Ab Initio Hartree-Fock and Density Functional Theory Study on Molecular Structures, Energies, and Vibrational Frequencies of 2-Amino-3-, 4-, and 5-Nitropyridine

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The molecular structures, vibrational frequencies, and corresponding vibrational assignments of 2-amino-3-, 4-, and 5-nitropyridine have been calculated by using ab initio Hartree-Fock (HF) and density functional theory (B3LYP) methods with 6-311++G(d,p) basis set level. The calculated vibrational frequencies and optimized geometric parameters (bond lengths and bond angles) were found to be in well agreement with the experimental data. The comparison of the observed and the calculated results showed that the scaled B3LYP method is superior to the scaled HF method for both the vibrational frequencies and the geometric parameters. For well fitting the calculated and the experimental frequencies we used scale factors obtained from the ratio of the frequency values of the strongest peaks in the calculated and the experimental spectra. These obtained scales seem to cause the better agreement of the gained vibrations to the experimental data.

Key words: Amino Nitropyridine; Vibrations; IR Spectra; Raman Spectra; HF; DFT.

1. Introduction

Studying vibrational spectra of substituted pyridines, mainly amino pyridine, has attracted the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. Amino pyridines serve as good anesthetic agents. Hence, they are used to prepare drugs for certain brain disease [1]. 2-amino-4-nitropyridine is of interest because its compounds with other chemicals may exhibit valuable physical properties, e. g. ferroelectricity and second harmonic generation. Oszust et al. have analysed the structural and vibrational properties of the 2-amino-4-nitropyridine crystal [2]. 2-amino-5-nitropyridine is a necessary raw material for preparing azo-compounds, which are widely used as colouring matter. It has a nitro group as an electron donor and an amino group as an electron acceptor while the pyridine ring acts as a cationic bonding site. Because of this molecular characteristic it has been commonly used as molecular building block of nonlinear optical materials. In order to improve the process of chemical synthesis of 2-amino-5-nitropyridine molecules, some of the thermodynamic properties have been studied in detail [3].

In this paper we have calculated the optimized structures, energies, and vibrational spectra of all the title molecules using ab initio Hartree-Fock (HF) and density functional theory (B3LYP) methods with a 6-311++G(d,p) basis set, and compared the calculated results with the experimental data.

2. Computational Method

The optimized molecular structure, energies, and vibrational frequencies of the molecules have been calculated by using HF and B3LYP methods at 6-311++G(d,p) basis set level. All the computations were performed by using a Gauss-View molecular visualization program [4] and Gaussian 03 package on the personal computer [5]. The scale factors of 0.9051 and 0.9614 were used for HF and B3LYP with 6-311++G (d,p) basis set, respectively [6].

3. Results and Discussion

The chemical formula of 2-amino-3-, 4-, and 5-nitropyridine molecules is $C_5H_5N_3O_2$ and therefore they have 39 normal modes of vibration. All the vibrations are active both in infrared (IR) and Raman (R)

Table 1. Experimental and calculated vibrational frequencies of 2-amino-3-nitropyridine. ν shows stretching, δ bending, γ out of plane bending, and ρ_r rocking modes.

Assignments	Experimental [8] Freq. (cm^{-1})		Calculated Freq. (cm^{-1}) [6-311++G(d,p)]					
			HF			B3LYP		
	IR	R	Freq.	IR inten. (km/mol)	R activity (Å^4/amu)	Freq.	IR inten. (km/mol)	R activity (Å^4/amu)
$\nu(NH^2)$			3607	126	23	3575	106	36
$\nu(NH_2)$	3442		3475	117	131	3438	89	186
$\nu(CH)$	3095		3073	3	75	3098	4	98
$\nu(CH)$	3075	3080	3051	3	99	3082	3	112
$\nu(CH)$	3025	3000	3009	20	101	3029	17	134
$\nu(ring)+\delta(NH_2)+\delta(CH)+(CN)$	1590	1580	1649	958	12	1592	506	19
$\nu(ring)+\delta(CH)+\nu(NO)+(NH_2)$	1560	1560	1612	106	23	1549	109	13
$\nu(NO_2)+\nu(ring)+\delta(CH)+\delta(NH_2)$	1520		1591	285	30	1534	83	27
$\nu(ring)+\nu(NO_2)+\delta(NH)+\delta(CH)$	1480	1480	1563	100	12	1493	159	17
$\delta(CH)+\delta(NH)+\nu(ring)$	1420	1440	1463	422	69	1420	43	4
$\delta(NH_2)+\delta(CH)+\nu(ring)+\nu(NO_2)$		1400	1451	58	3	1414	105	7
$\delta(CH)+\nu(CN)+\delta(NH_2)+\nu(NO_2)$	1330	1330	1414	128	120	1326	49	6
$\delta(CH)+\delta(NO_2)+\nu(CN)+\nu(ring)$	1300		1331	6	26	1306	149	128
$\delta(CH)+\delta(CN)+\delta(NO_2)+\nu(ring)$	1250	1260	1274	13	1	1249	16	20
$\nu(ring)+\delta(CH)+\delta(CN)+\delta(NH)+\nu(CN)$	1230	1230	1178	164	15	1235	338	93
$\delta(CH)+\nu(CN)+\nu(NO)$	1120	1170	1138	16	21	1128	9	8
$\delta(CH)+\rho_r(NH_2)+\nu(CN)+\delta(ring)$	1060	1076	1086	99	30	1063	48	23
$\delta(CH)+\nu(ring)+r_r(NH_2)+\nu(CC)$		1040	1068	14	24	1054	10	32
$\rho_r(NH_2)+\delta(CH)+\nu(ring)$	1010	990	1015	∼ 0	∼ 0	969	2	2
$\gamma(CH)$	966	920	1007	∼ 0	∼ 0	955	1	∼ 0
$\gamma(CH)$			982	35	12	953	1	∼ 0
$\delta(ring)+\nu(CN)+\delta(NO_2)$	900		899	40	1	878	17	2
$\delta(NO_2)+\nu(ring)+\nu(CN)$	808		844	18	27	811	15	39
$\gamma(CH)$	760	800	786	26	2	765	32	1
$\gamma(CN)+\gamma(ring)$	721	680	750	9	∼ 0	722	11	∼ 0
$\gamma(ring)+\gamma(CH)+\gamma(NO_2)$			735	54	1	688	12	∼ 0
$\tau(ring)+\delta(NO)$	665		669	9	6	661	3	5
twist(NH_2)	610	580	585	3	∼ 0	617	6	∼ 0
$\delta(ring)+\nu(CN)$	565		567	1	9	560	1	12
$\rho_r(NO_2)+\rho_r(NH_2)+\rho_r(ring)$	523	520	537	14	1	525	8	3
$\gamma(CH)+\gamma(ring)$	520		529	12	∼ 0	520	7	∼ 0
$\gamma(ring)+\gamma(CH)$		420	414	6	∼ 0	409	16	∼ 0
$\rho_r(NH_2)+\delta(NO)$		380	405	5	3	393	4	7
$\rho_r(NH_2)$			381	3	2	374	3	3
$\rho_r(NH_2)$ out of plane		270	279	5	1	310	194	∼ 0
$\rho_r(NO_2)+\rho_r(NH_2)+\rho_r$ (ring)			269	249	∼ 0	278	5	1
$\rho_r(NH_2)$ out of plane+ρ_r(ring) out of plane		165	230	1	1	225	2	1
ρ_r(ring) out of plane+(NH_2)			120	∼ 0	1	113	∼ 0	1
twist$(NO_2)+\rho_r$(ring) out of plane			51	3	∼ 0	64	2	∼ 0

spectra. For an N-atomic molecule 2N-3 of all vibrations are in plane and N-3 are out of plane [7]. Thus, for the title molecules, 27 of all possible 39 vibrations are in plane and 12 are out of plane. This has been checked by the visual inspection of the vibrations using a Gauss-View visualization program.

The experimental IR and R spectra of 2-amino-3- and 5-nitropyridine have been obtained from the web page of Sigma-Aldrich cooperation [8] and that of 2-amino-4-nitropyridine from [2]. The symmetries of the title molecules belong to the C_1 group instead of the Cs group because the two H atoms of the NH_2 group are slightly out of the molecular plane. The experimental and the calculated vibrational frequencies for all title molecules are given in Table 1 – 3. The tables also report the theoretical infrared intensities and the Raman activities. As seen from the tables the calculated vibrational frequencies are in good agreement with the experimental values.

Table 4 shows the calculated optimized structure parameters (bond lengths and bond angles). In this table are also given the experimental parameters ob-

Table 2. Experimental and calculated vibrational frequencies of 2-amino-4-nitropyridine. ν shows stretching, δ bending, γ out of plane bending, and ρ_r rocking modes.

Assignments	Experimental [2] Freq. (cm^{-1})		Calculated Freq. (cm^{-1}) [6-311++G(d,p)] HF			B3LYP		
	IR	R	Freq.	IR inten. (km/mol)	R activity (Å^4/amu)	Freq.	IR inten. (km/mol)	R activity (Å^4/amu)
$\nu(\mathrm{NH_2})$	3566		3553	47	41	3568	42	50
$\nu(\mathrm{NH_2})$	3442	3444	3448	71	141	3453	71	201
ν(CH)		3122	3089	6	65	3116	6	75
ν(CH)	3092	3076	3074	6	50	3094	5	57
ν(CH)	3030	3031	3023	17	100	3041	16	126
ν(ring)+$\delta(\mathrm{NH_2})$+δ(CH)+δ(CN)+ (CN)	1594	1586	1666	117	5	1600	190	13
$\delta(\mathrm{NH_2})$+ν(CC)+ ν(CN)	1573	1573	1627	754	23	1574	136	3
$\nu(\mathrm{NO_2})$+ν(ring)+δ(CH)+δ(NH)			1611	35	4	1549	113	12
ν(ring)+$\nu(\mathrm{NO_2})$+δ(CH)+δ(CN)	1524	1522	1599	266	6	1529	331	14
δ(CH)+ν(ring)+δ(NH)	1442	1452	1497	33	25	1449	6	6
ν(CN)+δ(NH)+δ(CH)+ν(ring)	1386	1384	1477	244	34	1402	113	5
ν(CN)+$\delta(\mathrm{NO_2})$+δ(CH)	1320	1337	1422	131	4	1326	214	89
δ(CH)+δ(CN)+δ(NH)+ν(CN)	1287	1289	1314	~ 0	5	1298	8	11
ν(ring)+$\rho_r(\mathrm{NH_2})$+δ(CH)	1276	1275	1276	34	13	1266	33	6
δ(CH)+ν(CN)		1229	1154	85	8	1249	26	13
$\rho_r(\mathrm{NH_2})$+δ(CH)+ν(CN)	1094	1099	1121	4	8	1093	~ 0	9
δ(CH)+ν(CC)+ν(CN)	1059	1069	1096	8	9	1060	21	18
$\rho_r(\mathrm{NH_2})$+δ(CH)+ν(CN)	996	991	1015	30	13	1011	5	~ 0
δ(ring)+ν(CN)	964		1001	~ 0	1	966	8	17
γ(CH)	952	955	978	18	22	949	~ 0	~ 0
ν(CN)+δ(CH)+$\delta(\mathrm{NO_2})$+ν(ring)	935	937	940	1	2	913	~ 0	12
γ(CH)+γ(ring)	877	875	888	35	~ 0	849	26	~ 0
$\delta(\mathrm{NO_2})$+ν(CN)+δ(ring)			844	58	13	814	40	17
γ(CH)	830	830	833	15	1	803	15	~ 0
γ(ring)+γ(CH)+$\gamma(\mathrm{NO_2})$			752	42	2	721	11	1
$\gamma(\mathrm{NO_2})$+γ(CH)+γ(ring)	737	737	731	7	~ 0	699	13	~ 0
δ(ring)+δ(CH)+δ(NO$_2$	692	693	691	23	4	678	14	3
τ(ring)+$\nu(\mathrm{NH_2})$		572	572	18	2	558	2	7
γ(CH)+γ(ring)+twist(NH$_2$)	549	561	563	2	4	546	2	~ 0
$\rho_r(\mathrm{NH_2})$+ρ_r(ring)+$\rho_r(\mathrm{NO_2})$			527	12	2	517	4	3
twist(NH$_2$)	435		474	254	2	442	61	~ 0
γ(NH)+γ(CH)+γ(ring)	412	421	435	38	~ 0	416	60	~ 0
$\rho_r(\mathrm{NH_2})$	383	389	397	1	1	388	12	1
$\rho_r(\mathrm{NH_2})$+δ(NO)+δ(CH)			369	5	6	359	9	5
γ(CH)			351	60	~ 0	341	182	1
$\rho_r(\mathrm{NO_2})$+$\rho_r(\mathrm{NH_2})$+ρ_r(ring)	213	250	215	1	1	208	1	1
γ(CH)+$\rho_r(\mathrm{NH_2})$ out of plane+γ(ring)	190	190	211	12	1	198	9	1
ρ_r(ring) out of plane+γ(NH)			164	4	1	156	3	1
twist(NH$_2$)+ρ_r(ring) out of plane+$\rho_r(\mathrm{NH_2})$ out of plane			26	~ 0	~ 0	38	~ 0	~ 0

tained by the X-ray structure analysis of 2-amino-4-nitropyridine in [2]. For all the mentioned molecules the correlation factors between the experimental and the calculated data at both levels are listed in Table 5. From the correlation values in Table 5 we can say that the calculated vibrational frequencies and the optimized geometric parameters (bond lengths and bond angles) correspond well with the experimental values. The comparison of the calculated and the experimental data at HF and B3LYP level shows that the scaled B3LYP method is superior to the scaled HF method for both the vibrational frequencies and the geometric parameters. The largest differences between calculated geometries and experimental ones are: 0.184 Å (HF) compared with 0.198 Å (B3LYP) for the bond lengths and 3.30° (HF) compared with 3.28° (B3LYP) for the bond angles.

The sum of electronic and zero-point energies of all title molecules at HF and B3LYP 6-311++G(d,p) level are given in Table 6. As seen from the table the energy values of the molecules are very close to each other but those calculated at B3LYP level are lower.

Table 3. Experimental and calculated vibrational frequencies of 2-amino-5-nitropyridine. ν shows stretching, δ bending, γ out of plane bending, and ρ_r rocking modes.

Assignments	Experimental [8] Freq. (cm^{-1})		Calculated Freq. (cm^{-1}) [6-311++G(d,p)]					
			HF			B3LYP		
	IR	R	Freq.	IR inten. (km/mol)	R activity (Å^4/amu)	Freq.	IR inten. (km/mol)	R activity (Å^4/amu)
$\nu(\mathrm{NH_2})$	3585		3578	60	46	3589	54	61
$\nu(\mathrm{NH_2})$	3460	3460	3462	117	179	3466	129	297
$\nu(\mathrm{CH})$	3086		3068	2	64	3095	3	70
$\nu(\mathrm{CH})$	3071		3061	1	59	3074	1	67
$\nu(\mathrm{CH})$	3057	3060	3033	5	77	3059	7	96
$\nu(\mathrm{ring})+\delta(\mathrm{NH_2})+\delta(\mathrm{CH})$	1580	1580	1643	670	10	1588	566	51
$\nu(\mathrm{ring})+\delta(\mathrm{NH_2})+\delta(\mathrm{CH})$			1624	515	70	1565	23	23
$\rho_\mathrm{r}(\mathrm{NH_2})+\nu(\mathrm{ring})+\delta(\mathrm{CH})+\nu(\mathrm{NO_2})$	1560	1560	1607	65	54	1558	167	15
$\nu(\mathrm{ring})+\delta(\mathrm{NH})+\nu(\mathrm{NO_2})+\delta(\mathrm{CH})$	1503		1569	48	6	1498	141	16
$\delta(\mathrm{CH})+\nu(\mathrm{ring})+\delta(\mathrm{NH_2})$	1460	1450	1494	12	56	1456	61	38
$\nu(\mathrm{ring})+\delta(\mathrm{CH})+\delta(\mathrm{NH})+\nu(\mathrm{CN})$	1380	1380	1449	620	243	1390	61	4
$\delta(\mathrm{CH})+\nu(\mathrm{CN})+\nu(\mathrm{NO_2})$			1406	325	39	1309	193	197
$\nu(\mathrm{CN})+\delta(\mathrm{CH})+\nu(\mathrm{NO_2})+\nu(\mathrm{ring})$	1305	1306	1318	29	13	1307	387	211
$\nu(\mathrm{ring})+\delta(\mathrm{CH})+\rho_\mathrm{r}(\mathrm{NH_2})+\nu(\mathrm{NO})$	1290	1280	1301	77	6	1284	59	88
$\delta(\mathrm{CH})+\nu(\mathrm{NO})$	1264		1206	12	25	1271	142	58
$\delta(\mathrm{CH})$		1120	1150	36	66	1129	8	21
$\delta(\mathrm{CH})+\nu(\mathrm{CN})+\rho_\mathrm{r}(\mathrm{NH_2})$	1082		1107	100	13	1092	123	39
$\rho_\mathrm{r}(\mathrm{NH_2})+\delta(\mathrm{CH})$	1001	1000	1037	11	5	1002	4	3
$\delta(\mathrm{ring})+\delta(\mathrm{CH})+\rho_\mathrm{r}(\mathrm{NH_2})$	984		1010	~ 0	~ 0	984	7	1
$\gamma(\mathrm{CH})$	958	960	998	7	1	955	1	~ 0
$\gamma(\mathrm{CH})$	921	940	994	3	1	938	5	1
breathing(molecule)$+\delta(\mathrm{NO_2})$	854	840	877	30	25	848	15	48
$\delta(\mathrm{NO_2})+\nu(\mathrm{CN})+\delta(\mathrm{ring})+\delta(\mathrm{CH})$	825		832	18	8	812	10	~ 0
$\gamma(\mathrm{CH})$			827	34	3	802	32	~ 0
$\gamma(\mathrm{CH})+\gamma(\mathrm{ring})$	725		754	27	2	728	4	1
$\gamma(\mathrm{NO_2})+\gamma(\mathrm{CH})$	683		738	7	~ 0	693	10	1
$\gamma(\mathrm{C\text{-}NH_2})+\delta(\mathrm{ring})+\delta(\mathrm{CH})+\delta(\mathrm{NO_2})$	641		645	20	~ 0	634	12	3
$\tau(\mathrm{ring})+\rho_\mathrm{r}(\mathrm{NH_2})$			631	1	5	625	~ 0	5
$\rho_\mathrm{r}(\mathrm{NH_2})+\rho_\mathrm{r}(\mathrm{NO_2})+\rho_\mathrm{r}(\mathrm{ring})$	543		529	14	1	517	7	3
twist$(\mathrm{NH_2})+\gamma(\mathrm{CH})+\gamma(\mathrm{ring})$	508	507	501	5	~ 0	503	2	~ 0
twist$(\mathrm{NH_2})+\gamma(\mathrm{CH})$	458	460	450	48	~ 0	454	28	~ 0
$\gamma(\mathrm{ring})+$twist$(\mathrm{NH_2})$			415	1	~ 0	408	2	~ 0
$\rho_\mathrm{r}(\mathrm{NH_2})+\rho_\mathrm{r}(\mathrm{NO_2})+\rho_\mathrm{r}(\mathrm{ring})$			395	6	~ 0	386	5	~ 0
$\nu(\mathrm{C\text{-}NO_2})+\nu(\mathrm{C\text{-}NH_2})+\delta(\mathrm{ring})$			361	4	2	353	~ 0	2
$\gamma(\mathrm{CH})+\gamma(\mathrm{ring})+\rho_\mathrm{r}(\mathrm{NH_2})$ out of plane			281	244	8	258	5	~ 0
$\rho_\mathrm{r}(\mathrm{NH_2})+\rho_\mathrm{r}(\mathrm{NO_2})+\rho_\mathrm{r}(\mathrm{ring})$			265	89	3	213	1	1
$\rho_\mathrm{r}(\mathrm{NH_2})$ out of plane			220	2	1	198	257	6
$\rho_\mathrm{r}(\mathrm{NH_2})$ out of plane$+\rho_\mathrm{r}$ (ring) out of plane		110	107	~ 0	1	99	~ 0	1
twist$(\mathrm{NO_2})+$twist(ring)			62	1	~ 0	58	1	~ 0

The relative energy value between 2-amino-3-nitropyridine and 2-amino-4-nitropyridine is 3.7 kcal/mol (HF) and 3.9 kcal/mol (DFT), respectively, while it is 0.93 kcal/mol (HF) and 0.96 kcal/mol (DFT) between 2-amino-3-nitropyridine and 2-amino-5-nitropyridine.

For well fitting the calculated to the experimental frequencies we have also used the scale factors obtained from the ratio of the frequency values of the strongest peaks in the calculated and the experimental IR spectra. These frequencies in the experimental spectra are 1590 cm^{-1} for 2-amino-3-nitropyridine, 1594 cm^{-1} for 2-amino-4-nitropyridine, and 1580 cm^{-1} for 2-amino-3-nitropyridine and those in the calculated spectra are non-scale frequency values corresponding to these experimental frequencies (see Table 1 – 3). So, the obtained scale factors are 0.8726 (HF) and 0.9601 (B3LYP) for 2-amino-3-nitropyridine, 0.8658 (HF) and 0.9579 (B3LYP) for 2-amino-4-nitropyridine, and 0.8705 (HF) and 0.9564 (B3LYP) for 2-amino-5-nitropyridine. These values are very close to the scale factors (0.9051 for HF and 0.9614 for B3LYP) at the same level of the theory

Table 4. Experimental and calculated optimized structure parameters of all title molecules.

Parameters	Experimental [2]	Calculated					
		2-amino-3-nitropyridine		2-amino-4-nitropyridine		2-amino-5-nitropyridine	
		HF	B3LYP	HF	B3LYP	HF	B3LYP
Bond lengths (Å)							
N(1)-C(2)	1.333	1.336	1.352	1.316	1.340	1.324	1.345
N(1)-C(6)	1.323	1.307	1.323	1.322	1.335	1.316	1.328
C(2)-C(3)	1.400	1.413	1.426	1.404	1.411	1.410	1.416
C(2)-N(13)	1.335	1.339	1.347	1.370	1.373	1.355	1.361
C(3)-C(4)	1.401	1.389	1.396	1.365	1.379	1.365	1.376
C(3)-N(10)	1.473	1.444	1.453				
C(4)-C(5)	1.369	1.372	1.381	1.384	1.391	1.394	1.398
C(4)-H(9)	1.000	1.072	1.082				
C(5)-C(6)	1.358	1.392	1.401	1.378	1.390	1.379	1.393
C(5)-H(8)	1.000	1.072	1.082	1.070	1.079		
C(6)-H(7)	0.990	1.077	1.087	1.076	1.086	1.073	1.084
N(10)-O(11)	1.219	1.188	1.226	1.185	1.222	1.189	1.228
N(10)-O(12)	1.206	1.196	1.238	1.186	1.223	1.190	1.229
N(13)-H(14)	0.810	0.990	1.008	0.994	1.007	0.992	1.005
N(13)-H(15)	0.930	0.992	1.007	0.995	1.008	0.994	1.008
C(3)-H(9)	1.000			1.071	1.081	1.074	1.084
C(4)-N(10)	1.473			1.476	1.489		
C(4)-H(8)	1.000					1.072	1.082
C(5)-N(10)	1.473					1.445	1.457
Bond angles (°)							
C(2)-N(1)-C(6)	117.9	120.0	118.0	118.9	118.2	118.3	118.0
N(1)-C(2)-C(3)	121.7	121.2	120.0	122.3	122.3	122.5	121.7
N(1)-C(2)-N(13)	116.8	117.0	116.0	117.2	116.6	116.4	116.5
C(3)-C(2)-N(13)	121.4	123.6	121.0	120.4	121.2	121.0	121.4
C(2)-C(3)-C(4)	116.9	120.0	117.0	116.6	116.9	119.0	118.0
C(2)-C(3)-N(10)	121.3	122.7	122.6				
C(4)-C(3)-N(10)	121.8	118.0	118.0				
C(3)-C(4)-C(5)	123.0	122.0	120.0	122.3	122.1	120.0	122.0
C(3)-C(4)-H(9)	118.4	119.0	118.3				
C(5)-C(4)-H(9)	118.5	122.0	119.0				
C(4)-C(5)-C(6)	115.6	116.5	116.0	115.4	115.7	117.0	119.0
C(4)-C(5)-H(8)	122.0	122.0	122.0	122.1	122.0		
C(6)-C(5)-H(8)	122.0	121.3	121.0	122.4	122.0		
N(1)-C(6)-C(5)	124.8	124.6	124.0	124.5	124.5	123.0	123.0
N(1)-C(6)-H(7)	112.5	116.0	113.0	113.0	114.0	115.0	113.0
C(5)-C(6)-H(7)	122.7	122.0	121.2	120.1	120.1	121.0	121.0
C(3)-N(10)-O(11)	118.3	118.0	118.5				
C(3)-N(10)-O(12)	118.0	118.4	118.3				
O(11)-N(10)-N(12)	123.7	123.6	123.2	125.0	125.0	123.0	124.0
C(2)-N(13)-H(14)	119.0	120.0	120.2	118.1	119.0	119.7	121.0
C(2)-N(13)-H(15)	121.0	118.0	119.3	118.0	118.5	118.2	118.0
H(14)-N(13)-H(15)	118.0	119.0	118.0	116.0	117.0	118.0	118.0
C(2)-C(3)-H(9)	121.3			121.8	122.3	120.5	121.0
C(4)-C(3)-H(9)	121.8			121.4	120.5	121.2	121.0
C(3)-C(4)-N(10)	118.4			118.5	118.5		
C(5)-C(4)-N(10)	118.5			119.0	119.3		
C(4)-N(10)-O(11)	118.0			117.2	117.4		
C(4)-N(10)-O(12)	118.3			117.5	117.6		
C(3)-C(4)-H(8)	121.8					121.5	121.8
C(5)-C(4)-H(8)	122.7					120.1	120.0
C(4)-C(5)-N(10)	121.3					119.0	120.2
C(6)-C(5)-N(10)	121.8					120.3	120.2
C(5)-N(10)-O(11)	118.0					117.0	118.0
C(5)-N(10)-O(12)	118.3					117.5	118.0

Table 5. Correlation factors between experimental and calculated values for all title molecules.

Molecule	Frequencies		Bond lengths		Bond angles	
	HF	B3LYP	HF	B3LYP	HF	B3LYP
2-amino-3-nitropyridine	0.9984	0.9998	0.9667	0.9763	0.7144	0.8853
2-amino-4-nitropyridine	0.9989	0.9998	0.9557	0.9709	0.8732	0.8797
2-amino-5-nitropyridine	0.9938	0.9999	0.9608	0.9755	0.7780	0.7803

Table 6. Sum of electronic and zero-point energies calculated at 6-311++G(d,p) level for all title molecules (hartree/particle).

Molecule	HF	B3LYP
2-amino-3-nitropyridine	−505.226478	−508.197743
2-amino-4-nitropyridine	−505.220563	−508.191507
2-amino-5-nitropyridine	−505.227975	−508.196214

Table 7. % Error between experimental and calculated frequencies.

Molecule	% Error HF [6–311++G(d,p)]		% Error B3LYP [6–311++G(d,p)]	
	Our scale	Ref's scale (0.9051)	Our scale	Ref's scale (0.9614)
2-amino-3-nitropyridine	0.1999	0.2287	0.2155	0.2166
2-amino-4-nitropyridine	0.1857	0.2210	0.2045	0.2075
2-amino-5-nitropyridine	0.1459	0.1786	0.1595	0.1640

given in [6]. If we compare our and the reference's scale by means of the % error between the experimental and calculated vibrational frequency values, defined by

$$\%\ \text{error} = \frac{\text{calculated}\ (\varpi_i) - \text{experimental}\ (\varpi_i)}{\text{calculated}\ (\varpi_i)},$$

where ϖ_i are the calculated and experimental frequencies of mode i. We find that the % errors for our scales are lower than those for the reference's scales. All the % error values are given in Table 7. Thus, we can say that our scales for the title molecules are more reasonable than those of the literature. This comment has also been given for the vibrational analysis of xanthine and its methyl derivatives in our previous study [9].

4. Conclusion

The vibrational frequencies, optimized molecular structures, and corresponding vibrational assignments of 2-amino-3-, 4-, and 5-nitropyridine have been calculated using HF and B3LYP methods at 6-311++G(d,p) basis set level. The comparison of the calculated and the experimental results indicates that the B3LYP method is superior to the HF method for both the vibrational frequencies and the geometric parameters. The scale factors obtained from the ratio of the frequency values of the strongest peak in the calculated and the experimental spectra seem to cause the better agreement of the gained vibrations with the experimental data.

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