

Molecular structure and vibrational analysis of 2,5-pyridine-dicarboxylic acid using experimental and theoretical methods

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Abstract. The FTIR and FT-Raman spectra of 2,5-pyridine-dicarboxylic acid (PDA) has been recorded in the range 4000-450 cm^{-1} and 4000-50 cm^{-1} , respectively. The optimized geometry and vibrational frequencies were computed using density functional theory (DFT) employing B3LYP functional with 6-311++G(d,p) basis set. The rms error between observed and calculated frequencies is obtained as 10.8 cm^{-1} . A normal coordinate analysis was carried out for all the vibrations of this molecule by solving inverse vibrational problem (IVP) using a 74-parameter modified valence force field employing overlay technique. This reproduced 35 observed frequencies of this molecule with an error of 9.28 cm^{-1} in the zero-order calculations, demonstrating the transferability of the force field obtained in our earlier work on some related pyridine-dicarboxylic acids. PED and eigen vectors calculated in the process were used to make unambiguous vibrational assignments of all the fundamentals of the molecule.

1. Introduction

We have been investigating the molecular structure and vibrational analysis of pyridine-carboxylic acids by recording their infrared and Raman spectra; and subjecting them to normal coordinate analysis using density functional theory (DFT) and solving inverse vibrational problem (IVP). The force constants thus obtained in the process were utilized to demonstrate their transferability to the related pyridine-carboxylic acids. In our earlier paper, we reported the results of experimental and theoretical study of 2,3-, 2,4- and 3,4-pyridine-dicarboxylic acids; and evaluated their optimized geometries and valence force field [1]. In continuation of this work, we now investigated 2,5-pyridine dicarboxylic acid (PDA) for its structure and vibrational assignments.

Pyridine-dicarboxylic acids have immense importance in several fields of scientific research such as coordination chemistry, biochemistry, pharmaceuticals and medicine. They are used in coordination chemistry as multifunctional ligands capable of forming extended networks of different dimensionalities with transition metals, yielding materials having interesting topologies and physical properties [2, 3]. In biochemistry, they find application as enzyme inhibitors [4], plant preservatives [5] and food sanitizers [6]. NMR, UV and IR absorption spectra of 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridine-dicarboxylic acids were reported by Wasylina et al [7]. They proposed tentative assignments for very few IR bands on the basis of qualitative considerations, leaving many other observed vibrational frequencies unassigned. Monomeric and dimeric structures of 3,5-pyridine-dicarboxylic acid or dinicotinic acid were studied by Nataraj et al by recording FT-Raman, FTIR and UV spectra and making DFT and ab initio calculations [8]. Dinicotinic acid and its dianions were investigated, both experimentally (Raman and infrared spectra) and theoretically, by Kathleen McCann and Jaan



Laane [9], whereas its Raman spectra in microcrystalline form was reported by Alexandre et al [10]. Thermochemical and theoretical studies of 2,3-; 2,5- and 2,6-pyridine-dicarboxylic acids are also available along with that of dimethyl pyridine-2,6-dicarboxylate [11].

From the above, it is clear that the experimental (Raman and infrared) and theoretical investigation of 2,5-pyridine-dicarboxylic acid (PDA) is not yet appear in the literature. Hence, a systematic investigation of vibrational spectra of this molecule employing experimental and theoretical methods is undertaken. The purpose of this investigation is:

- i) To record FTIR and FT-Raman spectra of PDA to get complete information on its vibrational frequencies.
- ii) To make DFT (Density Functional Theory) calculations in order to make geometry optimization so as to identify the most stable rotational isomer of the molecule in the ground state and calculate theoretical vibrational frequencies using scaling.
- iii) To test the transferability of force constants obtained for the related molecules by solving inverse vibrational problem using optimized geometry by Wilson's GF-matrix method employing overlay least-squares technique.
- iv) To make unambiguous vibrational assignment of all the fundamental vibrations of the molecule using PED and eigen vectors obtained in the results of both DFT and IVP computations.

2. Experimental Details

The compound PDA was obtained from TCI Chemical Company, Japan and used as such for the spectral measurements. The room temperature FTIR spectra is recorded using Bruker IFS 66V spectrometer employing KBr optics in the spectral range 4000-450 cm^{-1} with a scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ with spectral width 2.0 cm^{-1} . The FT-Raman spectra is recorded in the range 4000-50 cm^{-1} using FRA 106 Raman module equipped with Nd:YAG laser source operating at 200 mw power with spectral resolution of 2 cm^{-1} . The wavelength of the exciting radiation used was 1064 nm.

3. Computational details

3.1. The Quantum Chemical Calculations – Molecular geometry

As the determination of the most stable conformation is the starting point for further calculations, the molecule was subjected to a rigorous conformational analysis around free rotation bonds using Gaussian 09w software package [12]. The standard density functional triply-parameter hybrid model DFT/B3LYP [13, 14] with 6-311++G(d,p) basis set was employed for the computations. The optimized geometry of the molecule corresponding to minimum on the potential energy surface was obtained by solving self-consistent field equation iteratively. These computations yielded eight stable rotational conformers for PDA as shown in Fig.1.

The conformer in Fig.1(d) has the lowest global minimum energy for PDA. Hence, this is accepted as the most stable conformer for optimizing the geometry of the molecule PDA. Subsequent calculations were performed with this optimized structure as shown in Fig. 2. The same figure contains numbering of atoms also. The optimized structure parameters in the most stable conformation are given in Table 1.

As per the computations, the molecule PDA C_s point group symmetry. The molecule consists of 17 atoms. Hence, it has 45 fundamentals, distributed as 31 in-plane vibrations of a' -species and 14 out-of-plane vibrations of a'' -species in C_s symmetry. All the vibrations of C_s symmetry are active in both IR absorption and Raman scattering.

Detailed description of vibrational modes using the full set of 58 primitive internal coordinates containing 13 redundancies, normal coordinate analysis using the MOLVIB 7.0 program and scaling of the force constants was made according to scaled quantum mechanical procedure as discussed in our earlier work [1]. For plotting simulated IR and Raman spectra, a pure Lorentzian band shape was

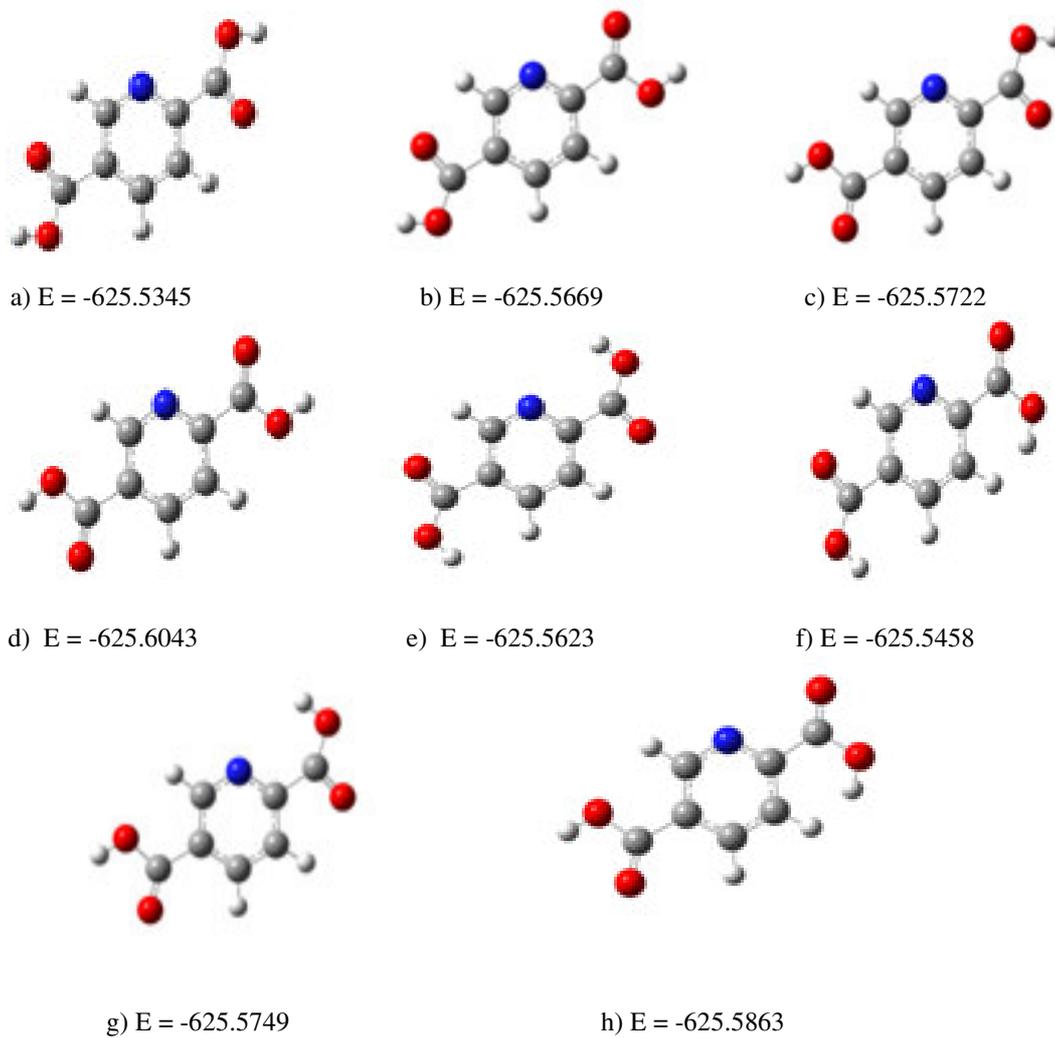


Fig.1. Conformers of PDA (Energy, E in Hartree)

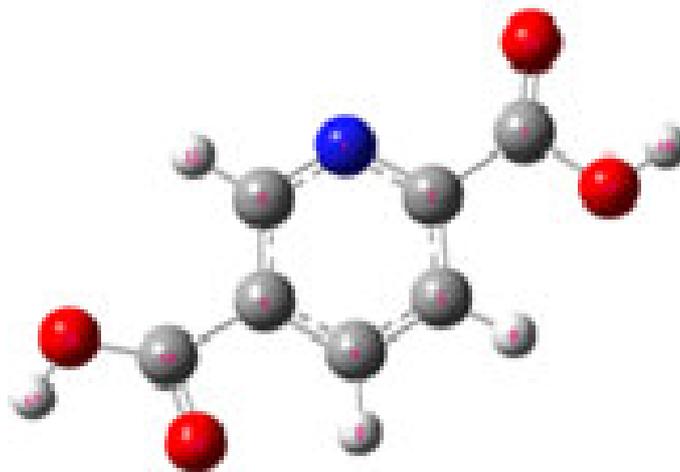


Fig.2. Optimized structure of PDA

Table 1. Optimized geometrical parameters of PDA

Bond	Bond length	Bond angle	Value (in °)	Torsional angle	Value (in °)
N1-C2	1.336	N1-C2-C3	123.34	N1-C2-C3-C4	0.00
C2-C3	1.398	C2-C3-C4	118.32	C2-C3-C4-C5	0.00
C3-C4	1.388	C3-C4-C5	118.81	C3-C4-C5-C6	0.00
C4-C5	1.394	C4-C5-C6	118.33	C6-N1-C2-C7	180.00
C5-C6	1.402	N1-C2-C7	115.32	N1-C2-C3-H8	180.00
C6-N1	1.334	C2-C3-H8	120.34	C2-C3-C4-H9	-180.00
C2-C7	1.507	C3-C4-H9	121.66	C3-C4-C5-C10	180.00
C3-H8	1.081	C4-C5-C10	118.89	C4-C5-C6-H11	180.00
C4-H9	1.083	C5-C6-H11	120.24	N1-C2-C7-O12	0.0
C5-C10	1.488	C2-C7-O12	125.60	N1-C2-C7-O13	180.0
C6-H11	1.084	C2-C7-O13	111.49	C2-C7-O13-H14	-180.0
C7-O12	1.200	C7-O13-H14	106.93	C4-C5-C10-O15	0.0
C7-O13	1.359	C5-C10-O15	124.48	C4-C5-C10-O16	180.0
O13-H14	0.968	C5-C10-O16	112.71	C5-C10-O16-H17	-180.00
C10-O15	1.207	C10-O16-H17	107.23	*	*
C10-O16	1.352	*	*	*	*
O16-H17	0.968	*	*	*	*

* Not applicable

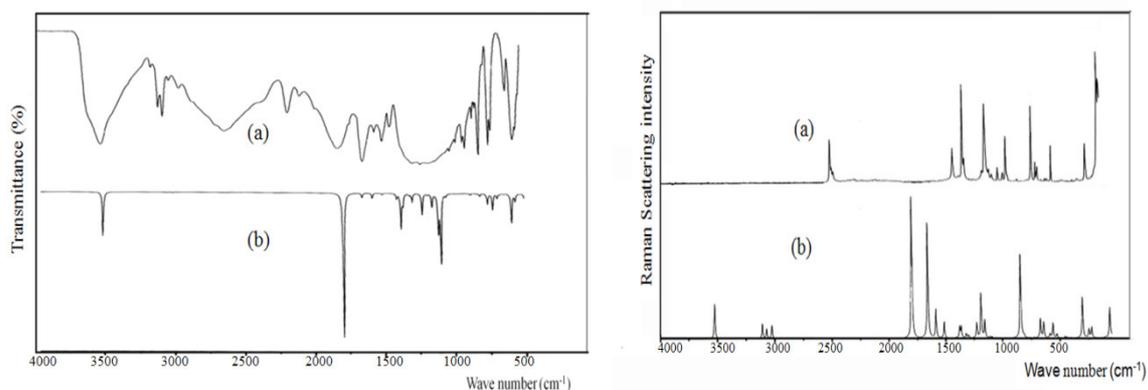


Fig.3. FTIR and FT-Raman spectrum of PDA: (a) Observed, (b) Simulated with DFT

used with a full width at half maximum (FWHM) of 10 cm^{-1} . The observed and simulated FTIR and FT-Raman spectra of this molecule are presented in Fig. 3. The observed frequencies (both IR and Raman) and calculated frequencies (both un-scaled and scaled) and vibrational modes of PDA are reported in Table 2.

It is necessary to determine the goodness of fit between the calculated and observed frequencies to lend credence to the reliability of the computations. This is achieved by calculating root mean square (rms) error between the calculated and experimental frequencies using the following relation

$$\text{rms} = \sqrt{\left\{ \frac{1}{n-1} \sum_{i=1}^n [(v_i)^{\text{cal}} - (v_i)^{\text{exp}}]^2 \right\}}$$

where, $(v_i)^{\text{cal}}$ is the i^{th} calculated frequency, $(v_i)^{\text{exp}}$ is the i^{th} experimental frequency, and n is the number of experimental frequencies. The rms error between un-scaled frequencies and observed

frequencies for PDA was found to be 35.8 cm^{-1} . On using the refined scaling factors, this deviation was reduced to 10.8 cm^{-1} for this molecule.

3.2. Calculations based on Classical Mechanics

A zero-order normal coordinate analysis of all the vibrations of PDA was made by solving inverse vibrational problem (IVP) using Wilson's GF-matrix method employing overlay technique as discussed in our earlier work on pyridine-dicarboxylic acids [1]. The initial set of 74 force constants was transferred there from for this molecule. This reproduced 35 observed frequencies of this molecule with an error of 9.28 cm^{-1} in the zero-order calculations. This should be considered as good, as the force constants are not refined. This demonstrates the transferability of force constants obtained in our earlier work [1]. Observed frequencies, calculated frequencies using the above set of force constants by IVP method, frequencies computed by DFT and the vibrational modes of PDA are presented in Table 2.

Table 2. Observed, calculated frequencies (in cm^{-1}) with DFT/B3LYP/6-311++G and IVP; and vibrational modes of PDA

S.No	Mode ^a	Obs. frequency		Cal. frequency		
		IR	Raman	DFT		IVP
				Un-scaled	Scaled	
a'- species						
1	$\nu(\text{C-N})1$	807	813	814	804	802
2	$\nu(\text{C-C})8a$	-	1622	1617	1614	1628
3	$\nu(\text{C-N})8b$	1609	1602	1608	1611	1610
4	$\nu(\text{C-C})14$	1270	-	1250	1261	1267
5	$\nu(\text{C-C})19a$	1519	-	1541	1520	1521
6	$\nu(\text{C-C})19b$	1464	-	1471	1480	1468
7	$\nu(\text{C-H})2$	3071	3082	3273	3065	3060
8	$\nu(\text{C-H})7a$	3108	3100	3220	3108	3110
9	$\nu(\text{C-H})20b$	-	3064	3120	3076	3072
10	$\nu(\text{C-C}_\alpha)7b$	-	1020	1041	1024	1027
11	$\nu(\text{C-C}_\alpha)20a$	-	-	1358	1312	1304
12	$\beta(\text{CH})3$	-	1228	1241	1224	1221
13	$\beta(\text{CH})9b$	-	1138	1152	1134	1137
14	$\beta(\text{CH})18a$	1187	1172	1160	1184	1185
15	$\beta(\text{CC}_\alpha)9a$	-	110	139	111	112
16	$\beta(\text{CC}_\alpha)18b$	-	263	240	267	264
17	$\beta(\text{CCC})6a$	-	360	331	352	351
18	$\beta(\text{CCC})6b$	496	-	462	498	486
19	$\beta(\text{CCC})12$	693	-	711	698	694
a''- species						
20	$\pi(\text{CH})5$	863	-	871	861	
21	$\pi(\text{CH})11$	787	792	785	780	787
22	$\pi(\text{CH})17a$	930	-	912	932	937

23	$\pi(\text{CC}_\alpha)$ 10b	-	-	181	165	163
24	$\pi(\text{CC}_\alpha)$ 17b	-	128	141	124	125
25	$\tau(\text{CCCC})$ 4	764	-	751	761	763
26	$\tau(\text{CCCC})$ 16a	563	-	585	565	563
27	$\tau(\text{CCCC})$ 16b	-	440	422	441	442
Vibrations of acid groups						
a'- species						
28	$\nu(\text{C}_\alpha=\text{O})_1$	1790	-	1763	1786	1791
29	$\nu(\text{C}_\alpha=\text{O})_2$	-	1730	1741	1735	1728
30	$\nu(\text{C}_\alpha-\text{O})_1$	-	1328	1341	1321	1327
31	$\nu(\text{C}_\alpha-\text{O})_2$	-	1328	1338	1320	1337
32	$\delta(\text{OH})_1$	-	1372	1342	1370	1371
33	$\delta(\text{OH})_2$	-	1372	1348	1375	1376
34	$\nu(\text{O}-\text{H})_1$	3521	-	3652	3522	3531
35	$\nu(\text{O}-\text{H})_2$	3521	-	3652	3524	3538
36	$\delta(\text{C}_\alpha=\text{O})_1$	676	667	681	671	666
37	$\delta(\text{C}_\alpha=\text{O})_2$	-	639	671	648	641
38	$\gamma(\text{C}_\alpha-\text{O})_1$	-	-	581	562	571
39	$\gamma(\text{C}_\alpha-\text{O})_2$	464	-	438	467	461
a''- species						
40	$\tau(\text{CC}_\alpha)_1$	-	75	91	78	73
41	$\tau(\text{CC}_\alpha)_2$	-	-	80	84	81
42	$\omega(\text{OH})_1$	516	-	530	511	517
43	$\omega(\text{OH})_2$	-	-	415	428	424
44	$\omega(\text{C}_\alpha=\text{O})_1$	-	857	842	856	860
45	$\omega(\text{C}_\alpha=\text{O})_2$	-	857	851	861	864

^a: Mode in Wilson's notation [15]. C_α represents Carbon atom of acid group; ν , stretching; β , in-plane bending; δ , deformation; γ , in-plane rocking; π , out-of-plane bending; τ , torsion; ω , wagging

4. Results and Discussion

The bond-distance between the pyridine ring and each of the two acid groups in the present study is found as 1.507 and 1.488 Å in PDA. The calculated bond length of C-N in this molecule is 1.336 Å. This value is in good agreement with the experimental values available in literature [7, 9]. The optimized structure of the molecule and the torsional angles presented in Table 1 reveal that the two acid groups are within the plane of pyridine ring due to the presence of non-bonding electrons on the nitrogen atom and thus, possess C_s symmetry. Wasylina et al [7] studied the NMR, UV and IR spectra and made vibrational assignments for some vibrations of the molecule under investigation and the symmetry of the molecule was not reported. The other structure parameters computed in the present study are in good agreement with the literature values [7, 9].

4.1. Vibrational assignments

Vibrational assignments of the molecule are made by using density functional theory (DFT) as well as solving classical inverse vibrational problem. In DFT computations, the assignments are arrived at by referring to potential energy distribution (PED) and deriving considerable help from Gauss View

program, which shows oscillations (or displacements) of atoms of the molecule in each mode of vibration. PED and eigen vectors were used to make vibrational assignments in classical inverse vibrational problem. There are no significant differences between the PED and hence the vibrational assignments, arrived at on the basis of both the methods. Hence, results of DFT computations are taken as reference in the discussion of vibrational assignments, as they are obtained from general valence force field, derived from quantum chemical principles, which is the best at the present state of our knowledge. The results presented in Tables 2 are self-explanatory. Hence, the detailed discussion is unwarranted.

5. Conclusion

Geometry optimization has yielded structure parameters that agree well with their experimental counter parts. A complete vibrational analysis of 2,5-pyridine-dicarboxylic acid is performed using the DFT method at B3LYP/6-311++(d,p) level of theory and solving inverse vibrational problem using optimized molecular geometry. All the fundamental frequencies of the molecule are assigned unambiguously based on the PED and eigen vectors obtained from normal coordinate analysis. The rms error between un-scaled frequencies and observed frequencies for PDA was found to be 35.8 cm^{-1} . On using the refined scaling factors, this deviation was reduced to 10.8 cm^{-1} for this molecule. Transferability of 74-parameter force field obtained in our earlier work for the related molecules has been demonstrated for the molecule under investigation and reproduced 35 experimental frequencies with an error of 9.28 cm^{-1} in the zero-order calculations. This should be considered as good, as the force constants are not refined.

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