



Quantum chemical calculations of pyridine-2,6-dicarbonyl dichloride

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ABSTRACT

The solid phase FT-IR and FT-Raman spectra of pyridine-2,6-dicarbonyl dichloride (PDD) have been recorded in the regions 4000-400 cm^{-1} and 3500-100 cm^{-1} , respectively. Geometry and vibrational wavenumbers are calculated using *ab-initio* Hartree-Fock (HF) and Density Functional Theory (DFT) methods employing the 6-311+G (d,p) basis set. The observed FT-IR and FT-Raman vibrational frequencies have been analyzed and assigned to different normal modes of the molecule. Using PEDs, the contributions are determined for different modes to each wavenumber.

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Introduction

N-Heterocyclic, especially, pyridine ring system occurs in the structures of a wide variety of natural products, pharmaceuticals and agrochemical compounds. It plays a central role in the structure and properties of nucleic acids. Its biological importance is substantiated by the fact that pyridine ring plays a very important role in the fundamental metabolism in two ways: (i) as an oxidizing system by effective hydride abstraction in nicotinamide adenine dinucleotide and (ii) in dehydrogenase enzymes, and in transamination reactions, an important aspect of amino acid metabolism[1-3], as vitamin B6.

Nitrogen in the pyridine ring has a lone pair of electrons which is not delocalized with the aromatic π -electron system and is easily available for protonation. The basicity becomes more pronounced if electron-donating groups are present on the ring at adjacent positions of N because of the increased electron density on the nitrogen atom[4-6].

Intensive studies on pyridine and substituted pyridines have been made in the past keeping in view their industrial importance both as a fundamental building block and as a solvent and reagent in organic syntheses[7]. The spectroscopic studies of N-heterocyclic molecules including substituted pyridines have become quite interesting as they are the constituents[8-10] of DNA and RNA.

Literature survey reveals that to the best of our knowledge, the results based on quantum chemical calculations, FT-IR and FT-Raman spectral studies on pyridine-2,6-dicarbonyl dichloride (PDD) have no reports.

Hence in the present work, we reported detailed interpretations of the infrared and Raman spectra based on the experimental and theoretical results, which are acceptable and supportable to each other. Attempts have been made to find out an optimum method using a reasonable basis set to get a close agreement between the computed and the experimental data.

Methodology

Experimental and theoretical methods

The compound PDD was provided by Lancaster Chemical Company, UK, with a stated purity of 98% and it was used as such without further purification. The spectral measurements were carried out at Central Electro Chemical Research Institute (CECRI), Karaikudi (Tamilnadu), India. The FT-Raman spectrum of PDD was recorded using 1064nm line of Nd:YAG laser as excitation wavelength in the region 3500-100 cm^{-1} on thermo electron corporation model Nexus 670 spectrometer equipped with FT-Raman module accessory. FT-IR spectral measurement was carried out at St. Joseph College, Tiruchirappalli, India. The FT-IR spectrum of the title compound was recorded in the region 4000-400 cm^{-1} on Perkin Elmer Spectrophotometer in KBr pellet. The spectrum was recorded at room temperature with a scanning speed of 30 $\text{cm}^{-1}\text{min}^{-1}$ and the spectral width of 2.0 cm^{-1} . The observed experimental FT-IR and FT-Raman spectra are shown in Figs.1 and 2, respectively.

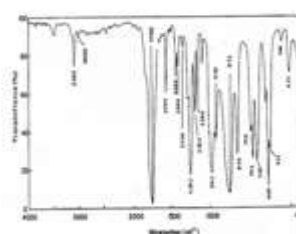


Fig. 1 FT-IR spectra of pyridine-2,6-dicarbonyl dichloride

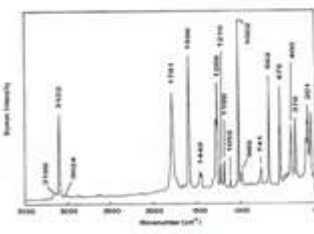


Fig. 2 FT-Raman spectra of pyridine-2,6-dicarbonyl dichloride

Computational method

Geometry optimization and vibrational frequencies of pyridine-2,6-dicarbonyl dichloride were calculated at the HF[11] and DFT levels with B3LYP (Becke-3-Lee-Yang-Parr three parameters) hybrid functional with correlation function such one proposed by Lee, Yang and Parr[12,13]. B3LYP is most promising in providing reasonably acceptable vibrational wave numbers for organic molecules. Standard 6-311+G (d,p) basis

set has been used in both methods in order to see the effect of correlation. Gaussian 09 software package[14] and the methods implemented therein have been utilized to accomplish all the calculation. All the parameters were allowed to relax and all the calculations were converged to an optimized geometry which corresponds to a true energy maximum, as revealed by the lack of imaginary values in the wavenumber calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming the molecule belongs to C_s point group symmetry. The transformation of force field from Cartesian to internal local symmetry coordinates the scaling, the subsequent normal coordinate analysis (NCA), calculation of potential energy distribution (PED) were done on a PC with the version V7.0-G77 of the MOLVIB program written by Tom Sundius[15].

A detailed description of vibrational modes can be given by means of normal coordinate analysis, for this purpose the full set of 50 standard internal coordinates (containing 11 redundancies) for the title compound is presented in Table 1. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Pulay and Fogarasi[16,17] which are presented in Table 2. The theoretically calculated DFT force fields were transformed to this set of vibrational coordinates and used in all subsequent calculations.

Results and discussion

Geometric structure

The optimized structural parameters (Table. 3) and global minimum energy of PDD were calculated by C_s point group symmetry with HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels. In accordance with the atom numbering scheme is given in Fig. 3. The global minimum energies of PDD are -1389.9530 and -1394.1538 hartrees for HF/6-311+G(d,p) and B3LYP/6-311+G(d,p) levels, respectively. The computed harmonics were scaled by 0.8901 for wavenumbers less than 1700 cm^{-1} and 0.9813 for higher wavenumbers. The computed bond lengths and bond angles by both levels show satisfactory agreement with experimental[18] observation.

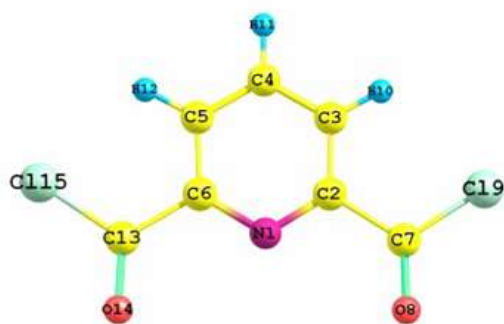


Fig. 3. – Molecular structure of pyridine-2,6-dicarbonyl dichloride

Vibrational assignments

The 39 normal modes of PDD are distributed among the symmetry species as $\Gamma_{3N} - 6 = 27 A'$ (in-plane) + $12 A''$ (out-of-plane) by assuming C_s point group symmetry. The detailed vibrational assignments of fundamental modes of PDD along with observed and calculated frequencies, IR intensities, Raman scattering activities and normal mode descriptions have been reported in Table 4. It is convenient to discuss the vibrational spectra of PDD in terms of characteristic spectral region as described below:

C-H vibrations — The hetero aromatic organic compounds commonly exhibit multiple weak bands in the region $3100\text{-}3000\text{ cm}^{-1}$ due to C-H stretching vibrations[19]. In this region, the bands are not affected appreciably by the nature of substituents. In this title molecule, the bands have been assigned at $3191, 3103, 3020\text{ cm}^{-1}$ in IR and $3188, 3102, 3024\text{ cm}^{-1}$ in Raman to C-H stretching vibrations. The scaled values computed by B3LYP/6-311+G(d,p) level coincide well with the experimental observation. The C-H in-plane[20] ring bending vibrations normally occurred as number of strong to weak intensity sharp bands in the region $1300\text{-}1000\text{ cm}^{-1}$. The bands for C-H in-plane bending vibrations of the title compound identified at $1282, 1208, 1120\text{ cm}^{-1}$ in infrared and 1288 and 1210 cm^{-1} in Raman. The theoretically computed frequency for C-H in-plane bending vibrations by B3LYP/6-311+G(d,p) method shows excellent agreement with recorded spectra as well as literature[10] data.

The C-H out-of-plane bending vibrations[10, 21] are strongly coupled vibrations and normally observed in the region $950\text{-}800\text{ cm}^{-1}$. In the present case, the bands are identified at $1002, 970$ and 871 cm^{-1} for C-H out-of-plane bending. Except first two bands, the assigned frequency is found to be well within the characteristic regions. In the case of C-H out-of-plane bending vibrations of present molecule are slightly pulled up fairly. This view of pull of vibrations is purely by the heavy mass of carbonyl chloride group vibration.

C-N vibrations — The pyridine absorbs strongly in the region $1600\text{-}1500\text{ cm}^{-1}$ due to the C=N ring stretching vibrations[22]. Accordingly, a medium strong band is observed at 1448 cm^{-1} in infrared and 1449 cm^{-1} in Raman in the title molecule. The C-N stretching vibrations[22] are always mixed with other bands and are usually assigned with region $1266\text{-}1382\text{ cm}^{-1}$. The C-N stretching is observed at 1184 and 1188 cm^{-1} in IR and Raman, respectively and is mixed with C-H in-plane bending vibrations. This frequency is also at the lower end of the expected range which may be due to the interaction of C-C vibration, whose frequency extends up this value. This view is supported by the literature[22,23].

C-C vibrations — The ring carbon-carbon stretching vibrations[24] occur in the region $1625\text{-}1430\text{ cm}^{-1}$. The in-plane deformation vibration is at higher frequencies than the out-of-plane vibrations. In the present work, the frequencies observed in the FT-IR spectrum at $1595, 1561, 1480, 1350, 992$ and 720 cm^{-1} have been assigned to C-C stretching vibrations. The same vibrations appear in the FT-Raman spectrum at $1596, 1349$ and 989 cm^{-1} . The theoretically computed values by B3LYP/6-311+G(d,p) method for C-C vibrations are good agreement with FT-IR experimental values.

C-Cl vibrations — Strong characteristic absorption due to C-X stretching vibration is observed and the position of the band is influenced by neighboring atoms or groups the smaller the halide atom the greater the influence of the neighbors. Unlike aliphatic compounds there appears to be no pure C-X stretching vibration band for aromatic halogen compounds. The C-Cl stretching absorption is observed in the broad region between 850 and 550 cm^{-1} . In view of this, the bands in IR at 754 and 741 cm^{-1} having a Raman counterpart at 741 cm^{-1} are assigned to the C-Cl stretching of PDD. The C-Cl in-plane bending modes of the title compound are observed at 421 and 400 cm^{-1} in Raman.

C=O vibrations — The carbonyl stretching vibration C=O is expected in the region $1715\text{-}1680\text{ cm}^{-1}$ and in the present study, the bands observed at 1781 and 1745 cm^{-1} in the Raman spectrum are assigned as C7=O8 and C13=O14 stretching

modes. B3LYP calculations give these modes at 1784 and 1740 cm^{-1} . The mode $\nu_{\text{C}=\text{O}}$ is simultaneously active in IR and Raman spectra which clearly explains a charge transfer between the donor and acceptor through a π -conjugated path. The fundamentals of C=O in-plane and out-of plane bending vibrations are presented in Table 4. These assignments are in good agreement with the literature[25,26] values for heterocyclic compounds.

Conclusion

The pyridine-2,6-dicarbonyl dichloride is of biological and pharmaceutical importance belongs to C_s point group symmetry. The Fourier transforms infrared and Raman spectra of the title molecule were recorded in the region of 4000-400 cm^{-1} and 3500-100 cm^{-1} . The optimized geometrical parameters such as bond lengths, bond angles and dihedral angles were measured by using Gaussian package. Comparison between the calculated and experimental structural parameters indicates that B3LYP results are in good agreement with experimental value. The infrared intensities, Raman activities, reduced masses and force constants of the title compound were determined and the vibrational assignments have been analyzed. The difference between the observed and scaled frequency values of most of the fundamentals is very small. On the basis of agreement between the calculated and observed results, assignments of fundamental vibrational modes of PDD are examined. Therefore, the assignments made at higher level of theory with higher basis set with only reasonable value seem to be correct. From the vibrational discussion, it was concluded that the substitution of H atom by the COCl group distort the ring geometries to small extent and the planarity of the molecule.

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Table 1 — Definition of internal coordinates of pyridine-2,6-dicarbonyl dichloride

No(i)	Symbol	Type	Definition
Stretching			
1-3	r_i	C-H	C3-H10, C4-H11, C5-H12
4-5	R_i	C-C	C2-C7, C6-C13
6-7	P_i	C=O	C7-O8, C13-O14
8-11	q_i	C-C	C2-C3, C3-C4, C4-C5, C5-C6
12-13	t_i	C-Cl	C7-C19, C13-C115
14-15	S_i	C-N	C2-N1, C6-N1
In-plane bending			
16-21	α_i	C-C-H	C2-C3-H10, C4-C3-H10, C3-C4-H11, C5-C4-H11, C4-C5-H12, C6-C5-H12
22-25	β_i	C-C-C	N1-C2-C7, C3-C2-C7, N1-C6-C13, C5-C6-C13
26-27	γ_i	C-C-O	C6-C13-O14, C2-C7-O8
28-29	σ_i	C-C-Cl	C2-C7-C19, C6-C13-C115
30-35	δ_i	Ring	N1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-N1, C6-N1-C2
Out-of-plane bending			
36-38	ω_i	C_{ar} -H	H10-C3-C2-C4, H11-C4-C5-C3, H12-C5-C4-C6
39-40	ω_i	C_{ar} -C	C7-C2-C3-N1, C13-C6-N1-C5
41-42	ω_i	C-O	O8-C7-C2-C3(N1), O14-C13-C6-C5(N1)
43-44	ω_i	C-Cl	C19-C7-C2-C3(N1), C115-C13-C6-C5(N1)
45-50	τ_i	tRing	C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-N1, C5-C6-N1-C2, C6-N1-C2-C3, N1-C2-C3-C4

For numbering of atom refer Fig. 3

Table 2 — Definition of local symmetry coordinates of pyridine-2,6-dicarbonyl dichloride

No(i)	Symbol ^a	Definition ^b
1-3	CH_{ar}	r_1, r_2, r_3
4-5	CC	R_4, R_5
6-7	CO	P_6, P_7
8-11	CC	q_8, q_9, q_{10}, q_{11}
12-13	CCl	t_{12}, t_{13}
14-15	CN	S_{14}, S_{15}
16-18	CCH	$(\alpha_{16}-\alpha_{17})/\sqrt{2}, (\alpha_{18}-\alpha_{19})/\sqrt{2}, (\alpha_{20}-\alpha_{21})/\sqrt{2}$
19-20	CCC	$(\beta_{22}-\beta_{23})\sqrt{6}, (\beta_{24}-\beta_{25})\sqrt{6}$
21-22	CCO	γ_{26}, γ_{27}
23-24	CCCl	$\sigma_{28}-\sigma_{29}$
25-27	Rring	$(\delta_{30}-\delta_{31}+\delta_{32}-\delta_{33}+\delta_{34}-\delta_{35})/\sqrt{6},$ $(-\delta_{30}-\delta_{31}+2\delta_{32}-\delta_{33}-\delta_{34}+2\delta_{35})/\sqrt{12},$ $(\delta_{30}-\delta_{31}+\delta_{33}-\delta_{34})/2,$
28-30	CH	$\omega_{36}, \omega_{37}, \omega_{38}$
31-32	CC	ω_{39}, ω_{40}
33-34	CO	ω_{41}, ω_{42}
35-36	CCl	ω_{43}, ω_{44}
37-39	tring	$(\tau_{45}-\tau_{46}+\tau_{47}-\tau_{48}+\tau_{49}-\tau_{50})/\sqrt{6},$ $(\tau_{45}-\tau_{46}+\tau_{48}-\tau_{50})/2,$ $(-\tau_{45}+\tau_{46}-\tau_{47}-\tau_{48}+2\tau_{49}-\tau_{50})/\sqrt{12}$

^aThese symbols are used for description of the normal modes by PED in Table 4

^bThe internal coordinates used here are defined in Table 2.

Table 3 — Optimized geometrical parameter of pyridine-2,6-dicarbonyl dichloride obtained by HF/6-31+G(d,p) and B3LYP/6-31+G(d,p)

Parameters	Exp ^a	Bond length(Å)		Parameters	Exp ^a	Bond angle(°)		Parameters	Dihedral angle(°)	
		HF	B3LYP			HF	B3LYP		HF	B3LYP
N1-C2	1.340	1.347	1.346	C2-N1-C6	117.3	118.94	119.00	C6-N1-C2-C7	180.00	180.00
N1-C6	1.340	1.347	1.346	N1-C2-C3	123.7	122.43	122.34	C2-N1-C6-C13	180.00	180.00
C2-C3	1.395	1.403	1.401	N1-C2-C7		113.76	113.61	N1-C2-C3-C4	0.0004	0.00
C2-C7		1.491	1.489	C3-C2-C7		123.79	124.04	N1-C2-C3-H10	179.99	180.00
C3-C4	1.394	1.397	1.394	C2-C3-C4	118.51	118.30	118.32	C7-C2-C3-C4	-180.00	-180.00
C3-H10		1.080	1.077	C2-C3-H10		120.50	120.59	C7-C2-C3-H10	-0.00	-0.01
C4-C5	1.394	1.397	1.394	C4-C3-H10		121.18	121.08	N1-C2-C7-O8	0.03	0.00
C4-H11	1.081	1.083	1.079	C3-C4-C5	118.5	119.56	119.67	N1-C2-C7-C19	179.96	179.99
C5-C6	1.395	1.403	1.401	C3-C4-H11	120.2	120.21	120.16	C3-C2-C7-O8	179.96	180.00
C5-H12	1.081	1.080	1.077	C5-C4-H11		120.21	120.16	C3-C2-C7-C19	-0.03	-0.01
C6-C13		1.491	1.489	C4-C5-C6	118.5	118.30	118.32	C2-C3-C4-C5	-0.01	-0.01
C7-O8		1.202	1.193	C4-C5-H12	120.2	121.18	121.08	C2-C3-C4-H11	180.00	179.99
C7-C19		1.909	1.925	C6-C5-H12		120.50	120.59	H10-C3-C4-C5	-180.00	-180.00
C13-O14		1.202	1.197	N1-C6-C5	123.6	122.43	122.34	C3-C4-C5-H12	-180.00	-180.00
C13-C115		1.909	1.925	N1-C6-C13		113.76	113.62	H11-C4-C5-C6	179.99	179.99
				C5-C6-C13		123.79	124.04	C4-C5-C6-C13	-180.00	-180.00
				C2-C7-O8		127.66	128.13	H12-C5-C6-N1	179.99	180.00
				C2-C7-C19		113.73	113.54	H12-C5-C6-C13	-0.01	-0.01
				O8-C7-C19		118.59	118.31	N1-C6-C13-O14	0.04	0.00
				C6-C13-O14		127.66	128.13	N1-C6-C13-C115	179.95	179.99
				C6-C13-C115		113.73	113.54	C5-C6-C13-O14	179.95	180.00
				O14-C13-C115		118.59	118.32	C5-C6-C13-C115	0.03	0.01

^aTaken from Ref. 18**Table 4 — Vibrational assignment of fundamental observed frequencies and calculations frequencies using HF/6-311+G and B3LYP/6-311+G levels with basis sets[Wave number cm⁻¹, IR intensities using(KM mole⁻¹); Raman activity (Normalized to 100) Reduced mass(amu); Force constant(mdyme A⁻¹)]**

No.	Species	Observed frequencies (cm ⁻¹)		Computational frequencies(cm ⁻¹)			IR Intensity		Raman activity		Reduced Mass		Force Constant		Assignments /(%PED)
		IR	Raman	Unscaled		Scaled B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	
				HF	B3LYP										
1	A'	3191w	3188w	327 6	3248	3192	0.00	0.00	108.97	104.97	1.09	1.09	6.93	6.82	vCH (99)
2	A'	3103s	3102s	327 3	3245	3102	2.75	1.39	27.96	27.99	1.09	0.09	6.89	6.77	vCH (99)
3	A'	3020w	3024w	323 5	3206	3022	3.54	4.79	84.42	82.52	1.09	0.09	6.73	6.61	vCH (99)
4	A'	1784vs	1781s	182 7	1807	1784	405.03	436.77	124.88	127.60	13.19	13.18	25.97	25.36	vC=O (98)
5	A'		1745w	182 2	1801	1740	27.09	31.84	73.50	75.94	13.13	13.11	25.69	25.06	vC=O (97)
6	A'	1595vs	1596vs	162 1	1606	1601	19.93	20.86	47.14	48.87	4.74	4.44	7.35	6.76	vC-C (95)
7	A'	1561w		161 0	1592	1565	4.44	3.97	77.83	75.94	5.95	5.54	9.09	8.29	vC-C (95)
8	A'	1480ms		149 7	1487	1478	11.31	10.92	21.52	48.87	2.12	2.07	2.80	2.70	vC-C (94)
9	A'	1448ms	1449ms	143 3	1415	1445	6.61	5.73	3.80	75.45	3.50	3.41	4.23	4.03	vCN (87)
10	A'	1350w	1349w	134 8	1321	1309	0.05	0.03	6.30	25.42	6.62	5.82	7.09	5.99	vC-C (93)
11	A'	1282vs	1288s	127 3	1260	1285	1.38	0.39	73.58	2.08	5.40	5.50	5.16	5.15	δCH (77)

Table 4 — Vibrational assignment of fundamental observed frequencies and calculations frequencies using HF/6-311+G and B3LYP/6-311+G levels with basis sets[Wave number cm^{-1} , IR intensities using(KM mole^{-1}); Raman activity (Normalized to 100) Reduced mass(amu); Force constant(mdyne A^{-1})] — Contd

No.	Species	Observed frequencies (cm^{-1})		Computational frequencies(cm^{-1})			IR Intensity		Raman activity		Reduced Mass		Force Constant		Assignments /(%PED)
				Unscaled		Scaled B3LYP									
		IR	Raman	H F	B3LYP		HF	B3LYP	HF	B3LYP	HF	B3LYP	HF	B3LYP	
21	A'	754w		761	756	758	19.60	18.51	1.70	1.37	1.92	2.01	0.65	0.68	vC-Cl (90)
22	A'	741s	741w	749	748	742	0.00	0.01	5.11	5.12	7.34	7.30	2.42	1.99	vC-Cl (91)
23	A'	720s		740	737	728	371.86	399.35	0.00	0.01	8.02	8.03	2.31	2.26	vC-C (90)
24	A''	660vs		675	672	666	0.39	0.29	17.68	18.92	8.48	8.52	2.28	2.27	γ C=O (58)
25	A'	621w		622	323	620	19.27	16.99	1.18	0.28	7.71	7.64	1.75	1.69	δ C-C (54)
26	A'	560ms	562s	506	508	512	0.38	0.60	1.51	1.60	7.85	7.73	1.18	1.15	δ C-C (55)
27	A''	475ms	475s	496	491	473	6.71	6.10	16.13	18.27	11.46	11.36	1.66	1.61	γ C-C (52)
28	A''		455w	456	451	455	0.00	0.00	1.24	1.09	6.18	6.18	0.75	0.74	γ C-C (50)
29	A'		421w	441	441	420	8.28	7.28	0.11	0.06	4.14	4.15	0.47	0.47	δ C-Cl (54)
30	A''	403vw	400ms	400	388	401	10.56	11.60	8.86	13.45	17.64	17.80	1.66	1.58	γ C=O (51)
31	A'		376ms	384	374	376	44.53	0.03	4.30	5.19	13.92	12.77	1.21	1.05	δ C-Cl (53)