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Spectroscopic and Quantum Mechanical studies of 4-Amino-3, 6-dichloro-2-pyridine carboxylic acid and 3, 6-Dichloro-2-pyridine carboxylic acid.

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ABSTRACT

A DFT level quantum mechanical analysis of 4-Amino-3, 6-dichloro-2-pyridinecarboxylic acid (AMPYD) and 3, 6-Dichloro-2-pyridinecarboxylic acid (CLPYD) has been performed to explore their electronic, structural and spectral behavior. In this theoretical analysis various geometrical parameters, band gap and assignment of important vibration frequencies are reported and analyzed for both the compounds. In AMPYD the C-Cl bond lengths are found to be 1.84 Å⁰ and 1.82 Å⁰ while in CLPYD the C-Cl bond lengths are 1.83 Å⁰ and 1.81 Å⁰. The C-C bonds of pyridine group of AMPYD are slightly longer than the C-C bonds of same group in CLPYD. It can be attributed to the presence of -NH₂ group in AMPYD. The bond length suggests that AMPYD is more reactive than CLPYD. Analysis also suggest that the active sites in both the compounds are lies on C-Cl bonds and on C-C bond present between pyridine ring and the substitute group of same bond. Both the compounds get stabilized by hydrogen bonding. Bond angle analysis reveals that all the C and N atoms in both undertaken compounds are in SP² hybridization. Analysis also suggests that O₂ is in SP³ hybridization. Since all C and N atoms are in trigonal planer orientation therefore structure of both compounds should be planer. Analysis of dihedral angles reveals that in both undertaken compounds pyridine ring and substitute group are planer. Both the -Cl attached with ring are also planer to ring. In AMPYD, -NH₂ group is also planer to ring. O₁, O₂, N₁ and N₂ are most negative elements while C₃ and C₆ are most positive elements it suggests maximum reactivity around C₃-N₂ and C₆-O₂ bonds. The total energy

of the two compounds is found to be -1404.26 a.u. and -1349.20 a.u. The band gap in undertaken molecules is found to be 4.89 eV (253.54 nm) and 5.30 eV (233.93 nm) respectively. Therefore, AMPYD is more polar than CLPYD. Analysis also reveals that AMPYD is soft and highly reactive. Zero-point vibration energy for both AMPYD and CLPYD is found to be 263289.5 Joules/Mol and 218865.6 Joules / Mol. The stoichiometric formula for AMPYD and CLPYD are calculated as $C_6H_4Cl_2N_2O_2$ and $C_6H_3Cl_2NO_2$ respectively and Deg. of freedom for both the compounds are 42 and 36 respectively. The dipole moment of AMPYD and CLPYD is computed as 6.22 and 3.61 Debye. Total thermal energy, Cv and entropy of AMPYD are computed as 69.691 Kcal / Mol, 39.716 Cal / Mol-kelvin, 104.545 Cal / Mol-kelvin, respectively and for CLPYD these values are computed as 58.255 Kcal / Mol, 34.072 Cal / Mol-kelvin, 99.027 Cal / Mol-kelvin, respectively.

Keywords: 4-Amino-3, 6-dichloro-2-pyridinecarboxylic acid (AMPYD), 3,6-Dichloro-2-pyridinecarboxylic acid, (CLPYD), DFT.

INTRODUCTION

Pyridine Herbicides have been an active area research because of their various biological applications. Herbicides are chemicals used to control unwanted plants. Modern herbicides are synthetic mimics of natural plant hormones that interfere with growth of the target plants. [1] Herbicides cross the cell wall and the plasma membrane of plant cell to reach its site of action and causes phytotoxicity. [2] Their resistance towards degradation and high water solubility increases its likelihood of transport. [3] Due to the lack of rotational programmes and continuous use of it with same sites of action, weeds develop resistance towards herbicides. [4] Herbicide activity, selectivity in dicots, and mechanism of phytotoxicity attributed to auxin-conjugating enzymes and auxin signal transduction components. [5] Studies have revealed that herbicides have carcinogenic, mutagenic, and teratogenic effects on humans. They also have negative effect on insects and rodents. [6-16] There is a risk of Parkinson's disease with exposure to herbicide. [17] Herbicide use has negative impact on Bird population and underground water. [18-20] They cause demasculinization in male frogs, therefore affect frog population negatively. [21] 4-Amino-3, 6-dichloro-2-pyridinecarboxylic acid or Aminopyralid and 3, 6-Dichloro-2-pyridinecarboxylic acid or Clopyralids are selective herbicides used to control broadleaf weeds. Both are in picolinic acid family and can enter the food chain via manure and affect potatoes, tomatoes, and beans. [22-28] Clopyralid is known for its ability to persist in dead plants and compost. It is a pyridine carboxylic acid, auxin-type herbicide that is adsorbed primarily by foliage and also through roots, after translocation to meristematic regions. It interferes with auxin growth hormones, affecting cell elongation and respiration, leading to growth defects and death in susceptible species. [26-28] Degradation of Clopyralid is due to formation of toxic intermediates through pyridine ring transformation, dichlorination and decarboxylation reactions. [29] Dissipation of clopyralid depends on environmental factors like temperature and soil water content. [30] Aminopyralid has great tendency of soil sorption [31] and has activity on Canada thistle. [32] It has greater biological activity at the target site than clopyralid. Aminopyralid has shorter half-life than clopyralid. It is relatively immobile in soil. Aminopyralid is a systemic auxin herbicide moves throughout the plant and deregulates plant growth metabolic pathways. They are structurally similar to the natural plant hormone auxin and induce same physiological and biochemical responses. The primary route of breakdown of Aminopyralid in soil is aerobic microbial degradation. [34-36] It is a water soluble weak acid herbicide that shows strong sorption towards clay minerals. Its off-target movement is very less. [37, 38] Its photolysis is mainly responsible for dissipation. [39-41] To the best of our knowledge, there is no report, available for quantum mechanical study of electronic, structural and spectral behavior of these compounds. In this analysis we provide, a DFT level computation of 4-Amino-3, 6-dichloro-2-pyridinecarboxylic acid and 3, 6-Dichloro-2-pyridinecarboxylic acid. Here 4-

Amino-3, 6-dichloro-2-pyridinecarboxylic acid is abbreviated as AMPYD and 3, 6-Dichloro-2-pyridinecarboxylic acid is termed as CLPYD.

METHODOLOGY

A quantum mechanical study of 4-Amino-3, 6-dichloro-2-pyridinecarboxylic acid and 3, 6-Dichloro-2-pyridinecarboxylic acid has been performed on the basis of density functional theory. [42, 43] Calculations were performed on a Pentium IV/ 1.6 GHz personal computer using the Gaussian 09W suite of programs [44]. The Becke 3LYP keyword, which invokes Becke three parameter hybrid method [45] using the correlation function of Lee et. al [46-48] and 3-21G (6D, 7F)-basis set [49, 50] was used to locate the optimized geometries of the undertaken complexes. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true minimum, as revealed by the lack of imaginary values in the wave number calculations. The Cartesian representation and the theoretical force constants has been computed at the fully optimized geometry by assuming the molecules belongs to Cs point group symmetry by combining the result of Gauss view programme [51] with symmetry consideration, vibration frequency assignments are made.

RESULTS AND DISCUSSION

Geometry of the molecule

The stoichiometric formula for AMPYD and CLPYD are computed as $C_6H_4Cl_2N_2O_2$ and $C_6H_3Cl_2NO_2$ respectively Molecular mass of both the compounds is calculated as 205.96498 amu and 190.95408 amu respectively.

Table 1: Various bond lengths in AMPYD and CLPYD in A^o R = -COOH

Bond length	C ₅ H ₃ Cl ₂ N ₂ -R	C ₅ H ₂ Cl ₂ N-R	Bond length	C ₅ H ₃ Cl ₂ N ₂ -R	C ₅ H ₂ Cl ₂ N-R
	AMPYD	CLPYD		AMPYD	CLPYD
C ₁ -C ₂ / C ₅ -C ₄	1.38	1.39	C ₂ -Cl ₁ / C ₄ -Cl ₁	1.82	1.81
C ₂ -C ₃ / C ₄ -C ₃	1.42	1.39	N ₂ -H ₃	1.01	-----
C ₃ -C ₄ / C ₃ -C ₂	1.40	1.38	N ₂ -H ₄	1.01	-----
C ₄ -C ₅ / C ₂ -C ₁	1.38	1.39	C ₃ -N ₂	1.35	-----
C ₅ -N ₁ / C ₁ -N ₁	1.30	1.30	C ₆ -O ₁	1.22	1.22
C ₆ -C ₁ / C ₅ -C ₆	1.50	1.49	C ₆ -O ₂	1.37	1.37
C ₁ -N ₁ / C ₅ -N ₁	1.35	1.35	O ₂ -H ₂ / O ₂ -H ₃	0.99	0.99
C ₄ -H ₁ / C ₂ -H ₂	1.08	1.08	H-bond	2.34	2.35
C ₅ -Cl ₂ / C ₁ -Cl ₂	1.84	1.83	C ₃ -H ₁	-----	1.08

In these herbicides substitute group shows a mono valent attachment to the C of pyridine ring. X-Ray crystal structure data of both the compounds is not available. Therefore, quantum mechanical analysis of these molecules becomes more relevant to optimize geometry at DFT level. Fig.1 and Fig.2 represent the optimized geometry of AMPYD and CLPYD respectively. It is found that the calculated bond lengths are in well conformity with the bond lengths expected from reported atomic radii. [52] In AMPYD the C-Cl (Pyridine group) bond lengths are found to be 1.84 \AA and 1.82 \AA that are higher than C-O bond lengths 1.37 \AA and 1.22 \AA of substitute group. In AMPYD the C-C bonds of pyridine group are slightly longer than the C-C bonds of pyridine group of CLPYD. Bond lengths also suggest that C-C bonds of AMPYD are less stable than CLPYD. It can be attributed to the presence of $-\text{NH}_2$ group in AMPYD. In AMPYD the C-O bonds are more stable than C-C bond. In CLPYD the C-Cl (Pyridine group) bond lengths are found to be 1.83 \AA and 1.81 \AA that are less than the same bond lengths in AMPYD. C-N bond in both the undertaken compounds is found to be 1.30 \AA . The carbonyl C₆-O₁ bond length in both the undertaken compounds is found to be 1.22 \AA . An important feature of the two compounds is that both the compounds get stabilized by hydrogen bonding. The (O-H) hydrogen bond length in AMPYD is 2.34 \AA while in CLPYD the same is 2.35 \AA . The bond length suggests that AMPYD should be more reactive than CLPYD. C-Cl Bonds in both the compounds are found longer than all other bonds and C-C bond between pyridine ring and substitute group in both the compounds are slightly longer, suggesting that active sites in both undertaken compounds are centered on the same bond.

The detailed data on bond lengths is shown in figure-1, figure2 and Table 1.

The optimized geometry of the AMPYD and CLPYD

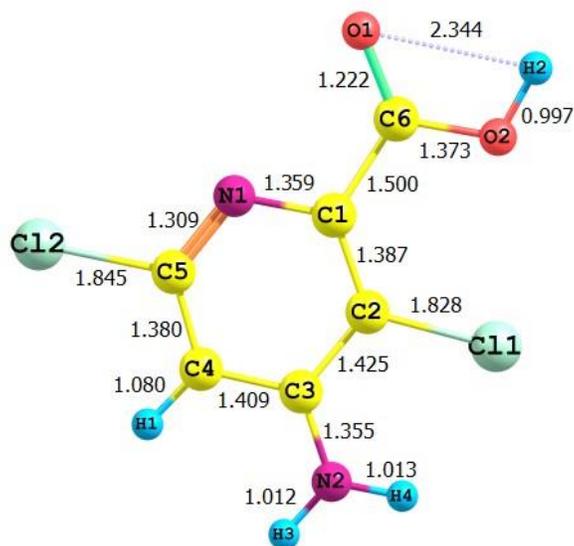


Figure-1: Optimized geometry of AMPYD

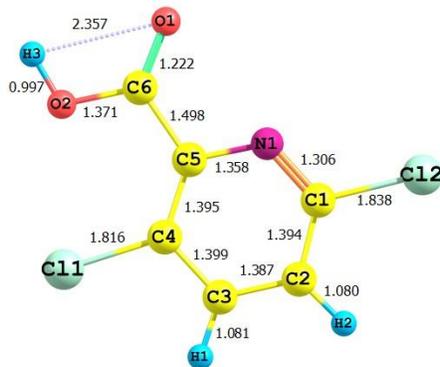


Figure-2: Optimized geometry of CLPYD

Table 2: Various bond angles (degree) in AMPYD and CLPYD R = -COOH

Angle	C ₅ H ₃ Cl ₂ N ₂ -R		Angle	C ₅ H ₂ Cl ₂ N-R	
	AMPYD	CLPYD		AMPYD	CLPYD
C ₁ C ₂ Cl ₁ / C ₅ C ₄ Cl ₁	124.6	125.4	C ₄ C ₅ Cl ₂ / C ₂ C ₁ Cl ₂	116.4	117.2
C ₁ C ₂ C ₃ / C ₅ C ₄ C ₃	121.1	116.3	H ₁ C ₄ C ₅ / H ₂ C ₂ C ₁	121.1	121.3
C ₂ C ₃ C ₄ / C ₄ C ₃ C ₂	116.2	119.6	C ₅ N ₁ C ₁ / C ₁ N ₁ C ₅	118.3	120.2
C ₂ C ₃ N ₂	122.2	-----	Cl ₂ C ₅ N ₁ / Cl ₂ C ₁ N ₁	117.5	118.1
Cl ₁ C ₂ C ₃ / Cl ₁ C ₄ C ₃	114.2	114.6	N ₁ C ₁ C ₆ / N ₁ C ₅ C ₆	111.9	112.6
C ₃ C ₄ C ₅ / C ₃ C ₂ C ₁	117.8	116.3	N ₁ C ₁ C ₂ / N ₁ C ₅ C ₄	120.4	119.2
C ₃ C ₄ H ₁ / C ₃ C ₂ H ₂	121.0	122.2	C ₁ C ₆ O ₂ / C ₅ C ₆ O ₂	112.9	112.2
C ₃ N ₂ H ₃	120.6	-----	C ₁ C ₆ O ₁ / C ₅ C ₆ O ₁	124.1	124.3
C ₃ N ₂ H ₄	120.1	-----	C ₆ O ₂ H ₂ / C ₆ O ₂ H ₃	107.9	108.3
N ₂ C ₃ C ₄	121.4	-----	O ₁ C ₆ O ₂ / O ₁ C ₆ O ₁	122.8	123.3
C ₄ C ₅ N ₁ / C ₂ C ₁ N ₁	125.9	124.5			

The bond angles in AMPYD and CLPYD are listed in Table 2. In both the compounds various bond angles around C and N₁ are almost 120° that suggests SP² hybridization in the C and N₁ atoms. N₁ is pyridine nitrogen. Here we can assume that non-bonding electron pair is not delocalized therefore cannot contribute in the resonance with the other π electrons in the cycle. In AMPYD N₂ is amine nitrogen. We can assess its hybridization sp². It can be attributed to the fact that all its surrounding bond angles are almost 120°. Here resonance interaction between the aromatic ring and the nitrogen delocalized lone pair can be predicted. O₁C₆O₂ angle in both undertaken molecules is more than 120° which can be attributed to high grade of repulsion between lp of both the oxygen atoms. C₆O₂H₂ angle in AMPYD and C₆O₂H₃ angle in CLPYD are less than 109° 28' it is due to lp-lp repulsion on oxygen atom. Bond angle around O₂ also suggests sp³ hybridization in O₂. Bond angles Cl₂C₅N₁, N₁C₁C₆, C₁C₆O₂, C₄C₅Cl₂

and Cl₁C₂C₃ in AMPYD and bond angles Cl₂C₁N₁, N₁C₅C₆ C₁, C₅C₆O₂, Cl₁C₄C₃, and C₂C₁Cl₂ in CLPYD are less than 120° it can be due to lp-bp repulsion.

Dihedral Angles

Table-3: Various Dihedral angles (degree) in AMPYD and CLPYD R= -C₂H₄COOH

Dihedral angles	C ₅ H ₃ Cl ₂ N ₂ -R		Dihedral angles	C ₅ H ₂ Cl ₂ N-R	
	AMPYD	CLPYD		AMPYD	CLPYD
H ₁ O ₂ C ₆ O ₁ / H ₃ O ₂ C ₆ O ₁	0.000	0.000	C ₂ C ₃ C ₄ C ₅ /C ₄ C ₃ C ₂ C ₁	0.001	-0.000
H ₁ O ₂ C ₆ C ₁ / H ₃ O ₂ C ₆ C ₅	-179.9	180	C ₂ C ₃ C ₄ H ₁ /C ₄ C ₃ C ₂ H ₂	-179.9	180
O ₂ C ₆ C ₁ C ₂ / O ₂ C ₆ C ₅ C ₄	-0.026	0.000	C ₃ C ₄ C ₅ Cl ₂ /C ₃ C ₂ C ₁ Cl ₂	179.9	-180
O ₂ C ₆ C ₁ N ₁ / O ₂ C ₆ C ₅ N ₁	179.9	179.9	C ₃ C ₄ C ₅ N ₁ /C ₃ C ₂ C ₁ N ₁	0.002	0.000
O ₁ C ₆ C ₁ C ₂ / O ₁ C ₆ C ₅ C ₄	179.9	180	H ₃ N ₂ C ₃ C ₄	-0.001	-----
O ₁ C ₆ C ₁ N ₁ / O ₁ C ₆ C ₅ N ₁	-0.05	-0.001	H ₄ N ₂ C ₃ C ₄	-179.9	-----
C ₆ C ₁ C ₂ Cl ₁ / C ₆ C ₅ C ₄ Cl ₁	0.002	-0.000	N ₂ C ₃ C ₄ H ₁ /H ₁ C ₃ C ₂ H ₂	-0.003	0.000
C ₆ C ₁ C ₂ C ₃ / C ₆ C ₅ C ₄ C ₃	179.9	179.9	N ₂ C ₃ C ₄ C ₅ /H ₁ C ₃ C ₂ C ₁	179.9	180
C ₆ C ₁ N ₁ C ₂ / C ₆ C ₅ N ₁ C ₁	-179.9	-180	H ₁ C ₄ C ₅ Cl ₂ /H ₂ C ₂ C ₁ Cl ₂	-0.01	0.000
C ₁ C ₂ C ₃ C ₄ / C ₅ C ₄ C ₃ C ₂	-0.009	0.000	H ₁ C ₄ C ₅ N ₁ /H ₂ C ₂ C ₁ N ₁	179.9	180
C ₁ C ₂ C ₃ N ₂ / C ₁ C ₄ C ₃ H ₁	-179.9	180	C ₄ C ₅ N ₁ C ₁ /C ₂ C ₁ N ₁ C ₅	0.001	0.000
Cl ₁ C ₂ C ₃ N ₂ / Cl ₁ C ₄ C ₃ H ₁	-0.015	-0.000	Cl ₂ C ₅ N ₁ C ₁ /Cl ₂ C ₁ N ₁ C ₅	-179.9	-180
Cl ₁ C ₂ C ₃ C ₄ / Cl ₁ C ₄ C ₃ C ₂	179.9	180	C ₅ N ₁ C ₁ C ₂ /C ₁ N ₁ C ₅ C ₄	-0.009	-0.001
C ₂ C ₃ N ₂ H ₃	179.9	-----	N ₁ C ₁ C ₂ Cl ₁ /N ₁ C ₅ C ₄ Cl ₁	-179.9	-179.9
C ₂ C ₃ N ₂ H ₄	0.055	-----	N ₁ C ₁ C ₂ C ₃ /N ₁ C ₅ C ₄ C ₃	0.01	0.000

The dihedral angles of AMPYD and CLPYD are listed in Table 3. Dihedral angles O₁C₆C₁C₂, O₁C₆C₁N₁, O₂C₆C₁C₂, and O₂C₆C₁N₁ in AMPYD are calculated to be 179.9⁰, -0.05⁰, -0.026⁰ and 179.9⁰ it reveals that substitute group is planer to pyridine ring. By analyzing dihedral angle data of N₁C₁C₂Cl₁, C₆C₁C₂Cl₁, Cl₁C₂C₃C₄, C₃C₄C₅Cl₂, H₁C₄C₅Cl₂, and Cl₂C₅N₁C₁, we can conclude that both substituted -Cl attached with ring are planer with this. Dihedral angles C₂C₃N₂H₃, C₂C₃N₂H₄, and N₂C₃C₄H₁ explain that -NH₂ attached with ring is also planer with ring.

In CLPYD dihedral angles O₁C₆C₅C₄, O₁C₆C₅N₁, O₂C₆C₅C₄, and O₂C₆C₅N₁ are calculated to be 180⁰, --0.001⁰, -0.000⁰ and 179.9⁰ these data reveal that in CLPYD substitute group and pyridine ring are almost planer. Dihedral data analysis also reveals that -Cl groups in CLPYD are planer to ring. We can also conclude by analyzing dihedral angle data of pyridine ring that this group in both the molecules is planer. Analysis of dihedral angles of substitute group also reveals that this group is planer in both the molecules.

Electronic Struction

Table 4: Mulliken Atomic charges (coulomb) on various atoms in AMPYD and CLPYD R = -COOH

Atomic charges	C ₅ H ₃ Cl ₂ N ₂ -R AMPYD	C ₅ H ₂ Cl ₂ N-R CLPYD	Atomic charges	C ₅ H ₃ Cl ₂ N ₂ -R AMPYD	C ₅ H ₂ Cl ₂ N-R CLPYD
C ₁ /C ₅	0.187	0.211	H ₂ /H ₃	0.373	0.377
C ₂ /C ₄	-0.297	-0.298	H ₃	0.326	-----
C ₃	0.455	-0.090	H ₄	0.342	-----
C ₄ /C ₂	-0.169	-0.169	Cl ₁	0.140	0.174
C ₅ /C ₁	0.044	0.054	Cl ₂	0.086	0.111
C ₆	0.678	0.679	O ₁	-0.455	-0.453
N ₁	-0.544	-0.526	O ₂	-0.557	-0.555
N ₂	-0.825	-----	H ₁	-----	0.247
H ₁ /H ₂	0.217	0.239			

Atomic charges depend on how the atoms are defined. [53] It plays an important role in the application of theoretical calculations to molecular system. The Milliken atomic charges calculated at B3LYP level with 6-31 +G (d, p) basis set on various atoms in molecules 1 and 2 are shown in table 4. Table shows that all hydrogen atoms in both the compounds carry positive charge it can be attributed to their electropositive nature. Milliken Atomic charges analysis reveals that O₁, O₂, N₁ and N₂ are most negative elements it can be attributed to their electronegative nature.

While C₃ and C₆ are most positive elements it suggests maximum reactivity around C₃-N₂ and C₆-O₂ bonds in these molecules. C₃ and C₈ are most positive element in both the undertaken compounds because it is attached to more electronegative elements like N and O. Carbonyl oxygen in both undertaken complexes has high grade of negative charge it can be attributed to high χ value of O. All C of pyridine ring that are attached with H are negative due to electro positivity of H. Due to larger size of Cl they are less electronegative and possess positive charge.

Table 5: R = -COOH

	C ₅ H ₃ Cl ₂ N ₂ -R AMPYD	C ₅ H ₂ Cl ₂ N-R CLPYD		C ₅ H ₃ Cl ₂ N ₂ -R AMPYD	C ₅ H ₂ Cl ₂ N-R CLPYD
Dipole Moment	6.22 Debye	3.61 Debye	HOMO	-0.250 Hartree	-0.282 Hartree

Total Energy	-1404.26 a.u.	-1349.20 a.u.	LUMO	-0.070 Hartree	-0.087 Hartree
Point group	C ₁	C ₁	Energy GAP	0.180 Hartree	0.195Hartree
			Energy GAP	4.89 eV	5.30 eV

The dipole moments, energies, the highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies and the energy gap for the studied molecules have been calculated and given in Table 5. The total energy is calculated to be -1404.26 a.u. and -1349.20 a.u. for AMPYD and CLPYD respectively. Zero-point vibration energy for AMPYD is found to be 263289.5 (Joules/Mol) or 62.92771 (Kcal/Mol) with zero-point correction 0.100282 (Hartree/Particle) and for CLPYD zero-point vibration energy is found 218865.6 (Joules / Mol) or 52.31015 (Kcal / Mol) with zero-point correction 0.083362 (Hartree / Particle). AMPYD has 104 electrons and 16 atoms while in CLPYD 96 electrons and 14 atoms are calculated and both are having neutral nature. The band gap of frontier molecular orbital HOMO and LUMO helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small band gap is more polarizable and is supposed to possess high chemical reactivity and can be termed as soft molecule [54,55]. HOMO is electron donor and LUMO is electron acceptor [56] the band gaps for AMPYD and CLPYD are computed to be 4.89 eV or 0.180 Hartree (253.54 nm) and 5.30 eV or 0.195 Hartree (233.93 nm) respectively. It suggests high chemical reactivity of AMPYD than CLPYD. The electron movement between these orbitals could easily occur [57] it makes molecule soft and more polarizable with a high chemical reactivity. 3D plots of HOMO and LUMO of the studied molecules are shown in Figure 3 and 4. The highest occupied molecular orbital and lowest unoccupied molecular orbital is concentrated around phenoxy group in both the compounds.

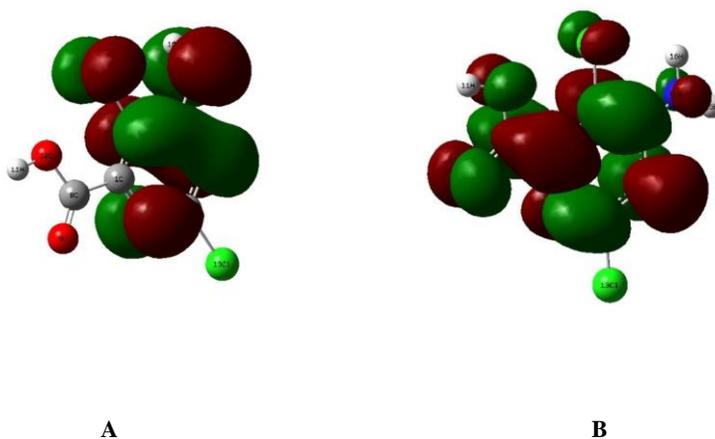


Figure-3: (A) HOMO and (B) LUMO molecular orbitals of AMPYD

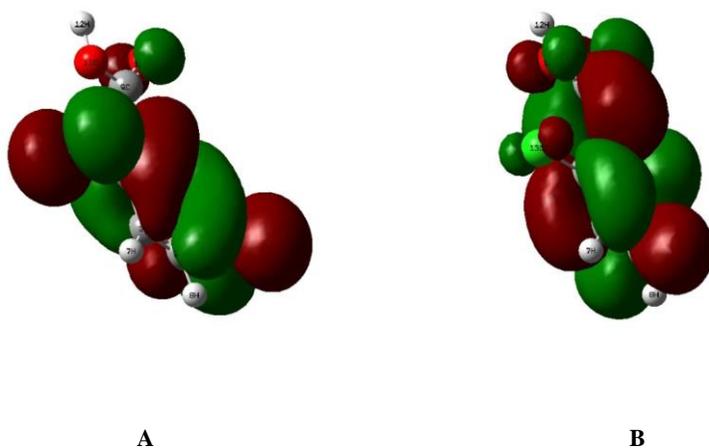


Figure-4: (A) HOMO and (B) LUMO molecular orbitals of CLPYD

Thermo chemical Analysis

The thermo chemical analysis of both undertaken molecules is also carried out. Total thermal energy, Cv and entropy of AMPYD are computed as 69.691 Kcal / Mol, 39.716 Cal / Mol-kelvin, 104.545 Cal / Mol-kelvin respectively and for CLPYD these values are computed as 58.255 Kcal / Mol, 34.072 Cal / Mol-kelvin, 99.027 Cal / Mol-kelvin, respectively.

Vibrational Analysis

Table-6: Computed stretching frequencies (cm^{-1}), force constants ($\text{mDyne}/\text{A}^\circ$), and atomic Cartesian displacement of vibration motions in AMPYD.

SN.	Frequency (Calculated)	Assignt.	Force Const	Cartesian Displacement
1.	3662.4(52.6)	Asym $\nu(\text{N}_2\text{-H}_3)$	8.7	$\text{H}_4(-0.63\text{X})+\text{H}_5(-0.55\text{Y})+\text{H}_3(-0.51\text{X})+\text{N}_2(0.08\text{X})$
2.	3543.5 (96.8)	Sym $\nu(\text{N}_2\text{-H}_4)$	7.7	$\text{H}_4(-0.73\text{X})+\text{H}_5(0.45\text{X})+\text{H}_3(0.48\text{Y})+\text{N}_2(-0.05\text{Y})$
3.	3485.6 (33.2)	$\nu(\text{O}_2\text{-H}_2)$	7.6	$\text{O}_2(-0.05\text{Y})+\text{O}_2(-0.03\text{X})+\text{H}_2(0.53\text{X})+\text{H}_2(0.847\text{Y})$
4.	3247.0(0.9)	$\nu(\text{C}_4\text{-H}_1)$	6.7	$\text{C}_4(-0.06\text{X})+\text{C}_4(-0.06\text{Y})+\text{H}_1(0.72\text{X})+\text{H}_1(0.69\text{Y})$
5.	1771.4 (163.2)	$\nu(\text{C}_6\text{-O}_1)$	19.5	$\text{C}_6(0.71\text{Y})+\text{C}_6(-0.23\text{X})+\text{O}_1(-0.44\text{Z})+\text{O}_1(0.16\text{X})$
6.	1606.9 (8.7)	$\nu(\text{C}_3\text{-N}_2)$	5.7	$\text{C}_1(0.15\text{Y})+\text{C}_5(0.27\text{Y})+\text{C}_3(0.34\text{Y})+\text{N}_2(-0.07\text{Y})$
7.	1555.0 (139.7)	$\nu(\text{C}_3\text{-C}_4)$	9.8	$\text{C}_3(0.43\text{X})+\text{C}_4(-0.26\text{X})+\text{C}_5(0.27\text{Y})+\text{C}_6(-0.27\text{X})$
8.	1459.2 (40.4)	$\nu(\text{C}_1\text{-C}_2)$	6.8	$\text{C}_1(0.37\text{Y})+\text{C}_2(-0.22\text{Y})+\text{C}_3(-0.31\text{Y})+\text{C}_4(0.01\text{X})$
9.	1443.4 (2.3)	$\nu(\text{C}_4\text{-C}_5)$	7.8	$\text{C}_2(-0.24\text{Y})+\text{C}_3(0.27\text{Y})+\text{C}_4(0.27\text{Y})+\text{C}_5(-0.31\text{Y})$
10.	1415.6 (2.4.1)	$\nu(\text{C}_1\text{-C}_6)$	3.0	$\text{C}_1(-0.11\text{X})+\text{C}_3(-0.15\text{X})+\text{C}_5(0.17\text{X})+\text{C}_6(0.18\text{X})$
11.	1352.9 (9.6)	$\nu(\text{C}_2\text{-C}_3)$	2.7	$\text{C}_1(-0.14\text{Y})+\text{C}_2(0.16\text{Y})+\text{C}_3(-0.11\text{X})+\text{C}_4(-0.05\text{Y})$

12.	1293.4 (9.5)	$\nu(\text{C}_1\text{-N}_1)$	4.7	$\text{C}_1(0.38\text{X})+\text{N}_1(-0.30\text{XY})+\text{C}_3(-0.19\text{X})+\text{C}_4(0.17\text{X})$
13.	1187.1 (291.2)	$\nu(\text{C}_5\text{-N}_1)$	1.6	$\text{C}_3(-0.02\text{Y})+\text{C}_4(0.08\text{Y})+\text{C}_5(0.16\text{X})+\text{N}_1(-0.09\text{X})$
14.	1098.3 (163.6)	$\nu(\text{C}_6\text{-O}_2)$	2.0	$\text{O}_1(-0.10\text{Y})+\text{C}_6(0.22\text{X})+\text{O}_2(-0.20\text{X})+\text{H}_2(0.59\text{X})$
15.	857.3 (46.1)	$\nu(\text{C}_5\text{-Cl}_2)$	4.0	$\text{C}_3(0.47\text{X})+\text{Cl}_2(-0.07\text{X})+\text{C}_4(-0.35\text{y})+\text{N}_1(0.18\text{Y})$
16.	516.2 (50.6)	$\nu(\text{C}_2\text{-Cl}_1)$	0.2	$\text{C}_2(0.14\text{X})+\text{Cl}_1(-0.17\text{X})+\text{C}_3(0.25\text{X})+\text{C}_4(0.30\text{X})$

Table 6.1: Computed stretching frequencies (cm^{-1}), force constants ($\text{mDyne}/\text{A}^\circ$), and atomic Cartesian displacement of vibration motions in CLPYD.

SN.	Frequency (Calculated)	Assignt.	Force Const	Cartesian Displacement
1.	3489.47(39.06)	$\nu(\text{O}_2\text{-H}_3)$	7.6	$\text{O}_2(0.04\text{X})+\text{O}_2(-0.05\text{Y})+\text{H}_3(-0.57\text{X})+\text{H}_3(0.82\text{Y})$
2.	3261.98(0.34)	Sym $\nu(\text{C}_2\text{-H}_2)$	6.8	$\text{C}_2(-0.06\text{X})+\text{C}_2(0.06\text{Y})+\text{H}_2(0.68\text{X})+\text{H}_2(-0.64\text{Y})$
3.	3241.08(0.46)	Asym $\nu(\text{C}_3\text{-H}_1)$	6.7	$\text{C}_3(-0.02\text{X})+\text{C}_3(-0.08\text{Y})+\text{H}_1(0.26\text{X})+\text{H}_1(0.90\text{Y})$
4.	1772.17(166.16)	$\nu(\text{C}_6=\text{O}_1)$	19.8	$\text{C}_6(0.22\text{X})+\text{C}_6(0.72\text{X})+\text{O}_1(-0.15\text{X})+\text{O}_1(-0.45\text{Y})$
5.	1589.57(23.80)	$\nu(\text{C}_3\text{-C}_4)$	9.2	$\text{C}_3(0.41\text{X})+\text{C}_3(-0.11\text{Y})+\text{C}_4(-0.17\text{X})+\text{C}_4(0.15\text{Y})$
6.	1562.94(13.79)	$\nu(\text{C}_1\text{-C}_2)$	7.6	$\text{C}_1(-0.07\text{X})+\text{C}_1(-0.21\text{Y})+\text{C}_2(0.26\text{X})+\text{C}_2(0.31\text{Y})$
7.	1469.19(154.39)	$\nu(\text{C}_1\text{-N}_1)$	2.6	$\text{C}_3(0.41\text{X})+\text{C}_3(-0.11\text{Y})+\text{C}_4(-0.17\text{X})+\text{C}_4(0.15\text{Y})$
8.	1423.68(100.03)	$\nu(\text{C}_5\text{-C}_6)$	4.7	$\text{C}_5(-0.21\text{X})+\text{C}_5(0.15\text{Y})+\text{C}_6(0.32\text{X})+\text{C}_6(-0.08\text{Y})$
9.	1349.10(14.12)	$\nu(\text{C}_5\text{-N}_1)$	2.8	$\text{C}_5(0.20\text{X})+\text{C}_5(-0.02\text{Y})+\text{C}_4(-0.10\text{X})+\text{C}_4(-0.04\text{Y})$
10.	1290.82(8.35)	$\nu(\text{C}_4\text{-C}_5)$	4.5	$\text{C}_4(-0.05\text{X})+\text{C}_4(-0.18\text{Y})+\text{C}_5(0.20\text{X})+\text{C}_5(0.28\text{Y})$
11.	1215.41(13.04)	$\nu(\text{C}_2\text{-C}_3)$	1.6	$\text{C}_2(-0.10\text{X})+\text{C}_2(-0.01\text{Y})+\text{C}_3(0.12\text{X})+\text{C}_3(-0.08\text{Y})$
12.	1097.13(124.23)	$\nu(\text{C}_6\text{-O}_2)$	2.3	$\text{C}_6(0.25\text{X})+\text{C}_6(-0.04\text{X})+\text{O}_2(0.04\text{X})+\text{O}_2(0.12\text{Y})$
13.	847.92(15.30)	$\nu(\text{C}_1\text{-Cl}_2)$	3.2	$\text{C}_1(0.37\text{X})+\text{C}_1(0.07\text{Y})+\text{Cl}_2(-0.05\text{X})+\text{Cl}_2(-0.01\text{Y})$
14.	320.73(1.54)	$\nu(\text{C}_4\text{-Cl}_1)$	1.7	$\text{C}_4(0.22\text{X})+\text{C}_4(0.09\text{Y})+\text{Cl}_1(0.54\text{X})+\text{Cl}_1(0.13\text{Y})$

Table-7: Computed Bending frequencies (cm^{-1}), force constants ($\text{mDyne}/\text{A}^\circ$), and atomic Cartesian Displacement of vibration motions in AMPYD.

SN	Frequency (Calculated)	Assignt.	Force Const	Cartesian Displacement
1	1689.2 (214.4)	$\pi \beta (\text{N-H})$	1.9	$\text{C}_3(-0.04\text{Y})+\text{N}_2(0.10\text{Y})+\text{H}_3(0.54\text{X})+\text{H}_4(-0.67\text{Y})$

2	1084.6 (12.6)	$\pi \beta$ (N-H)	4.2	$H_3(-0.53Y)+H_4(0.63Y)+N_2(-0.11X)+C_3(0.08X)$
3	1026.7 (34.8)	(Ring Breathing)	4.8	$C_2(0.53X)+C_4(-0.37X)+N_1(0.27Y)+C_5(-0.11X)$
4	970.6 (58.9)	$\pi \beta$ (C ₁ N ₁ C ₅)	4.2	$C_1(0.31Y)+C_4(0.17Y)+N_1(-0.31Y)+C_5(-0.19X)$
5	936.0(57.5)	W β (C-H)	1.0	$C_4(0.15Z)+H_1(0.95Z)+C_3(-0.05Z)+C_5(-0.22Z)$
6	863.1 (3.1)	$\tau \beta$ (C ₁ -C ₂)	2.5	$C_1(0.43Z)+C_2(-0.24Z)+C_3(0.09Z)+C_4(0.05Z)$
7	775.6 (31.1)	$\tau \beta$ (C ₂ -C ₃)	1.3	$C_1(-0.04Z)+C_2(-0.20Z)+C_3(-0.28Z)+C_4(-0.03Z)$
8	685.8 (0.007)	$\tau \beta$ (C ₅ -N ₁)	2.9	$C_3(-0.47Z)+C_4(-0.12Z)+N_1(-0.37Z)+C_5(0.61Z)$
9	667.9 (42.9)	$\pi \beta$ (O ₁ C ₆ O ₂)	1.2	$O_1(0.26X)+C_6(-0.19Y)+O_2(-0.23X)+H_2(-0.71X)$
10	636.0 (111.3)	$\tau \beta$ (C ₄ -C ₅)	0.3	$C_2(-0.03Z)+C_3(-0.05Z)+C_4(0.04Z)+C_5(-0.11Z)$
11	586.5 (49.4)	β (Total com)	1.2	$C_1(0.26X)+N_1(0.29X)+H_1(-0.30X)+H_2(0.31X)$
12	548.6 (2.8)	$\pi \beta$ (C ₄ C ₃ N ₂)	0.8	$C_3(-0.23Y)+C_4(0.10Y)+N_2(-0.20Y)+H_1(0.32Y)$
13	526.7 (228.5)	W β (N-H)	0.2	$N_2(0.11Z)+H_3(-0.23Z)+H_4(-0.77Z)+C_3(-0.03Z)$
14	499.1 (66.5)	W β (N-H)	0.2	$N_2(0.05Z)+H_3(-0.13Z)+H_4(-0.81Z)+C_3(0.09Z)$
15	472.4 (58.38)	$\tau \beta$ (N-H)	0.1	$C_3(0.01Z)+N_2(-0.07Z)+H_3(0.93Z)+H_4(-0.31Z)$
16	393.9 (6.3)	R β (N-H)	0.8	$C_3(-0.14Y)+N_2(-0.22Y)+H_3(-0.34X)+H_4(-0.41Y)$
17	351.7 (6.1)	R β (N-H)	0.4	$C_3(-0.06Y)+N_2(-0.29X)+H_3(0.50X)+H_4(0.35X)$
18	341.6 (7.7)	$\tau \beta$ (N-H)	0.3	$C_3(0.18Z)+N_2(-0.07Z)+H_3(-0.77Z)+H_4(0.09Z)$
19	316.5 (0.6)	R β (N-H)	1.4	$C_3(0.07Y)+N_2(-0.19X)+H_3(-0.31X)+H_4(-0.22X)$
20	284.3 (1.1)	R β (N-H)	0.3	$C_3(-0.12X)+N_2(-0.31X)+H_3(-0.44X)+H_4(-.35X)$
21	234.8 (1.6)	$\pi \beta$ (C ₁ C ₂ Cl ₂)	0.3	$C_1(0.12X)+C_2(0.08X)+Cl_2(-0.37Y)+C_6(0.20Y)$
22	215.6 (0.2)	$\tau \beta$ (C ₃ -C ₄)	0.1	$C_1(-0.12Z)+C_2(-0.04Z)+C_3(0.06Z)+C_4(0.39Z)$
23	167.5 (0.2)	$\pi \beta$ (Cl ₂ C ₅ N ₁)	0.2	$Cl_2(-0.36y)+C_5(0.12y)+N_1(0.17y)+C_6(0.17x)$
24	142.8 (4.0)	β (Total com)	0.1	$C_1(0.32Z)+C_2(0.20Z)+H_2(-0.45Z)+H_3(-0.37Z)$
25	69.8 (2.8)	β (Total com)	0.03	$H_1(0.31Z)+H_2(0.16X)+H_3(0.52Z)+H_4(0.36Z)$
26	34.2 (1.0)	$\tau \beta$ (C ₆ -O ₂)	0.007	$C_6(0.02Z)+O_1(0.49Z)+O_2(-0.63Z)+H_2(-0.58Z)$

Table-7.1: Computed Bending frequencies (cm^{-1}), force constants (mDyne/A^0), and atomic Cartesian Displacement of vibration motions in CLPYD.

SN	Frequency (Calculated)	Assign.	Force Const	Cartesian Displacement
1	1178.75(285.63)	R β (C-H)	2.0	$C_2(-0.08Y)+C_3(-0.02X)+H_1(-0.44X)+H_2(-0.59Y)$
2	1166.09(28.16)	$\pi \beta$ (C-H)	2.7	$C_2(-0.14X)+C_3(0.23Y)+H_1(0.51X)+H_2(-0.57Y)$
3	1042.82(0.03)	$\tau \beta$ (C-H)	0.9	$C_2(0.13Z)+C_3(-0.14Z)+H_1(0.70Z)+H_2(-0.68Z)$
4	1034.42(48.35)	(Ring Breathing)	5.1	$C_2(0.29Y)+C_3(-0.19Y)+C_4(0.43X)+C_5(0.20Z)$
5	890.22(37.80)	W β (C-H)	0.6	$C_2(-0.11Z)+C_3(-0.11Z)+H_1(0.67Z)+H_2(0.72Z)$
6	875.22(0.0089)	$\tau \beta$ (C-H)	3.7	$C_2(-0.11Z)+C_3(0.06Z)+H_1(0.58Z)+H_2(-0.13Z)$
7	762.76(25.08)	$\tau \beta$ (C-H)	2.0	$C_2(-0.15Z)+C_3(0.14Z)+H_1(0.35Z)+H_2(-0.56Z)$
8	700.49(16.15)	$\pi \beta$ (C ₃ -C ₄ -C ₅)	1.9	$C_2(0.13Y)+C_3(0.37Y)+C_4(-0.18X)+C_5(-0.08X)$
9	644.32(42.12)	$\pi \beta$ (O ₁ -C ₆ -O ₂)	1.3	$C_6(-0.15X)+O_1(0.23X)+O_2(-0.17X)+H_3(-0.60X)$
10	634.44(131.19)	W β (C-H)	0.3	$C_2(-0.05Z)+C_3(0.03Z)+H_1(-0.07Z)+H_2(-0.28Z)$
11	557.97(74.61)	$\pi \beta$ (C ₅ -C ₆ -O ₂)	1.7	$C_5(0.31X)+C_6(-0.21Y)+O_1(-0.22Y)+O_2(-0.19X)$
12	547.85(16.93)	W β (C-H)	0.4	$C_1(0.18Z)+C_4(0.24Z)+H_1(-0.44Z)+H_2(-0.27Z)$
13	482.41(30.16)	$\pi \beta$ (C ₃ -C ₄ -Cl ₁)	1.0	$C_3(0.32X)+C_4(-0.20Y)+Cl_1(-0.20X)+Cl_2(-0.13X)$
14	475.15(4.48)	$\tau \beta$ (C-C)	0.4	$C_2(-0.17Z)+C_3(0.21Z)+C_4(-0.11Z)+C_5(-0.22Z)$
15	381.90(0.65)	$\pi \beta$ (N ₁ -C ₅ -C ₆)	0.8	$C_5(-0.01Y)+N_1(0.29Y)+C_6(-0.16Y)+O_1(0.31X)$
16	313.06(0.33)	W β (C-C)	0.3	$C_1(-0.31Z)+C_2(-0.29Z)+C_3(0.28Z)+C_4(0.37Z)$
17	301.75(0.18)	$\pi \beta$ (C ₅ -C ₄ -Cl ₁)	0.4	$C_4(0.14Y)+C_5(0.13X)+Cl_1(-0.12X)+Cl_2(0.11Y)$
18	225.78(1.18)	$\pi \beta$ (C ₄ -C ₅ -C ₆)	0.5	$C_3(0.15Y)+C_4(0.11Y)+C_5(0.15Y)+C_6(0.28Y)$
19	165.34(0.16)	$\pi \beta$ (Cl ₂ -C ₁ -N ₁)	0.2	$C_1(-0.13Y)+N_1(-0.19Y)+Cl_1(-0.09X)+Cl_2(0.34Y)$
20	159.34(4.2)	W β (C-C)	0.1	$C_2(-0.13Z)+C_3(-0.11Z)+C_4(0.13Z)+C_5(0.34Z)$
21	81.74(2.66)	W β (C-H)	0.3	$C_2(0.39Z)+C_3(0.36Z)+H_1(0.48Z)+H_2(0.56Z)$
22	38.46(1.27)	$\tau \beta$ (C-O)	0.009	$C_6(0.01Z)+O_1(0.49Z)+O_2(-0.63Z)+H_3(-0.58Z)$

AMPYD has 16 atoms and in CLPYD 14 atoms are present result of it 42 and 36 fundamental modes of vibrations are present respectively in both the compounds. Among with 16 modes of vibrations are stretching vibrations in AMPYD and in CLPYD 14 modes of vibrations are stretching vibrations. Deg. of freedom for both the compounds is 42 and 36 respectively. The compounds belong to the Cs point group and all vibrations are supposed to IR as well as Raman active. Some relevant vibration modes, their computed frequencies along with their force constants and intensities are shown in Table 6, 6.1, 7, 7.1. The assignments have been made on the basis of earlier work [58-61] and Cartesian displacement of normal modes.

C- H Stretching Vibrations

Consideration of Cartesian displacements for AMPYD reveals that frequency appeared at 3247.0 cm^{-1} should be assigned to C-H stretching modes of pyridine group. Similarly, by analyzing Cartesian displacements in CLPYD 3261.98 cm^{-1} , and 3241.08 cm^{-1} , can be assigned to C-H stretching modes of pyridine group. These frequencies are shown in table 6 and 6.1.

C- C Stretching Vibrations

In AMPYD the frequencies calculated at 1555.0 cm^{-1} , 1459.2 cm^{-1} , 1443.4 cm^{-1} and 1352.9 cm^{-1} assigned to different C-C stretching modes in pyridine group and frequency computed at 1415.6 cm^{-1} belong to C₁-C₆ stretching mode in substitute group and are shown in Table 6. Similarly, in CLPYD the frequencies calculated at 1589.57 cm^{-1} , 1562.94 cm^{-1} , 1290.82 cm^{-1} and 1215.41 cm^{-1} are assigned to different C-C stretching modes in pyridine group. Similarly, frequency calculated at 1423.68 cm^{-1} represents C₅-C₆ stretching modes in substitute group and is shown in Table 6.1

O- H Stretching Vibrations

Frequencies computed at 3485.6 cm^{-1} and 3489.47 cm^{-1} are assigned to O-H (-COOH) stretching modes in substitute group of AMPYD and CLPYD respectively on the basis of their dependence of atomic coordinates. These frequencies are shown in table 6 and 6.1.

C- O Stretching Vibrations

On the basis of consideration of Cartesian displacements, vibration frequencies computed at 1771.4 cm^{-1} and 1772.17 cm^{-1} are assigned to C=O stretching modes in AMPYD and CLPYD respectively. In AMPYD the frequency calculated at 1098.3 cm^{-1} can be assigned to C₆-O₂ stretching modes similarly in CLPYD frequencies calculated at 1097.13 cm^{-1} can be assigned to C₆-O₂ stretching modes. These frequencies are shown in table 6 and 6.1.

C- Cl Stretching Vibrations

In pyridine group of AMPYD vibration frequencies calculated at 857.3 cm^{-1} and 516.2 cm^{-1} are assigned to C₅-Cl₂ and C₂-Cl₁ stretching modes while in same group of CLPYD frequencies calculated at 847.92 cm^{-1} and 320.73 cm^{-1} can be assigned to C₁-Cl₂ and C₄-Cl₁ stretching modes. These frequencies are shown in table 6 and 6.1.

N- H Stretching Vibrations

In AMPYD vibration frequencies computed at 3662.4 cm^{-1} and 3543.5 cm^{-1} are assigned to N₂-H₃ and N₂-H₄ stretching modes. These frequencies are shown in table 6. These vibrations are not found in CLPYD.

C- N Stretching Vibrations

In pyridine group of AMPYD vibration frequencies calculated at 1606.9 cm^{-1} , 1293.4 cm^{-1} and 1187.1 cm^{-1} are assigned to $\text{C}_3\text{-N}_2$, $\text{C}_1\text{-N}_1$ and $\text{C}_1\text{-N}_1$ stretching modes while in CLPYD frequencies calculated at 1469.19 cm^{-1} and 1349.10 cm^{-1} are assigned to $\text{C}_1\text{-N}_1$ AND $\text{C}_5\text{-N}_1$ stretching mode. These frequencies are shown in table 6 and 6.1.

Bending vibration modes

For AMPYD assignment of frequencies computed in the range 34.2-1689.2 cm^{-1} belong to different bending modes and are shown in Table 7. similarly for CLPYD assignment of frequencies computed in the range 38.46 -1178.75 cm^{-1} belong to different bending modes and are shown in Table 7.1. In AMPYD ring breathing is computed at 1026.7 cm^{-1} while in CLPYD ring breathing is computed at 1034.42 cm^{-1} . In AMPYD, $\pi \beta$ ($\text{C}_1\text{N}_1\text{C}_5$), $\tau \beta$ ($\text{C}_1\text{-C}_2$), $\tau \beta$ ($\text{C}_2\text{-C}_3$), $\tau \beta$ ($\text{C}_5\text{-N}_1$), $\pi \beta$ ($\text{O}_1\text{C}_6\text{O}_2$), $\tau \beta$ ($\text{C}_4\text{-C}_5$), $\pi \beta$ ($\text{C}_4\text{C}_3\text{N}_2$), $\pi \beta$ ($\text{C}_1\text{C}_2\text{Cl}_2$), $\tau \beta$ ($\text{C}_3\text{-C}_4$), $\pi \beta$ ($\text{Cl}_2\text{C}_5\text{N}_1$), and $\tau \beta$ ($\text{C}_6\text{-O}_2$) bending modes are calculated at 970.6 cm^{-1} , 863.1 cm^{-1} , 775 cm^{-1} , 685.8 cm^{-1} , 667.9 cm^{-1} , 636.0 cm^{-1} , 548.6 cm^{-1} , 234.8 cm^{-1} , 215.6 cm^{-1} , 167.5 cm^{-1} , and 34.2 cm^{-1} respectively while for CLPYD, $\pi \beta$ (C-H), $\text{W} \beta$ (C-H), $\tau \beta$ (C-H), $\pi \beta$ ($\text{C}_3\text{-C}_4\text{-C}_5$), $\pi \beta$ ($\text{O}_1\text{-C}_6\text{-O}_2$), $\pi \beta$ ($\text{C}_5\text{-C}_6\text{-O}_2$), $\text{W} \beta$ (C-H), $\pi \beta$ ($\text{C}_3\text{-C}_4\text{-Cl}_1$), $\tau \beta$ (C-C), $\pi \beta$ ($\text{N}_1\text{-C}_5\text{-C}_6$), $\pi \beta$ ($\text{C}_5\text{-C}_4\text{-Cl}_1$), $\pi \beta$ ($\text{C}_4\text{-C}_5\text{-C}_6$), and $\pi \beta$ ($\text{Cl}_2\text{-C}_1\text{-N}_1$) bending modes are calculated at 166.0 cm^{-1} , 890.2 cm^{-1} , 875.2 cm^{-1} , 700.4 cm^{-1} , 644.3 cm^{-1} , 557.9 cm^{-1} , 547.8 cm^{-1} , 482.4 cm^{-1} , 475.1 cm^{-1} , 381.9 cm^{-1} , 301.7 cm^{-1} , 225.7 cm^{-1} , and 165.3 cm^{-1} respectively.

CONCLUSION

Density function theory calculations are carried out for the undertaken compounds AMPYD and CLPYD with the objectives of suggesting their geometry, electronic structure, and bonding. The geometrical parameters, band gap and assignment of important vibration frequencies are reported.

It is found that the calculated bond lengths are in well conformity with the bond lengths expected from reported atomic radii. Theoretical calculations suggest that both the compounds get stabilized by hydrogen bonding. The bond length data suggests that AMPYD should be more reactive than CLPYD. It can also be concluded that the active sites in both undertaken compounds are centered on C-Cl bonds and on C-C bond lies between pyridine ring and the substitute group. Bond angle analysis suggests that all the C and N atoms in both undertaken compounds are in SP^2 hybridization. Analysis also reveals that O_2 in both undertaken compounds is in SP^3 hybridization. Analysis of dihedral angles reveals that in both undertaken compounds pyridine ring and substitute group are planer.

O_1 , O_2 , N_1 and N_2 are most negative elements while C_3 and C_6 are most positive elements it suggest maximum reactivity around $\text{C}_3\text{-N}_2$ and $\text{C}_6\text{-O}_2$ bonds. During quantum mechanical analysis, band gap of AMPYD is computed less than CLPYD therefore it is concluded that AMPYD is found more polar than CLPYD. We can also conclude that AMPYD is soft and highly reactive. Zero-point vibration energy for CLPYD and AMPYD is reported to be to be 263289.5 (Joules/Mol) and 218865.6 (Joules / Mol) respectively. The stoichiometric formula for AMPYD and CLPYD are calculated as $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2$ and $\text{C}_6\text{H}_3\text{Cl}_2\text{NO}_2$ respectively and the molecular mass of both the compounds is calculated as 205.96498 amu and 190.95408 amu respectively. Deg. of freedom for both the compounds is 42 and 36 respectively. The dipole moment of AMPYD is computed 6.22 Debye and for CLPYD it is 3.61 Debye. The entropy of AMPYD and CLPYD is computed as 104.545 and 99.027 Cal / Mol-kelvin respectively.

REFERENCES

1. Colborn, T., P Short; *Toxicol Ind Health*, **1999**. 15, p. 241–276.
2. Sterling, TM., *Weed Science*, **1994**. 42 (2): p. 263-276.
3. Smith., 8: Fate of herbicides in the environment, Handbook of Weed Management Systems. CRC Press. **1995**. p. 245-278.
4. R. F. Service; *Science*, **2013**. 341 (6152), p. 1329.
5. Mithila, J., *Weed Science*, **2011**. 59(4), p. 445-457.
6. Arbuckle, TE., *Int Arch Occup*. **2002**. 75, p. 406-414.
7. Arbuckle, TE., *Epidemiology*, **2001**. 109, p. 851-857.
8. Arbuckle TE., *Epidemiology*, **1999**. 10, p. 752-760.
9. Bhanti, M., *Chemosphere*, **2007**. 69, p. 63-68.
10. Bullman, TA., *Annu Rev Public Health*, **1994**. 15, p. 69-90.
11. Green, RM., *Int J Enviro. Res Public Health*, **2004**. 1, p. 124-131.
12. Kaioumova, DF., *Chemosphere*, **1998**. 37, p. 1755-1759.
13. Kavlock, R., *Crit Rev Toxicol*, **2005**. 35, p. 685-690.
14. Martin, SA., *Am J Ind Med*, **2002**. 41, p.202-209.
15. Moran, JM., *J Toxicol Environ Health A*, **2008**. 71, p.1457-1467.
16. Salehi, F., *J Toxicol Environ Health B Crit Rev*, **2008**. 11, p.301-321.
17. Gorell, JM., *Neurology*, **1998**. 50 (5), p. 1346-1350
18. Dinis-Oliveira, RJ., *Neurotoxicology*, **2006**. 27(6), p.1110-1122.
19. Reuber, MD., *Journal of Toxicology, and Environmental Health*, **1981**. 7(2), p.207-222.
20. MacKinnon, DS., *Journal of Applied Ecology*, **1993**. 30(3), p. 395-406.
21. Forouzesh, A., *Weed Research*, **2015**. 55, p. 334-358.
22. Aminopyralid - Compound Summary, PubChem. Dow Agro Sciences LLC September 8, 2008 at the Way Back Machine.
23. Hartzler, B., Department of Agronomy, Iowa State University, **2006**.
24. Moody, O., *Surrey*, UK British Crop Protection Council, **1997**. P.11
25. Reade, PH., *Weed Management Handbook*, (9thedn), Oxford Blackwell Science, **2002**.
26. Willoughby, I., *Forestry*, **2006**. 79 (5): p. 599-608.
27. Berberidou, C., *J Chem Tech Biotech*, **2016**. 91(9): p. 2510-2518.
28. Ahmad, R., *J Env Sci Health Part B*, **2009**. 57(5): p. 1960-1966.
29. Halstved, TM., *Weed Technology*, **2007**. 21(4): p. 890-894
30. Fast, BJ., *Weed Science*, **2010**. 58(4): p.484-489.
31. Enloe, SF., *Weed Science*, **2009**. 57(1): p. 10-15.
32. Milestone herbicide product label. Dow Agro Sciences Publication No. V01-880-029 (03/10) BR 01050805, IN: Dow Agro Sciences. 8 p.
33. United States Office of Prevention, Pesticides, Environmental Protection, and Toxic Substances. **2005**.
34. Senseman SA., *Herbicide Handbook*, (9thedn), Champaign, IL: Weed Science Society of America, **2007**. 331-332.
35. Bailey, GW., *Soil Sci Soc Am Proc*, **1968**, 32, p. 222-234.
36. Clay, DV., *Asp Appl Biol*, **1996**. 44, p. 39-46.
37. K.B. Kelley., *Pesticide Biochemistry and Physiology*, **2007**, 89(1), p. 1-11.

38. Eyheraguibel, B., *J Agric Food Che.*, **2009**. 57(5), p. 1960-1966.
39. Kohn, W., *Phys Rev*, **1965**. 140, p. 1133.
40. Hohenberg, P., *Phys Rev*, **1964**. 136, p. 864.
41. Frisch, MJ., et al., Gaussian 09, Revision A02, Gaussian Inc, Wallingford CT, **2009**.
42. Beack, AD., *J Chem Phys*, **1993**. 98, p. 5648.
43. Lee C., *Phys Rev*, **1998**, 37, p. 785.
44. Miehlich, B., *Chem Phys Lett*, **1989**. 157, p. 200.
45. Lee, C., *Phys. Rev.*, **1988**. 37, p. 787.
46. Francl, MM., *Journal of Chemical Physics*, **1982**. 77 p. 3654.
47. Ditch field, R., *J Chem Phys*, **1971**. 54, p. 724.
48. Frisch, A., Gauss view User's Manual, Gaussian Inc, Pittsburgh PA, **2000**.
49. Pekka, p., *Chemistry, A European Journal*, **2009**. 15 (46), p. 12770.
50. Sawant, AB., *Indian Journal of Pure and Applied Physics*, **2012**. 50, p. 308.
51. Kurtaran, R., *Polyhedron*, **2007**. 26, p. 5069.
52. Fleming, I., *Frontier Orbitals and Organic Chemical Reactions*, J Wiley, and Sons New York, **1976**.
53. Srivastav, RK., *Journal Of chemical and Pharmaceutical Research*, **2012**. 4, p. 3287.
54. Sagdinc, S., *Spectrochimica Acta A*, **2009**. 73, p. 181.
55. Chauhan, HPS., *Spectrochim Acta Part A*, **2009**. 74, p. 67.
56. Chaudhari, KR., *J Organometal Chem*, **2007**. 692, p. 928.
57. Yu, L., *J Organometal Chem*, **2004**. 620, p. 235.
58. Bhattacharya, S., *Spectrochim Acta Part A*, **2005**. 61, p. 3145.
59. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B*, (5thedn), John Wiley and Sons, New York, **1997**. 74.
60. Sathyanarayana, DN., *Vibrational Spectroscopy Theory, and Applications* (2ndedn), New Age International Limited: New Delhi, **2005**. 390.