignments have examined DFT method of computation and the values predicted by DFT / B3LYP at 6-311 ++G (d, P) have found to be nearly in good agreement with the experimental values of the compounds. The absorption maxima of synthesized compounds have obtained from HOMO- LUMO energy gap.

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