Theoretical Studies of Vibrational Spectral modes and HOMO, LUMO Studies of Some Synthetic Organic Compounds

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Abstract

The vibration modes of some synthetic compounds viz. derivatives of pyridines were examined experimentally and theoretically using Semi-empirical AM1 and PM3 methods. Apart from giving the comparison of the significant part of the spectra, the statistical correlation was also calculated for the theoretical spectra and methods to establish the use of these methods as alternative and supportive tool in analytical chemistry. Vibration modes for the compounds under study show a perfect correlation between theoretically and experimentally observed values. As well as, we report here frontier molecular orbitals (FMO) energy gap, molecular hardness (η), ionization energy (IE), electron affinity (EA), total energy and dipole moment of some pyridine derivatives supported by semi-empirical calculations, which properties provide the reactivity, stability and polarizabilities of the title compounds.

Keywords: Semi-empirical methods, AM1, PM3, vibration modes, correlation coefficient, frontier molecular orbital (FMO).

Introduction

Pyrazolone compounds refer to the class of compounds characterized by 5- membered ring structure composed of three carbon and two nitrogen atoms in the adjacent position, out of which one is basic nitrogen and other is neutral nitrogen. The aromatic nature these compounds arises from the four electrons and the unshared pair of electrons on the NH nitrogen[1]. Pyrazole derivative have a long history of application in agrochmicals as herbicides and insecticide and in pharmaceutical industry as antipyratic and anti- inflammatory drugs. Antipyrine is one of the earliest synthetic drugs and is named after its antipyratic properties. Pyrazolone compounds also have complex formation property. They can coordinate to metal ions via carbonyl oxygen atom and may be considered as good oxygen donor ligands. This fact has been established by various workers[1-3]. Some of the pyrazolone compounds have also found to show drug property[4,5]. Due to its wide range of biological activity, pyrazoles have received a considerable interest in the field of drug discovery and therefore, pyrazole ring constitutes a relevant synthetic target in pharmaceutical industry. In fact, such a heterocyclic moiety represents the core structure of a number of drugs[6].

Similar to pyrazolones, pyridines and its derivatives are the class of compounds which do have synthetic as well as medicinal importance. Benzyl pyridine shows a significant activity against specified microbes[7]. Due to this reason these compounds were also considered as compounds of interest for studies by the workers in past[8,9].

Density Functional Theory, molecular mechanics, semi-empirical and ab-initio methods are often employed to calculate molecular properties. These methods give information regarding vibration modes, molecular geometry, heat of formation, force constants, electron densities, dipole moments, population analysis, chemical reaction pathways and thermodynamic properties etc.

Semi-empirical methods provide the information of approximate calculations of different chemical properties using different methods viz. AM1, PM3, MNDO and ZINDO[9,10]. Since the other quantum chemical calculation methods are time consuming, so, semi-empirical AM1 and PM3 methods are in use with reasonably good results.

In this paper we wish to report the vibration modes analysis of some selected pyridine derivatives using AM1 and PM3 methods and their comparison with their real spectra. Compounds taken for the studies here are (i) 2-Amino pyridine (2-APy); (ii) 3-Amino pyridine (3-APy) and (iii) 4-Amino pyridine (4-APy). Structures of these compounds are given in figure-1.

2-Amino pyridine (2-APy)

3-Amino pyridine (3-APy)
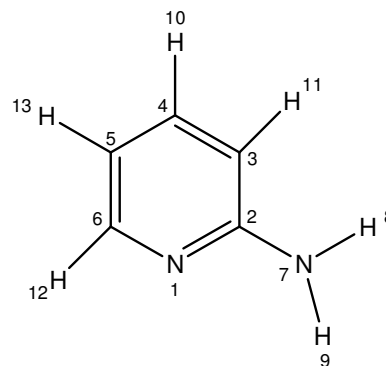
4-Amino pyridine (4-APy)
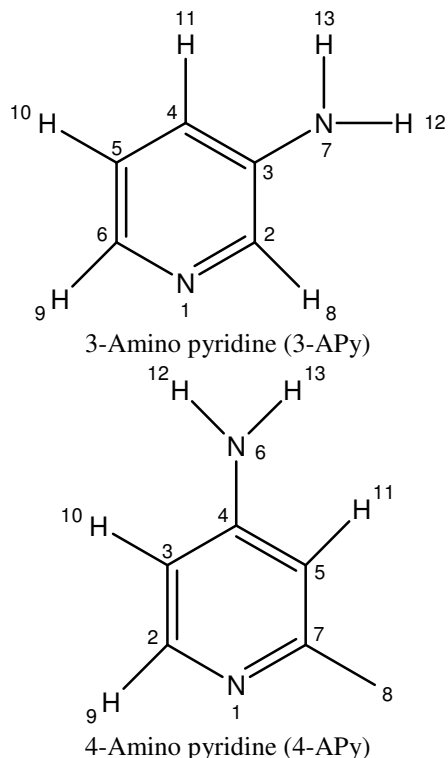
Figure-1
Molecular Structures of pyridine derivatives with numbering atoms adopted in the quantum chemical calculation

Material and Methods

Experimental: The compounds under study were procured from the reliable sources as E-Merck, Loba Chemie and C.D.H. etc. Their purities were checked by checking their melting points. The I.R. spectral studies of these compounds were carried out at Sophisticated Analytical Instrumentation Facility (S.A.I.F), Central Drugs Research Institute (C.D.R.I.) Lucknow using KBr/CsI pallets in the range 4000- 400 cm^{-1} [11].

Computational details: The AM1 and PM3 quantum chemical methods in MOPAC package software were used to calculate the molecular geometry, Net atomic charge, electron density, Frontier Molecular Orbital energies and total energy etc. The calculations for vibration modes of the pyridine derivatives under study were also done using same package. Structures of the compounds were drawn on the PCMODEL package of Serena software and then were optimized which were then used as input to MOPAC. All these calculations were done on the Pentium–III machine with configuration: P-III/866Mhz/20GB/52X/SCROLL MOUSE/56 KBPS.

Results and Discussion

The computed molecular geometry, Net atomic charge, electron density, Frontier Molecular Orbital energies and other computed results are of theoretical interest. The computed vibration modes along with their experimental values are given in the tables-1-3. It has also been tried to match the computed spectral peaks with their experimental values. Recorded spectral data match well with the theoretically computed data for the compounds under study. The observed results are well within earlier work[12-13].

Table-1
Computed and observed vibration modes values (cm^{-1}) for 2-Amino pyridine (2-APy) compound

Experimental (cm^{-1})	AM1	PM3
445	443.81	444.54
------	498.87	448.20
565	566.85	564.85
630	629.68	631.43
774	742.92	758.58
----	822.01	824.86
910	906.94	909.85
966	966.14	966.58
------	997.40	998.05
------	1099.55	1099.58
1140	1139.70	1140.87
-----	1188.17	1186.57
------	1208.19	1209.64
1230	1229.12	1230.51
------	1299.63	1298.67
1350	1349.70	1365.68
------	1466.78	1464.58
------	1583.19	1592.27
1650	1656.75	1646.75
------	1722.63	1729.43
------	1785.46	1785.08

The notable peaks in these compounds are carbonyl stretching frequency υ (C=N); υ (C-N-C) bending; ring breathing and deformation and ring stretching etc which appear well within the range as reported by earlier workers[12-15].

Correlation coefficient between computed and experimental vibration modes for the different pyridine derivatives under study using AM1 and PM3 methods respectively are computed and are listed here: i. 2-Amino pyridine (2-APy) **-- 0.999473** (AM1) and **0.999917** (PM3), ii. 3- Amino pyridine (3-APy) **-- 0.997847** (AM1) and **0.992439** (PM3), iii. 4-Amino pyridine (4-APy) **-- 0.999996** (AM1) and **0.991169** (PM3).

Table-2
**Computed and observed vibration modes values (cm⁻¹) for
3- Amino pyridine (3-APy) compound**

Experimental (cm⁻¹)	AM1	PM3
445	442.37	408.14
------	519.64	486.19
565	579.91	544.33
630	632.36	636.83
774	671.16	644.39
----	843.82	874.86
910	922.81	889.73
966	965.17	977.29
------	988.45	997.95
------	1120.88	1050.55
1140	1151.51	1079.61
-----	1192.16	1085.17
------	1221.66	1123.04
1230	1243.51	1151.18
------	1280.96	1188.88
1350	1359.76	1221.57
------	1470.40	1365.58
------	1602.01	1542.28
1650	1665.32	1567.05
------	1732.26	1673.43
------	1780.86	1763.98

Table-3
**Computed and observed vibration modes values (cm⁻¹) for 4-
Amino pyridine (4-APy) compound**

Experimental (cm⁻¹)	AM1	PM3
445	445.73	411.26
------	506.76	493.94
565	542.53	540.94
630	594.57	643.01
774	683.06	662.40
----	688.91	817.96
910	862.14	845.60
966	966.30	939.27
------	970.59	964.10
------	1131.78	1041.48
1140	1209.31	1103.86
-----	1246.95	1148.26
------	1305.06	1174.96
1230	1342.26	1243.89
------	1506.58	1378.21
1350	1532.92	1492.83
------	1687.14	1584.84
------	1736.81	1676.30
1650	1748.82	1739.78
------	1769.71	1769.58

These correlation coefficient values among computed and experimental vibration modes for the pyridine derivatives under study clearly indicates that computed values are approximately in correlation with the experimental values. The linear graphs between computed and experimental values for vibration modes for the pyridine compounds under studies are given in the figure-2.

Net atomic charge (NAC) and electron density (ED) on different atoms were also computed using AM1 and PM3 semi-empirical methods of the pyridine derivatives under study. These properties on Nitrogen, Carbon and hydrogen atoms of title compounds have been listed in table-4-6. Their variation graphs are also plotted and are shown in the figure-3 for various pyridine derivatives.

Frontier Molecular Orbital (FMO) Analysis: The frontier molecular orbital such as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the chemical species are very important in defining organic compounds reactivity[16,17]. Higher value of HOMO of a molecule has a tendency to donate electrons to appropriate acceptor molecule with low energy and empty molecular orbitals. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies, hardness (η), ionization energy (IE), total energy and dipole moment have been calculated and are given in table-4. Based on AM1 and PM3 optimized geometry, the total energies of the title compounds have been calculated by these quantum chemical methods, which are range to -1009.002 to -1136.4201 eV. An electronic system of the organic compounds with a larger frontier molecular orbital gap should be less reactive than one having smaller gap[18]. The ionization energy (IE) can be expressed through HOMO orbital energies as IE = - ϵ_{HOMO} and electron affinity (EA) can be expressed through LUMO orbital energies as EA = - ϵ_{LUMO}, which are also reported in the same table.

The hardness (η) corresponds to the energy gap between the HOMO and LUMO frontier molecular orbital energies. In the respect, highest stability of the chemical system has larger HOMO-LUMO orbital energy gap[19]. In the present study, the HOMO-LUMO gap of the molecules under study are reported on the basis of AM1 and PM3 semi-empirical quantum chemical methods, respectively are shown in table-7, which clearly indicates that the molecules are very stable. The ionization potential values obtained by all these theoretical quantum chemical methods also support the stability of the molecules under study. The calculated dipole moment values indicate the polarizabilities of the molecules.

Conclusion

On comparison among the AM1 and PM3 semi-empirical methods tested in the present study for the title compounds, AM1 semi-empirical method can be considered as the most

appropriate method to facilitate the vibration frequencies identifications of such compounds as I.R. frequencies simulated by this method exhibit the best linearity between computed and experimental frequencies data. Thus this may be concluded that Quantum- chemical semi-empirical calculations can be successfully used for the prediction of vibration modes and simulation of I.R. spectra as well as for Frontier Molecular Orbital (FMO) studies for the organic compounds. The assignments made with minimal basis set and reasonable deviations from the experimental values seem to be correct. The calculated HOMO-LUMO orbital energies can be used to estimate the ionization energy, molecular hardness and other physical parameters semi-quantitatively. HOMO-LUMO energy gap, molecular hardness, ionization energy, electron affinity and total energy are very important physical parameters for chemical reactivity and biological activities of the compounds under study.
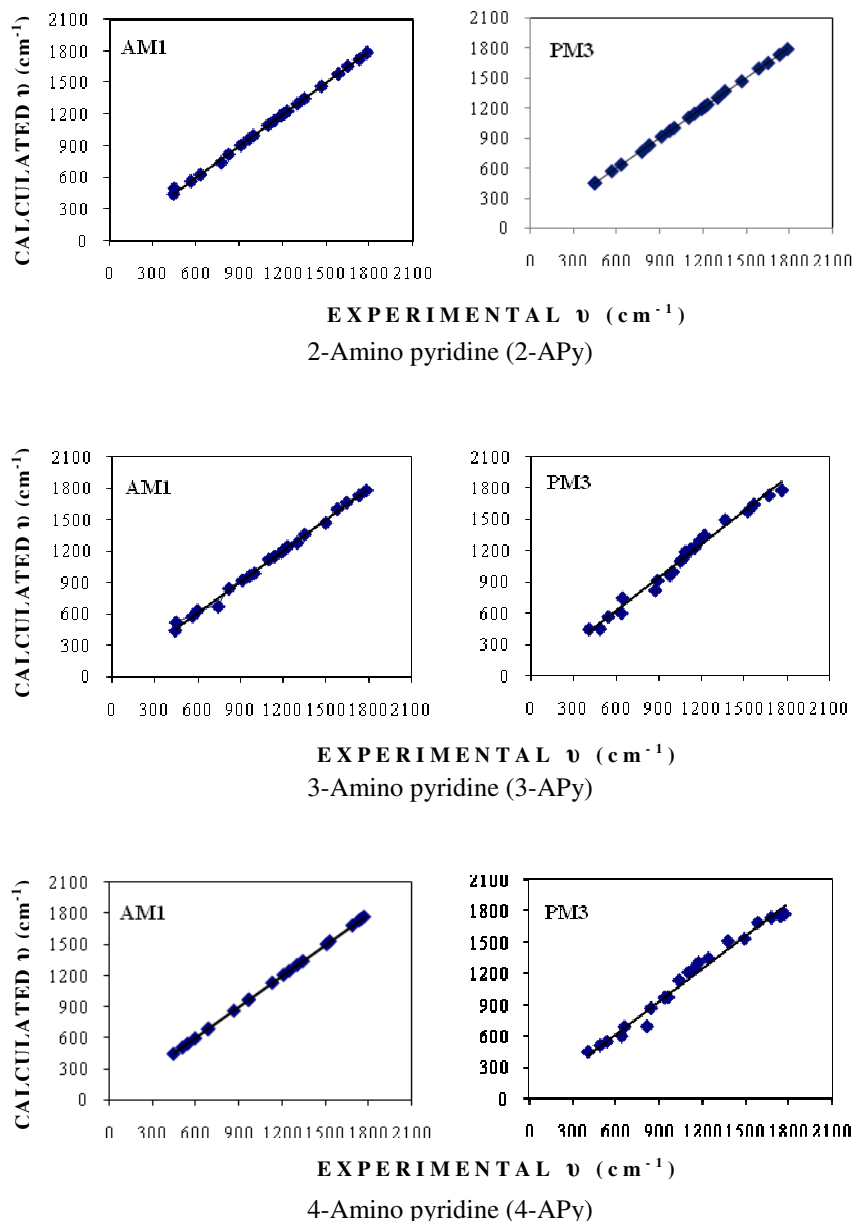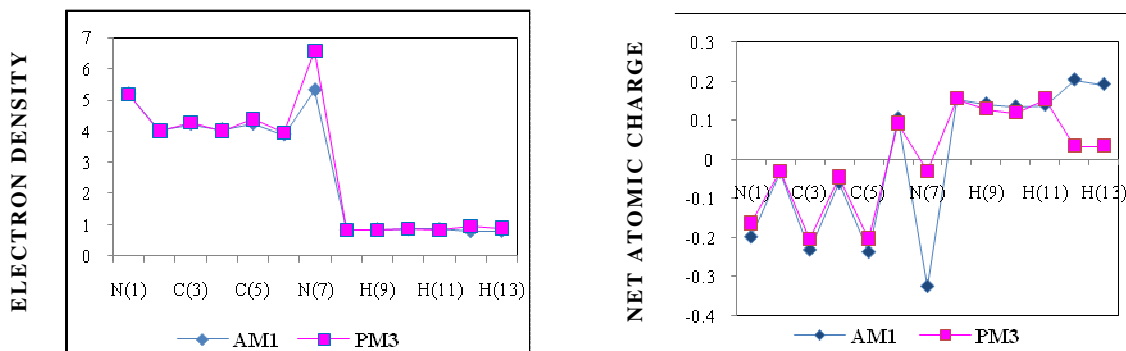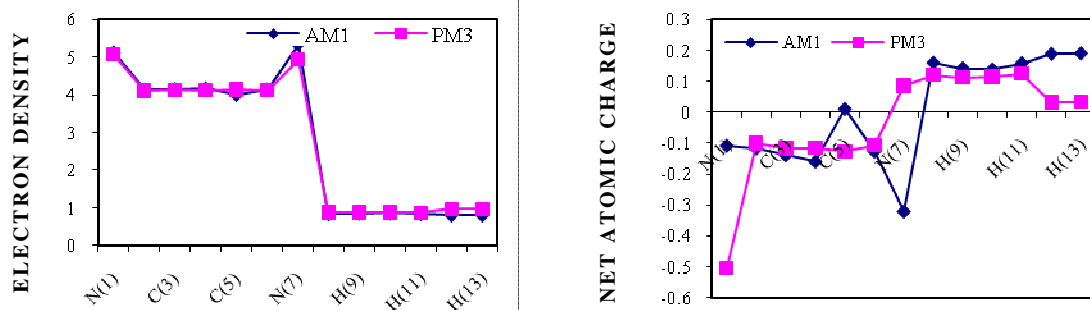

2-Amino pyridine (2-APy)

3-Amino pyridine (3-APy)

4-Amino pyridine (4-APy)

Figure-2
Correlation graphs between Computed and experimental values of vibration modes of various pyridine compounds under study

A T O M S   A N D   I T S   N U M B E R I N G
2-Amino pyridine (2-APy)

A T O M S   A N D   I T S   N U M B E R I N G
3-Amino pyridine (3-APy)
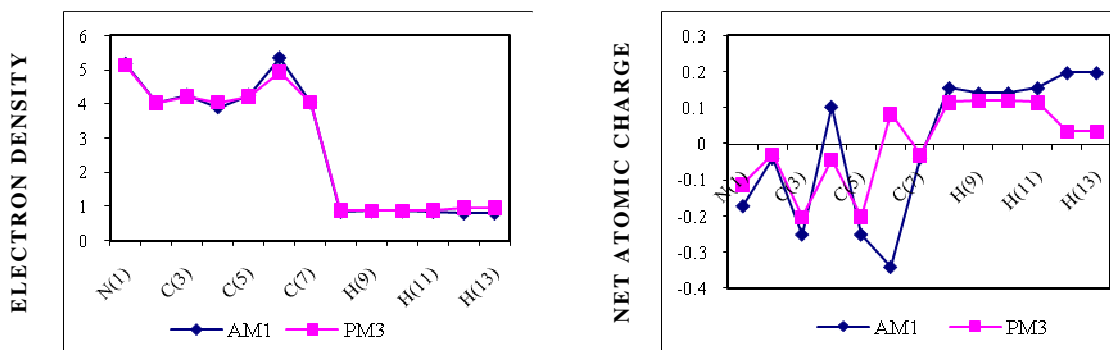
A T O M S   A N D   I T S   N U M B E R I N G
4-Amino pyridine (4-APy)

Figure-3
Computed values for Net Atomic Charge (NAC) and Electron Density (ED) of various pyridine compounds under study

Table-4
Net atomic charges (NAC) and Atom electron density (ED) calculated by AM1 and PM3 Semi-empirical methods for 2-aminopyridine (2-APy)

ATOM & NUMBER	AM1		PM3	
	NAC	ED	NAC	ED
N(1)	-0.1972	5.1972	-0.1624	5.1856
C(2)	-0.0313	4.0313	-0.0297	4.0198
C(3)	-0.2303	4.2303	-0.2030	4.2865
C(4)	-0.0589	4.0589	-0.0449	4.0195
C(5)	-0.2357	4.2357	-0.2023	4.3989
C(6)	0.1055	3.8945	0.0928	3.9523
N(7)	-0.3233	5.3233	-0.0303	6.5869
H(8)	0.1562	0.8438	0.1551	0.8456
H(9)	0.1426	0.8574	0.1297	0.8467
H(10)	0.1354	0.8646	0.1199	0.8679
H(11)	0.1401	0.8599	0.1548	0.8485
H(12)	0.2043	0.7957	0.0348	0.9680
H(13)	0.1926	0.8074	0.0349	0.9048

Table-5
Net atomic charges (NAC) and Atom electron density (ED) calculated by AM1 and PM3 Semi-empirical methods for 3-aminopyridine (3-APy)

ATOM & NUMBER	AM1		PM3	
	NAC	ED	NAC	ED
N(1)	-0.1094	5.1094	-0.502	5.0502
C(2)	-0.1183	4.1183	-0.1005	4.1005
C(3)	-0.1406	4.1406	-0.1173	4.1173
C(4)	-0.1609	4.1609	-0.1153	4.1153
C(5)	0.0092	3.9908	-0.1265	4.1265
C(6)	-0.1277	4.1277	-0.1070	4.1070
N(7)	-0.3219	5.3219	0.0845	4.9155
H(8)	0.1586	0.8414	0.1198	0.8802
H(9)	0.1408	0.8592	0.1113	0.8887
H(10)	0.1369	0.8631	0.1134	0.8866
H(11)	0.1573	0.8427	0.1236	0.8764
H(12)	0.1872	0.8128	0.0315	0.9685
H(13)	0.1887	0.8113	0.0327	0.9673

Table-6
Net atomic charges (NAC) and Atom electron density (ED) calculated by AM1 and PM3 Semi-empirical methods for 4-aminopyridine (4-APy)

ATOM & NUMBER	AM1		PM3	
	NAC	ED	NAC	ED
N(1)	-0.1719	5.1719	-0.1124	5.1124
C(2)	-0.0385	4.0385	-0.0297	4.0297
C(3)	-0.2512	4.2512	-0.2030	4.2030
C(4)	0.1037	3.8963	-0.0444	4.0444
C(5)	-0.2510	4.2510	-0.2023	4.2023
N(6)	-0.3415	5.3415	0.0828	4.9172
C(7)	-0.0388	4.0388	-0.0303	4.0303
H(8)	0.1560	0.8440	0.1151	0.8849
H(9)	0.1406	0.8594	0.1197	0.8803
H(10)	0.1412	0.8588	0.1199	0.8801
H(11)	0.1555	0.8445	0.1148	0.8852
H(12)	0.1980	0.8020	0.0348	0.9652
H(13)	0.1980	0.8020	0.0349	0.9651

Table-7
Computed HOMO-LUMO energy, hardness (η), ionization energy (IE), electron affinity (EA), total energy and dipole moment for pyridine compounds under study as obtained by AM1 and PM3 methods

Computed Parameters	2-Apy		3-Apy		4-Apy	
	AM1	PM3	AM1	PM3	AM1	PM3
ϵ_{HOMO} (eV)	-8.83604	-8.96850	-8.78722	-8.89580	-9.13960	-9.10112
ϵ_{LUMO} (eV)	-0.32333	-0.0825	-0.25914	-0.03858	-0.30398	-0.06417
ϵ_{HOMO} - ϵ_{LUMO}	8.51271	8.8860	8.52808	8.85722	8.83562	9.03695
Hardness(η) = ½(ϵ_{HOMO} - ϵ_{LUMO})	4.25636	4.4430	4.26404	4.42861	4.41781	4.51848
IE = - ϵ_{HOMO}	8.83604	8.6426	8.78722	8.89580	9.13960	9.10112
EA = - ϵ_{LUMO}	-0.32333	-0.04587	-0.25914	-0.03858	-0.30398	-0.06417
Total Energy (eV)	-1136.2403	-1008.561	-1136.3761	-1009.002	-1136.4201	-1009.033
Dipole moment (Debyes)	1.887	2.054	2.852	2.547	3.278	2.897

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