Vibrational Investigation of "2-Arsanyl-Pyridine" Using First Principle

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Abstract

Spectroscopic investigations along with theoretical quantum chemical studies on "2-Arsanyl-Pyridine (C_5H_7AsN)" have been carried out. The quantum chemical density functional method at B3LYP/6-31+g(d,p) level, is used to obtain the equilibrium geometries of the title compound. We have also performed vibrational analysis of the title compound at their equilibrium geometries and established the complete assignments of the significant vibrational modes. The calculated vibrational frequencies are shown to be in perfect agreement with the theoretically observed FTIR spectra of the molecule under study.

1. INTRODUCTION

Yridine is a heterocyclic aromatic tertiary amine, also called azabenzene and azine, is characterized by a six member ring composed of five carbon atoms and a nitrogen atom which replace one carbon-hydrogen unit in the benzene ring (C_5H_5N). Pyridine is a base with chemical properties similar to tertiary amines. Nitrogen in the ring system has an equatorial lone pair of electrons that does not participate in the aromatic π-bond. Pyridine and its derivatives are very important in industry as well as in bio chemistry. Pyridine and its derivatives are used as solvents and starting material for the synthesis of target compounds for instance insecticides, herbicides, medicines, vitamins, food flavorings, feed additives, dyes, rubber chemicals, explosives, disinfectants, and adhesives. It is also used as a denaturant for antifreeze mixtures, as a dyeing assistant in textiles and in fungicides. 2-Arsanyl-Pyridine is an intermediate for the synthesis further pyridine derivatives especially for agrochemical field [1]. The aim of the present study is to investigate in detail the vibrational spectra of the important biological molecule 2-Arsanyl-Pyridine, a derivative of pyridine having commercial interest find application in market areas where bioactivity is important, as in medicinal drugs and in agricultural products such as herbicides, insecticides, fungicides, and plant growth regulators [2].

2. MATERIALS AND METHODS

The model molecular structure of the title compound is shown fig 1. The title molecule is an asymmetric top with rotational symmetry number equal to 1. The theoretical FT-IR spectra plotted is shown in fig 2.

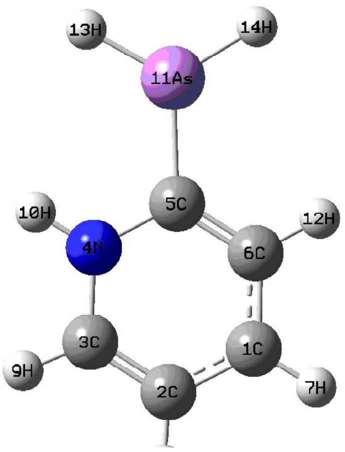

Fig.1: Model molecular structure of 2-Arsany l-Pyridine

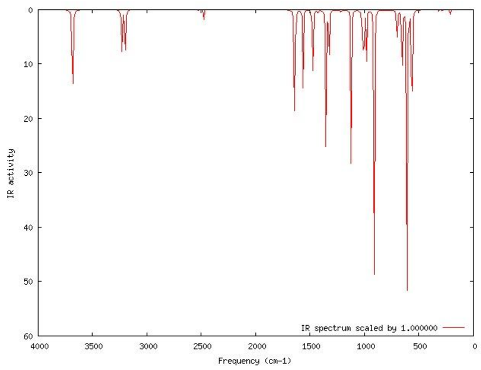

Fig.2: Theoretical FT-IR spectra of 2-Arsany l-Pyridine

3. RESULT AND DISCUSSION

All the calculations were performed on an AMD dual core/2.71 GHz personal computer by the B3LYP [3, 4] method using the 6-31+g(d,p) level basis set of Density functional theory [5]. All computations were carried out with the Gaussian 09 package [6]. By combining the results of the Gaussview 5.0 program package [7] with symmetry considerations and the VEDA 4 program to calculate the PED values [8].

3.1 Geometry Optimization

The optimized geometrical parameters of 2-Arsanyl-Pyridine are listed in table 1, showing bond lengths, in plane bond angles, out of plane wag and torsional vibrations. The optimized geometry of the title compound calculated by the B3LYP method of DFT agrees well with the experimental results. By allowing the relaxation of all parameters, the calculations converged to optimize geometries, which also correspond to the true energy minima, as revealed by the lack of imaginary frequencies in the vibrational mode calculation. Subsequently, the zero point vibrational energy obtained for structure optimization of 2-Arsanyl-Pyridine with B3LYP/ 6-31+g(d,p) sets is approximately -64.11121 (Kcal/ Mol).

Table-1 : Optimized Parameters of 2-Arsanyl-Pyridine using B3LYP/6-31+g(d,p) method

S.No.	Parameter	DFT Values	S.No.	Parameter	DFT Values
	Stretching				
1	R(1,2)	1.42	2	R(1,6)	1.42
3	R(1,7)	1.08	4	R(2,3)	1.37
5	R(2,8)	1.09	6	R(3,4)	1.41
7	R(3,9)	1.08	8	R(4,5)	1.4
9	R(4,10)	1.01	10	R(5,6)	1.37
11	R(5,11)	1.87	12	R(6,12)	1.09
13	R(11,13)	1.47	14	R(11,14)	1.46
	Bending		15	A(2,1,6)	118.26
16	A(2,1,7)	121.35	17	A(6,1,7)	120.39
18	A(1,2,3)	120.56	19	A(1,2,8)	120.85
20	A(3,2,8)	118.59	21	A(2,3,4)	120.11
22	A(2,3,9)	124.36	23	A(4,3,9)	115.54
24	A(3,4,5)	120.52	25	A(3,4,10)	118.87
26	A(5,4,10)	120.61	27	A(4,5,6)	119.55
28	A(4,5,11)	116.45	29	A(6,5,11)	123.99
30	A(1,6,5)	121	31	A(1,6,12)	119.9
32	A(5,6,12)	119.1	33	A(5,11,13)	120.9
34	A(5,11,14)	119.78	35	A(13,11,14)	119.32
	Dihedral Angles				
36	D(6,1,2,3)	0.00	37	D(6,1,2,8)	-180.00
38	D(7,1,2,3)	-180.00	39	D(7,1,2,8)	0.00
40	D(2,1,6,5)	0.00	41	D(2,1,6,12)	179.99
42	D(7,1,6,5)	179.99	43	D(7,1,6,12)	-0.01
44	D(1,2,3,4)	0.00	45	D(1,2,3,9)	-180.00
46	D(8,2,3,4)	180.00	47	D(8,2,3,9)	0.00
48	D(2,3,4,5)	0.01	49	D(2,3,4,10)	179.94
50	D(9,3,4,5)	-180.00	51	D(9,3,4,10)	-0.07
52	D(3,4,5,6)	-0.01	53	D(3,4,5,11)	179.99
54	D(10,4,5,6)	-179.94	55	D(10,4,5,11)	0.06
56	D(4,5,6,1)	0.01	57	D(4,5,6,12)	-179.99
58	D(11,5,6,1)	-179.99	59	D(11,5,6,12)	0.01
60	D(4,5,11,13)	0.05	61	D(4,5,11,14)	180.00
62	D(6,5,11,13)	-179.95	63	D(6,5,11,14)	0.00

3.2 Thermodynamical and Electronic Parameters

The thermodynamic functions-internal thermal energy (*E*), constant volume heat capacity (*Cv*), and entropy (*S*) are shown in table 2. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is termed as a soft molecule [9,10] and vice versa. According to the present DFT calculations the frontier orbital gap in case of the molecule 2-Arsanyl-Pyridine is calculated as 0.2639 Hartee or 7.144 eV. The rotational constants are calculated as 5.38400 0.99018 0.83637 GHz respectively.

Table-2: Thermodynamic and Electronic Parameters of 2-Arsanyl-Pyridine with B3LYP/6-31+g(d,p) basis set

Parameters	**E (Thermal)** KCal/Mol	**C_V** Cal/Mol-Kel	**S** Cal/Mol-Kel
Total	68.056	23.777	82.642
Electronic	0.000	0.000	1.377
Translational	0.889	2.981	41.043
Rotational	0.889	2.981	28.668
Vibrational	66.278	17.815	11.553
Rotational constants (GHz)	5.38400	0.99018	0.83637
Zero-point vibrational energy	64.11121 (Kcal/Mol)		
HOMO =	-8.10288 eV		
LUMO =	-0.885904 eV		
Energy Band Gap =	7.14408 eV		

3.3 Normal Mode Analysis

3.3.1 ν(N-H) Stretch:

The N-H stretching vibrations occur in the region 3500-3300 cm^{-1} [11-p-240] This mode is calculated at 3528 cm^{-1} having IR intensity 47.33 in the calculated spectra. The other mode of vibration is calculated at 1414, 1075, 1034, 974, 964 & 661 cm^{-1} and represents the in plane bending and torsional modes.

3.3.2 ν(C-H) Stretch:

The aromatic structure ring R1 of the title compound shows the presence of C-H stretching vibration in the region 3100- 2900 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibration [12] identification of C-H stretching vibration. The calculated values of this mode are obtained at frequencies 3106, 3093, 3068 and 3062 cm^{-1} having IR intensities 3, 10, 12, and 9 respectively.

3.3.3 (As-H) Mode :

The calculated vibrational stretch ν(As-H) mode is obtained on 2422 and 2373 cm^{-1} with very weak absorption values. Two intense peaks are calculated at 873 and 863 cm^{-1} with boating and torsional modes respectively. These two peaks seem to be the **(Annexure-1)**

3.4 *Some Lower Region vibrational Modes*

The study of low frequency vibrations is of great significance because it provides the information for weak intermolecular interactions, which occurs in enzyme reactions [14]. Study of low frequency modes is also useful for the interpretation of the effect of electromagnetic radiation on biological systems [15]. In present study, the important calculated lower order modes are obtained at frequencies 674 (ring-breathing), 627(torsion and wagging) and 584 cm^{-1} (torsion) with IR intensities equal to 10, 31 and 61 respectively.

4. CONCLUSION

This paper reports a comprehensive theoretical quantum chemical study on 2-Arsanyl-Pyridine. The molecular geometry, vibrational wavenumbers, infrared intensities, electronic and thermodynamic properties of the title molecule have been calculated using DFT (B3LYP) method adopting at 6-31+g(d,p) basis set. Normal modes analysis provides detailed description of the vibrational spectra of the molecules in question. A good agreement between experimental and calculated normal modes of vibrations is achieved. The aim of this paper is to obtain direct information on lower and higher frequency vibrations of such biological molecule. In the absence of experimental vibrational spectra of the title compound, the theoretically calculated spectra should provide an important path for experimentalists. All the measurements were made for the gas phase.

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(Annexure-1)

Table-3: Frequency assignments for 2-Arsanyl-Pyridine at B3LYP/6-31+g(d,p) method in cm-1, with PED % in Square Brackets [PED]

S. No.	Calculated Freq		IR Freq	Assignment Modes [PED]
	Unscaled	Scaled	Intensity	
1	3683	3528	47.23	ν(N4-H10)[100]
2	3242	3106	3.38	ν(C1-H7)[30] + ν(C2-H8)[30] + ν(C3-H9)[26]
3	3229	3093	10.17	ν(C1-H7)[32] + ν(C2-H8)[30] + ν(C3-H9)[25]
4	3203	3068	11.67	ν(C1-H7)[36] + ν(C2-H8)[26]+ ν(C3-H9)[20]+ν(C5-H12)[10]
5	3196	3062	8.9	ν(C1-H7)[12] + ν(C2-H8)[30]+ν(C5-H12)[12]
6	2528	2422	0.23	ν(As11-H14)$_{asym}$[14] + ν$_{sym}$(As11-H13)[86]
7	2477	2373	2.22	ν(As11-H14)[86] + νsym(As11-H13)[14]
8	1641	1572	48.39	R$_{defor}$ [51]
9	1564	1498	16.16	ν(C2-C3)[19] + ν(C1-C6)[19] + Φ(H10-N4-C5)[32]
10	1476	1414	25.29	ν(C5-C6)[11] + Φ(H10-N4-C5)[46] + Φ(H8-C2-C1)[13]
11	1428	1368	1.91	Φ(H12-C6-C5)[35] + Φ(H8-C2-C3)[26] + Φ(H7-C1-C6)[10]
12	1355	1298	42.7	R$_{deform}$ [76]
13	1326	1270	19.15	Φ(H12-C6-C5)[30] + Φ(H12-C6-C1)[28]
14	1218	1167	1.43	ν(N4-C3)[11] + Φ(H9-C3-N4)[26]
15	1122	1075	31.21	ν(N4-C3)[11] + Φ(H9-C3-N4)[40]
16	1079	1034	0.08	ν(C1-C6)a[32] +Φ(C2-C3-N4)[32] + Φ(H7-C1-C6)[11]+Φa(C3-N4-C5)[10]
17	1017	974	19.1	ν(C1-C2)[18] +ν(N4-C3)[24] +Φ(N4-C3-C2)[15]+ Φ(C1-C2-C3)[14]
18	1006	964	20.12	ν(C1-C2)[22] +ν(N4-C3)[24] +Φ(C6-C5-N4)[14]
19	983	942	9.86	R$_{puck}$[47] + Φ(H14-As11-H13)[16]
20	920	881	1.09	τ(H9-C2-C3-H8)[66] + τ(H7-C1-C2-H8)[19]
21	911	873	53.65	Boat(As11-C5-C6-H12)[95]
22	901	863	4.5	τ(As11-C5-C6-H12)[85]
23	704	674	10.2	R$_{breath-in-plane}$[83]
24	690	661	0.38	τ(H7-C1-C2-C3)[38] + τ(H8-C2-C3-N4)[11] + ω(As11-N4-C6-C5)[30]
25	655	627	31.45	τ(H7-C1-C2-C3)[22] + τ(H8-C2-C3-C6)[49]
26	610	584	61.03	τ(H7-C1-C6-C5)[71] + τ(H8-C2-C1-C6)[12]
27	590	565	3.63	R$_{deform}$ [73]
28	569	545	16.46	τ(H7-C1-C6-C5)[15]+τ(H9-C3-C2-C1)[16]
29	561	537	14.04	Φ(H14-As11-H13)[86]
30	322	308	0.27	ν(As11-C5)$_{sym}$[59] + Φ(C2-C3-N4)[21]
31	285	273	0.4	R$_{out-of-plane-bending}$[84]
32	211	202	0.91	R$_{rock}$[86]
33	135	129	0.02	Rout-of-plane-bending[79]

Abbreviations: R-ring; deform: deformation; rock: rocking; puck: puckering