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Vibrational Spectroscopy



Elixir Vib. Spec. 87 (2015) 35674-35681

Vibrational Spectroscopic (FT-IR and FT-RAMAN) Investigation Using *AB INITIO* (HF) and DFT (B3LYP) Analysis on the Structure of 2,4-Dihydroxy-3-Nitropyridine

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ARTICLE INFO

Article history: Received: 30 September 2015; Received in revised form: 03 October 2015; Accepted: 08 October 2015;

Keywords DHNP, FT-IR, FT- Raman, HOMO-LUMO.

ABSTRACT

The FT-IR and FT Raman spectra of 2,4-dihydroxy-3-nitropyridine (DHNP) molecule have been recorded in the region 4000-400cm⁻¹ and 3500-50cm⁻¹ respectively. Optimized geometrical parameters, harmonic vibrational frequencies and depolarization ratio have been computed by HF and density functional theory (DFT) using B3LYP/6-311++G(d,p) method and basis sets. The observed FT-IR and FT-Raman vibrational frequencies are analysed and compared with theoretically predicted vibrational frequencies. The calculated HOMO and LUMO energies shows that charge transfer occur within molecule. Unambiguous vibrational assignments of all the fundamentals was made using the total energy distribution (TED).

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Introduction

The pyridine derivatives have an important position among the heterocylic compounds because they can be used as nonlinear materials and photochemicals [1-2]. The study of the vibrational spectra of substituted pyridine mainly nitro pyridine attracts the attention of many spectroscopists due to their wide application in pharmacology and agro-chemistry. Pyridine heterocycles are a repeated moiety in many large molecules with interesting photo physical, electrochemical and catalytic applications [3-10]. They serve as good anesthetic agent and hence they are used in the preparation of drugs for certain brain disease. These pharmaceutically acceptable salts and the predrugs are used for the treatment (or) prevention of diabetic neuropathy [11-12]. The pharmaceutical development of nitro pyridine derivatives has received considerable attention, since they have been fully employed as chiral nucleophilic catalysts in a wide range of asymmetric synthetic process [13]. The vibrational spectra of substituted pyridine have been the subject of several investigations [14-16]. More recently [17-18], FTIR and FT Raman spectra of nitro pyridine have been reported together with the vibrational assignments of the normal modes. HF/B3LYP detailed at 6-311++G(d,p)However. the comparative studies on the complete FT-IR and FT-Raman spectra of 2,4-dihydroxy-3-nitropyridine (DHNP) have not been reported so far. In this study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performance of the computational methods for ab initio (HF), hybrid density functional theory (B3LYP) at 6-311++G(d,p) basis sets are compared. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional ab initio Hartree-Fock calculations. In DFT

methods, Becke's three parameter exact exchange-functional (B3) [19] combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) [20-21] are the best predicting results for molecular geometry and vibrational wavenumbers for moderately larger molecule [22-24]. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, Raman activity, atomic charges, dipole moment, force constants, depolarization ratio and other thermodynamic parameters and Energy gap through HOMO and LUMO energy, are calculated using the Gaussian 09W packages.

Experimental Details

The compound under investigation namely 2,4-dihydroxy-3-nitropyridine (DHNP) was purchased from Lancaster Chemical Company (U.K.) and used as such for recording the spectra without any further purification. The FT-IR spectrum of DHNP in the region 4000-400 cm⁻¹ has been recorded with a BRUKER IFS 66V spectrophotometer using KBr pellet. The FT-Raman spectrum of the title compound was recorded in the region 3500-50 cm⁻¹ with a BRUKER RFS 100/s 66V spectrophotometer using KBr pellet technique. Raman module equipped with Nd:YAG laser source operating at 1064 nm line width 150 mw power. The spectra were recorded with a scanning speed of 50 cm⁻¹ min⁻¹ of spectral width 4 cm⁻¹. The reported wave numbers are believed to be accurate within ± 1 cm⁻¹.

Computational Details

Quantum chemical density functional theory calculations were carried out using the 2009 version of the Gaussian program package [25] with HF and B3LYP methods combined with the standard 6-311++G(d,p) basis set. The cartesian representation of the theoretical force constants has been computed at the optimized geometry by assuming C_1 point group symmetry.

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6-311++G(D,P) Basis Set								
Bond	Bond Value (Å)		Bond	Value (•)		Dihedral	Value (•)	
Length	HF/ 6- 311++G(d,p)	B3LYP/ 6-311++G(d,p)	Angle	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)	Angle	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
N1-C2	1.3044	1.3212	N1-C2-C3	121.836	121.955	C6-N1- C2-C3	0.0066	0.003
C2-C3	1.427	1.4371	C2-C3-C4	118.524	118.623	C6-N1- C2-O7	180.0027	-179.997
C3-C4	1.4131	1.4263	C3-C4-C5	117.671	117.539	C2-N1- C6-C5	-0.0038	-0.0066
C4-C5	1.3887	1.3946	C4-C5-C6	118.094	118.473	C2-N1- C6-H15	179.9973	179.9997
C5-C6	1.3712	1.384	C5-C6-N1	125.272	125.194	N1-C2- C3-C4	-0.0022	0.0081
C6-N1	1.3231	1.3371	C6-N1-C2	118.602	118.2146	N1-C2- C3-N9	-179.996	179.9851
C2-O7	1.3082	1.3262	N1-C2-O7	114.864	118.2146	N7-C2- C3-C4	-179.998	-179.992
O7-H8	0.9469	0.9805	С2-О7-Н8	111.481	115.6523	N7-C2- C3-O9	0.0085	-0.0149
C3-N9	1.4322	1.4269	C3-C2-O7	123.300	122.392	N1-C2- 07-H8	179.9251	179.9548
C4-O12	1.3101	1.328	C2-C3-O9	121.133	121.117	C3-C2- N7-H8	-0.0789	-0.0452
O12- H13	0.9484	0.9825	C4-C3-N9	120.343	120.259	C2-C3- C4-C5	-0.0051	-0.0157
C5-H14	1.0716	1.0813	C3-C4-O12	125.217	123.977	C2-C3- C4-O12	-180.007	179.9856
C6-H15	1.0762	1.0861	C5-C4-O12	117.112	118.483	N9-C3- C4-C5	179.9885	-179.993
N9-O10	1.1972	1.2429	C4-O12- H13	111.289	108.060	N9-C3- C4-O12	-0.0133	0.0084
N9-O11	1.1945	1.2394	С4-С5-Н14	119.4476	119.372	C2-C3- N9-O10	179.9767	179.9829
			С6-С5-Н14	122.4581	122.155	C2-C3- N9-O11	-0.0317	0.0007
			С5-С6-Н15	119.452	119.522	C4-C3- N9-O10	-0.0167	-0.0405
			N1-C6- H15	115.276	115.284	C4-C3- N9-O11	179.975	179.9773
			O10-N9- O11	122.031	121.007	C3-C4- C5-C6	0.0077	0.0126
			C3-N9- O10	118.666	119.260	C3-C4- C5-H14	179.9985	-179.998
			C3-N9- O11	119.303	119.7332	O12-C4- C5-C6	-179.991	-179.989
						O12-C4- C5-H14	0.0001	0.0011
						C3-C4- O12-H13	-0.0174	0.0151
						C5-C4- O12-H13	179.9808	-179.984
						C4-C5- C6-N1	-0.0036	-0.0016
						C4-C5- C6-H15	179.9952	179.9919
						H14-C5- C6-N1	-179.994	-179.991
						H14-C5- C6-H15	0.0048	0.0026

Table 1. Optimized Geometrical Parameters of 2-4-Dihydroxy-3-Nitropyridine Obtained By Hf And B3lyp Methods with 6-311++G(D.P) Basis Set

For numbering of atoms refer Fig.1

Scaling of the force field was performed according to the SQM procedure using selective scaling in the natural internal coordinate representation. Transformation of the force field and the subsequent normal coordinate analysis (NCA) including the least squares refinement of the scaling factors, and calculation of total energy distribution (TED) were done on a PC with the MOLVIB program (version 7.0-G77) written by Sundius [26-27].

The Raman activities (S_i) calculated with the GAUSSIAN 09W program are subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [28-30].

$$\mathbf{I}_{i} = \frac{f(\mathbf{v}_{0} - \mathbf{v}_{i})^{4} \mathbf{S}_{i}}{\mathbf{v}_{i} \left[1 - \exp\left(\frac{-hcv}{kT}\right)\right]}$$

where v_0 is the exciting frequency in cm⁻¹, v_i the vibrational wave number of the ith normal mode, h, c, k are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

Results and Discussion

 Table 2. Definition of Internal Coordinates Of 2,4

 Dihydroxy-3-Nitropyridine

No.	Symbol	Туре	Definition				
Stretching							
1-2	r _i	C-H	C5-H14,C6-H15				
3-4	p _i	O-H	O7-H8,O12-H13				
5-6	R _i	C-O	C2-O7,C4-O12				
7	qi	C-N	C3-N9				
8-9	Qi	N-O	N9-O10,N9-O11				
10-	T _i	C-C	N1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-				
15			N1				
In-pla	ne-bending	r					
16-	βi	Ring	N1-C2-C3, C2-C3-C4, C3-C4-C5,				
21	-		C4-C5-C6, C5-C6-N1, C6-N1-C2				
22-	γ_i	C-C-N	C2-C3-N9,C4-C3-N9				
23							
24-	θ_i	C-N-O	C3-N9-O10,C3-N9-O11				
25							
26	σi	O-N-O	O10-N9-O11				
27-	Пi	C-C-O	N1-C2-O7, C3-C2-O7, C3-C4-O12, C5-				
30			C4-O12				
31-	λi	C-O-H	С2-О7-Н8, С4-О12-Н13				
32							
33-	фi	C-C-H	C4-C5-H14, C6-C5-H14, C5-C6-H15, N1-				
36			C6-H15				
Out-of	-plane ben	ding					
37-	ω _i	C-H	H14-C5-C4-C6,H15-C6-C5-N1				
38							
39-	ψ_i	C-O-H	H8-O7-C2-(N1,C3),H13-O12-C4-				
40			(C3,C5)				
41-	ρ_i	C-O	07-C2-C3-N1, 012-C4-C5-C3				
42							
43	η_i	C-N	N9-C3-C4-C2				
Torsio	n		r				
44-	ti	tring	N1-C2-C3-C4, C2-C3-C4-C5, C3-C4-				
49			C5-C6,				
			C4-C5-C6-N1, C5-C6-N1-C2, C6-N1-				
			C2-C3				
50	t _i	t-NO ₂	C3-N9-O10-O11				
		wag					

Geometry Optimization

The molecular structure with the numbering scheme of 2,4– dihydroxy-3-nitropyridine is shown in Fig.1. Geometry optimization was performed on the compound yielding the C_1 symmetry. The calculated optimized geometrical parameters of DHNP obtained by the HF, DFT/B3LYP with 6-311++G(d,p) as basis set are presented in Table 1. A detailed description of vibrational modes can be given by means of normal coordinate analysis. The internal coordinates describe the position of the atoms in terms of distances, angles and dihedral angles with respect to an origin atom. For this purpose, a full set of standard internal co-ordinates containing 10 redundancies and non-redundant set of local symmetry coordinates were constructed, [31] and are listed in Table 2 and .3, respectively.

Table 3. Definition of Local Symmetry Coordinates Of 2	2,4-
Dihvdroxy- 3-Nitropyridine	

		Dinyuroxy- 5-1	and opymanic				
No.	o. Symbol Definition ^a		Scale factors used in the				
			calculations				
			HF/	B3LYP/			
			6-311++G(d,p)	6-311++G(d,p)			
1-2	СН	$\mathbf{r}_1, \mathbf{r}_2$	0.825	0.915			
3-4	OH	P_{3}, P_{4}	0.690	0.915			
5-6	CO	R ₅ ,R ₆	0.835	0.955			
7	CN sub	q ₇	0.859	0.990			
8	NO _{2 SS}	$(Q_8+_{09})/\sqrt{2}$	0.835	0.975			
9	NO ₂ ass	$(O_8 - O_9) / \sqrt{2}$	0.835	0.975			
10-	CC	T ₁₁ ,T ₁₂ ,T ₁₃ ,T ₁₄	0.859	0.985			
13		117 127 137 14					
14-	CNarr	T_{10}, T_{15}	0.859	0.990			
15		10, 10					
16	R trigd	$(\beta_{16} - \beta_{17} + \beta_{18} -$	0.859	0.955			
	U	$\beta_{19} + \beta_{20} - \beta_{21})/$					
		$\sqrt{6}$					
17	R symd	$(-\beta_{16}-\beta_{17}+2\beta_{18}-$	0.859	0.955			
		$\beta_{19} - \beta_{20} + 2 \beta_{21})/$					
		$\sqrt{12}$					
18	R asymd	$(\beta_{16} - \beta_{17} + \beta_{19} - \beta_{17})$	0.859	0.955			
	-	$\beta_{20})/2$					
19	b CN	$(\gamma_{22} - \gamma_{23})/\sqrt{2}$	0.859	0.955			
20	NO ₂	$(\theta_{24}, \theta_{25})/\sqrt{2}$	0.835	0.975			
	rock	· -· -·					
21	NO ₂	$(\sigma_{24+} \sigma_{25})/\sqrt{2}$	0.835	0.955			
	twist						
22	NO ₂ sisc	$(2\sigma i_{26} - \theta_{24} - \theta_{25})$	0.835	0.955			
		$\sqrt{6}$					
23-	bCO	$(\Pi_{27} - \Pi_{28})/\sqrt{2},$	0.859	0.955			
24		(П ₂₉ - П ₃₀)/ √2					
25	bOH	$(\lambda_{31} - \lambda_{32})/\sqrt{2}$	0.879	0.995			
26-	bCH	$(\phi_{33}, \phi_{34})/\sqrt{2},$	0.879	0.995			
27		(φ ₃₅ - φ ₃₆)/ √2					
28-	ωCH	ω ₃₇ , ω ₃₈	0.859	0.955			
30							
34	ψСОН	Ψ_{39}, Ψ_{40}	0.859	0.955			
35	ρCO	ρ_{41}, ρ_{42}	0.859	0.955			
36	ηCN	η_{43}	0.859	0.955			
37	t ring	$(\tau_{44} - \tau_{45} + \tau_{46} -$	0.859	0.955			
		$\tau_{47} + \tau_{48} - \tau_{49}) / \sqrt{6}$					
38	t R sym	$(\tau_{44} - \tau_{46} - \tau_{47} -$	0.859	0.955			
		τ ₄₉)/ 2					
39	t R	$(-\tau_{44}+2\tau_{45}-\tau_{56}-$	0.859	0.955			
	asym	τ_{47} +2 τ_{48} - τ_{49})/					
		√12					
40	τ	τ ₅₀	0.858	0.955			
	NO ₂ wag						

Vibrational Spectra

The vibrational frequencies IR intensities and Raman activities are calculated for DHNP at *ab initio* (HF) and DFT (B3LYP) level using 6-311++G(d,p) basis set have been collected in Table 4 and 5 along with the observed FT-IR and FT-Raman Spectral data. For visual comparison, the observed and calculated FT-IR and FT-Raman spectra of DHNP at HF and B3LYP level using 6-311++G(d,p) basis set are shown in Figs. 2 and 3, respectively.

3.7	Basis Set										
No. Symmetry Species		Observed frequency (am^{-1})		Calculated frequency (cm ⁻⁺)				Assignment with IED (%)			
		(CM)	ET					among type of internal coordinates			
		<i>Г I - I</i> K	FI- Paman	<i>HF/0-311</i>	++G(a,p) B3L1P/0-		n)				
			Naman	Unscaled	Scaled	Unscaled	Scaled	4			
1	А	3332vw	-	4052	3336	3493	3341	OH(100)			
2	A	3282ms	-	4024	3283	3453	3304	OH(100)			
3	A	3068m	3070vw	3385	3075	3217	3078	CH(99)			
4	А	2938vw	3023vw	3337	3030	3162	3025	CH(99)			
5	А	1645s	1635mw	1805	1646	1652	1638	CC(37), CNarr(22), bOH(13), bCO(8), Rasymd(8)			
6	А	1615ms	1612 m	1791	1618	1609	1595	CC(39), CNarr(11), bCN(11), bCH(11), Rsymd(6), CO(6)			
7	А	1577m	1577w	1751	1576	1587	1571	bOH (28), NO ₂ ass (15), bCN(14), CNarr(12), NO ₂ roc(8), CC(8)			
8	А	1487s	1494w	1631	1485	1495	1485	bOH(25), bCH(21), CO(16), CC(15), CNarr(8), NO ₂ ass(6)			
9	А	-	1460w	1602	1457	1465	1458	CO(24), bOH(21), CC(19), bCH(16), NO ₂ ass(8)			
10	А	1412ms	1414s	1562	1415	1423	1411	CO(28), CC(15), NO ₂ ss(13), Rtrigd(13), CNsub(7), bOH(6)			
11	А	1364s	1367ms	1484	1367	1373	1363	CNarr(32), bOH(23), CC(19), NO ₂ ass(13)			
12	А	-	-	1465	1340	1349	1336	bCH(36), CO(18), NO ₂ ass(14), CC(11), CNarr(8), bOH(6)			
13	А	1299s	1299vs	1428	1302	1319	1300	NO ₂ ss(35), NO ₂ sis(11), bOH(11), CO(9), CNarr(8), bCH(7)			
14	А	-	1246vw	1352	1249	1256	1246	CC(42), CNarr(18), bOH(16), CO(9)			
15	А	1220m	1220 vs	1281	1223	1242	1222	CNsub(21), CC(19), bOH(17), NO ₂ ss(14), NO ₂ sis(8), bCH(6)			
16	А	1143vs	1142w	1220	1143	1154	1145	bCH(27), CC(26), CNsub(25), Rtrigd(10), NO ₂ ss(6)			
17	А	1074m	1075vw	1172	1080	1090	1073	CC(30), bCN(18), CO(18), NO ₂ roc(7), bCO(7), bCH(6)			
18	А	1050m	1057vw	1166	1060	1080	1057	CNarr(27), bCH(18), CC(17), Rtrigd(12), CNsub(7), bCO(6)			
19	А	1000w	1003vw	1129	1006	1003	999	gCH(88), tRtrig(6)			
20	А	863w	861m	978	869	874	857	Rtrigd (35), NO ₂ sis(29), NO ₂ ss(12), CC(7)			
21	А	820ms	818vw	901	816	836	817	gCH(75), gCO(8), gOH(7)			
22	А	-	800s	888	802	818	802	NO ₂ sis(27), Rtrigd(18), Rasymd(16), CC(12), CO(11), Rsymd(7)			
23	А	-	-	824	730	746	729	gOH(44), gCN(21), tRtrig(13), gCO(12)			
24	А	-	-	787	713	735	718	tRtrig(35), gCO(31), tNO ₂ (14), gCN(11)			
25	А	694w	-	728	695	717	700	gOH(61), tNO ₂ (15), tRtrig(9), gCO(7)			
26	А		658vw	679	659	668	652	gCO(38), gCN(23), gOH(22), tRtrig(8)			
27	А	629m	627vw	679	629	646	631	gCO(30), gCN(24), NO ₂ twi(19), tRtrig(15), tRsymd(5)			
28	А	-	618w	647	618	632	620	Rasymd(21), CC(16), bCO(16), CNsub(11), NO ₂ sis(11), CO(8)			
29	А	591vw	592m	639	592	598	588	NO ₂ roc(36), bCO(19), bCN(18), CC(17)			
30	А	533m	534mw	582	532	539	530	Rsymd(62), Rasymd(12), CC(11), bCN(6)			
31	А	460m	-	513	457	470	459	NO ₂ twi (36), tRasym(21), gCO(10), gCN (10), tNO ₂ (9)			
32	А	442w	441vw	467	440	444	439	NO ₂ roc(55), bCO(34)			
33	А	426vw	431 m	461	426	435	427	bCO(40), Rasymd(11), CNsub(11), NO ₂ sis(7), CC(7), Rsymd(6)			
34	А	-	368w	407	370	377	370	bCO(43), Rasymd(17), CNsub(16), Rsymd(10)			
35	А	-	313vw	342	317	323	316	bCN(78)			
36	А	-	231w	267	230	241	235	gCN(63), NO ₂ twi(16), tNO ₂ (14)			
37	А	-	-	238	216	218	213	tRsymd(58), tRasym(14), gCH(12), gOH(8)			
38	А	-	108ms	114	106	111	109	tRasymd(28), gOH(27), tRsymd(14), gCN(11), tRtrig(8), NO ₂ twi(7)			
39	Α	-	-	72	65	94	91	$tNO_2(51), NO_2twi(45)$			

$Table \ 4. \ The \ Observed \ Ftir, \ Ft-Raman \ and \ Calculated \ (Unscaled \ And \ Scaled) \ Frequencies \ (Cm^{-1}) \ and \ Probable \ Assignments \ (Characterized \ By \ Ted) \ of \ 2,4-Dihydroxy-3-Nitropyridine \ Using \ Hf/6-311++G(D,P) \ and \ B3lyp/6-311++G(D,P) \ Methods \ and \ Methods \ And \ Scaled) \ Frequencies \ (Cm^{-1}) \ and \ Probable \ Assignments \ (Characterized \ By \ Ted) \ of \ 2,4-Dihydroxy-3-Nitropyridine \ Using \ Hf/6-311++G(D,P) \ and \ B3lyp/6-311++G(D,P) \ Methods \ and \ Methods \ And \ Scaled) \ Scaled \ And \ An$

Abbreviations: b-bending; g-out-of-plane bending; t-torsion; R-ring; ss-symmetric stretching; ass- asymmetric; arr – aromatic; rocrocking; sci-scissoring; twi-twisting: tNO_2 –wagging: asym-assymetic; sym-symmetric; vs-very strong; s-strong; ms-medium strong; m-medium; w-weak; vw-very weak.; arr-arromatic; sub-substitution.

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Fable 5. Calculated Fundamental Harmonic Frequencies (Cm-1), Force Constant (Mdyn A-1), Infrared - Intensity
(Km/Mol), Raman Activity (Å Amu-1) of 2,4-Dihydroxy-3-Nitropyridine are Analysed Based on Sqm Force Field
Calculation Using B3lvn/6-311++C(D P) and Hf/6-311++C(D P) Methods and Basis Set

HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
Frequency	Force Constants	IR Intensity	Raman Activity	Frequency	Force Constants	IR Intensity	Raman Activity
4052	10.313	368.850	56.347	3493	7.663	314.010	99.364
4024	10.167	179.098	19.534	3453	7.489	146.366	27.163
3385	7.402	0.188	114.983	3217	6.670	0.037	138.963
3337	7.169	15.842	98.776	3162	6.427	13.694	133.668
1805	18.849	1036.748	3.132	1652	8.200	329.002	15.153
1791	11.377	485.769	30.690	1609	9.742	607.902	9.508
1751	7.110	94.574	16.490	1587	5.272	76.272	20.093
1631	6.296	157.664	24.790	1495	3.289	28.376	1.358
1602	8.521	294.796	21.281	1465	3.402	211.995	5.225
1562	4.330	137.100	44.308	1423	5.608	91.759	5.096
1484	6.369	110.619	95.815	1373	3.776	48.332	23.023
1465	2.084	188.310	5.576	1349	2.078	43.248	6.678
1428	2.445	80.861	9.716	1319	3.872	98.370	80.951
1352	1.666	150.850	35.438	1256	2.830	381.092	8.668
1281	3.679	220.325	30.845	1242	2.240	334.633	86.591
1220	2.833	221.126	12.021	1154	1.863	25.040	3.766
1172	2.800	7.631	0.530	1090	2.698	16.726	2.394
1166	2.287	7.445	21.583	1080	2.038	2.435	6.360
1129	1.058	000	0.511	1003	0.832	0.169	0.283
978	6.278	35.646	8.672	874	4.391	8.403	11.385
901	0.675	32.590	0.140	836	0.555	9.149	0.030
888	3.700	0.428	11.475	818	3.596	0.031	23.387
824	3.678	1.601	0.053	746	0.413	108.553	0.522
787	3.955	28.973	0.741	735	0.896	2.303	0.102
728	1.428	0.066	0.321	717	0.494	19.580	0.455
679	2.581	22.345	7.027	668	0.885	124.453	0.016
679	0.292	147.720	0.358	646	1.243	6.039	0.119
647	1.303	26.435	3.263	632	2.410	14.695	10.818
639	0.260	162.039	0.206	598	1.109	20.812	3.641
582	1.934	3.892	6.885	539	1.672	3.566	11.216
513	0.556	5.036	0.470	470	0.476	4.456	0.652
467	1.096	8.649	0.933	444	1.099	6.874	1.461
461	0.834	1.366	2.037	435	0.824	0.281	7.025
407	0.833	0.520	0.362	377	0.612	0.952	0.569
342	0.643	14.680	0.593	323	0.530	15.351	0.464
267	0.359	0.665	0.331	241	0.310	1.708	0.025
238	0.208	1.436	0.724	218	0.174	1.379	0.633
114	0.059	0.264	0.677	111	0.058	0.124	0.477
72	0.045	0.197	0.613	94	0.074	0.247	0.286

C-C Vibrations

The benzene possesses six stretching vibrations of which the four with highest wave numbers occurring near 1650-1400 cm⁻¹ are good group vibrations [32]. With heavy substituents, the bonds tend to shift to somewhat lower wave numbers and greater the number of substituents on the ring, broader the absorption regions. In the title molecule, the FT-IR bands observed at 1645, 1615, 1074 cm⁻¹ and 1635, 1612, 1246 and 1075 cm⁻¹ in FT-Raman have been assigned to C-C stretching vibrations are due to the substituents in benzene ring. The higher percentage of total energy distribution (TED) obtained for this group encouraging and confirms the assignments proposed in this study for C-C stretching vibrations. The in-plane and out-of-plane bending vibrations of C-C group are also listed in Table.4.



Fig 1. Molecular Structure of 2,4-Dihydroxy-3-Nitropyrdine



Fig 2. Comparison of Observed and Calculated Ftir Spectra of 2,4-Dihydroxy-3-Nitropyridine (A) Observed In Solid Phase (B) Calculated With B3lyp/6-311++G(D,P) and (C) Calculated With Hf/6-311++G(D,P)

C-H Vibrations

The heteroaromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000 cm⁻¹ [33-35]. This is the characteristic region for the ready identification of C-H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substitutions. In the present investigation, the C-H vibrations are observed at 3068 and 2938 cm⁻¹ in the FT-IR spectrum and at 3070 and 3023 cm⁻¹ in the Raman for DHNP. The C-H in-plane and out-of-plane bending vibrations of the DHNP have also been identified and listed in Table 4.

O-H Vibrations

The precise positions of O-H band are dependent on the strength of hydrogen bond. The O-H stretching vibration is normally observed at about 3300 cm⁻¹. The O-H in-plane bending vibration is observed in the region 1440-1260 cm⁻¹ [36-37]. In DHNP, the bands appeared at 3332 and 3282 cm⁻¹ in FTIR spectrum were assigned to O-H stretching modes of vibrations. The in-plane bending vibrations of hydroxy groups have been identified at 1577, 1487 cm⁻¹ in IR and 1577, 1494 cm⁻¹ in FT Raman, respectively. O-H out-of-plane vibrations of the title compound have also been identified and listed in Table 4.



Fig 3. Comparison of observed and calculated FT-Raman Spectra of 2,4-dihydroxy-3-nitropyridine (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)

NO₂ vibrations

The characteristic group frequencies of the nitro group are relatively independent of the rest of the molecule which makes this group convenient to identify. For the assignments of NO₂ group frequencies, basically six fundamentals can be associated to each NO₂ group namely, NO₂(ss)-symmetric stretch, NO₂(ass)-antisymmetric stretch, NO₂(sciss)-scissoring, and NO₂(rock)-rocking which belong to in-plane vibrations. In addition, NO₂ (wag)-wagging and NO₂(twist)-twisting modes of NO₂ group would be expected to be depolarised for out-of-plane symmetry species.

The symmetric stretching frequencies are identified at 1299 cm⁻¹ in both FT-IR and FT-Raman spectra for DHNP. The bands observed at 800 cm⁻¹ in FT-Raman are assigned to scissoring [38]. Rocking, wagging and twisting vibrations of NO₂ group are also found well within the characteristic region and are summarized in Table 4.

C-N Vibrations

In aromatic compounds, the C–N stretching vibrations usually lie in the region 1400-1200 cm⁻¹ [40]. In the present work, the FT-IR band appeared at 1364 cm⁻¹ and 1367 cm⁻¹ in FT-Raman have been designated to C–N stretching vibrations. The in-plane and out-of-plane bending vibrations assigned in this study are also supported by the literature [39]. The identification of C–N vibration is a difficult task, since it falls in a complicated region of the vibrational spectrum. However, with the help of force field calculations, the C–N vibrations are identified and assigned in this work.

Calculations are made for a free molecule in vacuum, while experiments are performed for solid sample, so there are disagreements between the calculated and observed vibrational wave numbers. Comparison of the frequencies calculated at HF and B3LYP methods with experimental values reveals the overestimation of the calculated vibrational modes due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with HF frequency.

HOMO-LUMO Band Gap

This electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO[40]. Many organic molecule, containing conjugated π electrons are characterized by large values of molecular first hyper polarizabilities, are analyzed by means of vibrational spectroscopy. In most of the cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for DFT calculations in π conjugated system that predict exceptionally infrared intensities for the same normal modes. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by oneelectron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied orbital (LUMO). The LUMO; of π nature, (i.e. benzene ring) is delocalized over the whole C-C bond. The HOMO is located over benzene ring, iodine and the HOMO-LUMO transition implies an electron density transfer to the nitro group from benzene ring and oxygen

atom. Moreover, the compositions of the frontier molecular orbital for DHNP are shown in Fig 4.



Fig 4. Frontier Molecular Orbital For 2,4-Dihydroxy 3-Nitropyridine

The HOMO-LUMO energy gap of DHNP is calculated at B3LYP/6-311++G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor (EA) represents the ability to obtain an electron and HOMO represents ability to donate an electron (ED). The ED groups to the efficient EA groups through π -conjugated path.

Table 6. Thermodynamic Parameters of 2,4-Dihydroxy-3-Nitropyridine

Parameters	Method / Basis set				
	HF/	B3LYP/ 6-311++G(d,p)			
	6-311++G(d,p)				
Optimized global minimum	-600.0619	-603.42802			
Energy (Hartrees)					
Total energy (thermal) (kcal	30.165	68.025			
mol^{-1})					
Heat capacity (cal mol ⁻¹ k^{-1})	89.079	32.068			
Entropy (cal mol ⁻¹ k^{-1})					
Total	94.8493	90.116			
Translational	41.044	41.044			
Rotational	29.717	29.772			
Vibrational	18.318	19.300			
Zero point vibrational	68.40503	62.8161			
energy (Kcal mol ⁻¹)					
Rotational constants (GHZ)					
A	1.63678	1.60762			
В	1.30508	1.28096			
С	0.72611	0.71291			
Dipolemoment (Debye)					
μ _x	-0.5690565	-0.5957091			
μ _y	0.8207679	0.7861422			
μ _z	-0.0107157	-0.0105924			

The strong charge transfer interaction through π -conjugated bridge results in substantial ground state Donor-Acceptor (DA) mixing and the appearance of a charge transfer band in the electron absorption spectrum.

HOMO energy = -0.28102 a.u.

LUMO energy = -0.13571 a.u.

HOMO-LUMO energy gap =-0.145311 a.u.

The calculated self-consistent field (SCF) energy or optimized global minimum energy of DHNP is -603.393348237 Hartrees at B3LYP/6-311++G(d,p) and -600.011255480 Hartrees at HF/6-311++G(d,p). The HOMO and LUMO energy

gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

Other Molecular Properties

Several calculated thermodynamical parameters, rotational constants, rotational temperature, vibrational temperature and dipole moment have been presented in Table 6.

The zero-point vibrational energies, the entropy and the molar capacity at constant volume are calculated. The variation in the zero-point vibration energies seems to be insignificant. The changes in the total entropy of DHNP at room temperature at different methods are only marginal [41]. The dipole moment of the molecule is also calculated by *ab initio* HF and DFT/B3LYP using 6-311++G(d,p) basis set.

Conclusion

Attempts have been made in the present work for the molecular parameters and frequency assignments for 2,4dihydrocy-3-nitropyridine from the FT-IR and FT-Raman spectra. Vibrational frequencies, infrared intensities and Raman activities are calculated and analyzed by ab initio HF and DFT (B3LYP) levels of theory utilizing 6-311++G(d,p) higher basis set. The difference between the observed and scaled wavenumber values of most of the fundamentals is very small. Comparison between the calculated and experimental structural parameters indicates that B3LYP results are in good agreement with experimental values. The assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values seem to be correct. From the vibrational discussion, it is concluded that the substitution of H atom by the NO₂ group distorts the ring geometries to small extent and the planarity of the molecule. And also HOMO and LUMO energy gap explains that the eventual charge transfer interaction taking place within the molecule.

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