

Computational study of 3-pyridine carboxaldehyde

**SHEENA MARY Y¹, P.S. AMALA DEVI², MANIKANTAN NAIR¹, P. GEETHA³,
HEMA TRESA VARGHESE⁴, K. RAJU¹ and C. YOHANNAN PANICKER^{5*}**

¹Department of Physics, Univeristy College, Thiruvananthapuram (India).

²Department of Physics, S.N.College, Chempazhanthy, Thiruvananthapuram (India).

³Department of Physics, Govt. Arts and Science College, Calicut, Kerala (India).

⁴Department of Physics, Fatima Mata National College, Kollam - 691 001 (India).

⁵Department of Physics, TKM College of Arts and Science, Kollam - 691 005 (India).

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ABSTRACT

The vibrational wavenumbers of 3-pyridine carboxaldehyde were calculated using Gaussian03 software package at different levels and the fundamental modes are assigned. The predicted infrared and Raman activities are reported. The first hyperpolarizability is calculated and the title compound is an attractive object for future studies of non linear optics. The calculated wavenumbers are in agreement with the reported experimental values.

Key words: HF, DFT calculations, hyperpolarizability.

INTRODUCTION

Pyridine has been extensively studied spectroscopically, due to its applications in many chemical structures of high interest in a variety of biomedical and industrial fields.¹ Pyridine has the intrinsic interest of being the azine nearest to benzene. 3-pyridine carboxaldehyde is used in the preparation of 4H-chromines and analogs as activators of caspases and induces apoptosis in human leukemia cells and used as antirheumatic agents, antitumor agents, in the treatment of melanoma, neuroblasoma, insulinoma and colon carcinoma.² The title compound is widely used in the preparation of pyrido[4,3-g]quinoline – a photochromic compound which is useful for recording and as memory materials, light sensitive materials for radar and display devices.³ Nicotinic acid derivatives are used as antipruritic and for the prevention and treatment of acne vulgaris.^{4,5} Jose and Mohan⁶ reported the IR and Raman investigations of the title compound. In the present

study, we have calculated the vibrational wavenumbers by using HF and DFT methods and compared with the reported experimental values.

Computational details

Calculations of the title compound were carried out with Gaussian03 program⁷ using the Hartree-Fock and DFT (B3LYP) levels of theory using the standard 6-31G* set to predict the molecular structure and vibrational wavenumbers. Molecular geometry (Figure 1) was fully optimized by Berny's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minima of the potential surface. The wavenumber values computed contain known systematic errors and hence we have used scaling factors 0.8929 and 0.9613 for HF and DFT methods.⁸ The absence of imaginary wavenumbers of the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy. The

optimized geometrical parameters (DFT) are given in Table 1.

RESULTS AND DISCUSSION

The calculated scaled wavenumbers, experimental wavenumbers given by Jose and Mohan⁶ and the assignments are given in Table 2. The pyridine CH stretching vibrations are usually observed in the range⁹ 3100-3000 cm^{-1} and in the present case the DFT calculations give ν_{CH} in the range 3056-3093 cm^{-1} . Pyridine ring stretching vibrations^{10,11} ν_{Py} occur in the region 1600-1300 cm^{-1} . These modes involve stretching and contraction of all the bonds in the ring and interaction between the stretching modes. The bands at 1584, 1564, 1461, 1419 and 1379 cm^{-1} (DFT) are assigned as ν_{Py} modes. DFT calculations give the ring breathing mode at 1000 cm^{-1} as expected.¹² The pyridine CH in-plane and out-of-plane deformations are assigned at 1262, 1185, 1104, 1026 cm^{-1} and at 997, 967, 928, 814 cm^{-1} , respectively.^{10,11,13}

The aldehyde CH stretching mode¹⁴ is assigned at 2794 cm^{-1} which is expected in the range

2895-2650 cm^{-1} . The aldehyde CH vibrations are assigned at 1316, 939 cm^{-1} and C=O modes are assigned at 1735 cm^{-1} (stretching), 782, 652 cm^{-1} (deformations). The pyridine ring deformations, in-plane, out-of-plane and substituent sensitive vibrations are also identified (Table 2).

Analysis of organic molecules having conjugated π -electron systems and large hyperpolarizability using infrared and Raman

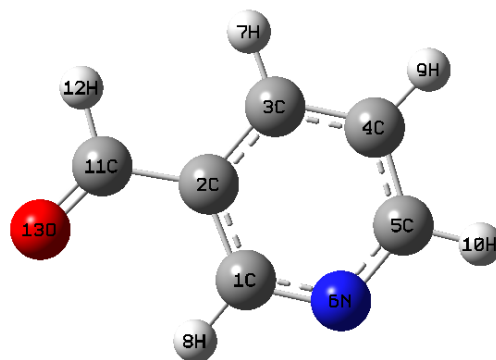


Fig. 1: Optimized geometry

Table 1: Geometrical parameters (DFT) of the title compound

Bond lengths (\AA)		Bond Angles ($^\circ$)		Dihedral Angles ($^\circ$)	
C_1-C_2	1.4046	A(2,1,6)	123.7	D(6,1,2,3)	-0.0
C_1-N_6	1.3341	A(2,1,8)	119.2	D(6,1,2,11)	-180.0
C_1-H_8	1.0876	A(6,1,8)	117.2	D(8,1,2,3)	180.0
C_3-C_2	1.3985	A(1,2,3)	118.2	D(8,1,2,11)	0.0
$\text{C}_{11}-\text{C}_2$	1.4805	A(1,2,11)	120.9	D(2,1,6,5)	0.0
C_3-C_4	1.3919	A(3,2,11)	120.9	D(8,1,6,5)	-180.0
C_3-H_7	1.0884	A(2,3,4)	118.8	D(1,2,3,4)	0.0
C_4-C_5	1.3967	A(2,3,7)	120.2	D(1,2,3,7)	180.0
C_4-C_9	1.0856	A(4,3,7)	121.1	D(11,2,3,4)	180.0
C_5-N_6	1.3423	A(3,4,5)	118.2	D(11,2,3,7)	0.0
C_5-H_{10}	1.0887	A(3,4,9)	121.4	D(1,2,11,12)	-180.0
$\text{C}_{11}-\text{H}_{12}$	1.1133	A(5,4,9)	120.4	D(1,2,11,13)	0.0
$\text{C}_{11}-\text{O}_{13}$	1.2151	A(4,5,6)	124.1	D(3,2,11,12)	0.0
		A(4,5,10)	120.2	D(3,2,11,13)	180.0
		A(6,5,10)	115.8	D(2,3,4,9)	180.0
		A(1,6,5)	117.1	D(7,3,4,5)	180.0
		A(2,11,12)	114.5	D(3,4,5,10)	180.0
		A(2,11,13)	124.6	D(9,4,5,6)	-180.0
		A(12,11,13)	120.8	D(10,5,6,1)	-180.0

spectroscopy has been evolved as a subject of research.¹⁵ The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement, by analyzing the vibrational modes

using the IR and Raman spectrum. The calculated first hyperpolarizability of the title compound is 2.13×10^{-30} esu, which is comparable with the reported values of similar derivatives.¹⁶ We conclude that the title compound is an attractive object for future studies of non linear optics.

Table 2: Calculated (scaled) wavenumbers and assignments

HF/6-31G*			B3LYP/6-31G*			$\nu_{(IR)}$ (cm^{-1})	$\nu_{(Raman)}$ (cm^{-1})	Assign- ments
$\nu(\text{cm}^{-1})$	IR Intensity	Raman Activity	$\nu(\text{cm}^{-1})$	IR Intensity	Raman Activity			
3039	1.58	174.56	3093	14.64	182.97	3091	3091	νCH
3037	20.87	51.02	3078	4.36	54.90			νCH
3013	22.24	82.87	3060	15.07	59.54	3059	3063	νCH
3002	6.52	70.13	3056	10.08	118.45	3035		νCH
2822	111.31	103.98	2794	132.53	121.97	2742	2742	νCH
1792	328.99	63.25	1735	211.53	66.45	1703	1700	νCO
1615	108.50	70.52	1584	66.43	63.53	1584	1584	νPy
1596	34.02	6.60	1564	39.63	20.72	1570	1570	νPy
1472	12.81	0.58	1461	3.93	0.84	1470		νPy
1426	13.30	0.29	1419	7.02	0.68	1428	1428	νPy
1387	20.35	4.74	1379	10.02	5.79	1386	1391	νPy
1321	17.52	1.65	1316	10.85	0.95	1321	1328	δCHO
1199	2.38	5.09	1262	7.10	3.71	1235	1238	δCH
1186	60.92	18.45	1188	44.02	25.68	1214	1214	$\nu\text{CX(X)}$
1134	10.14	10.61	1185	23.83	4.61		1184	δCH
1073	3.46	4.97	1104	6.89	1.21	1107	1110	δCH
1031	0.09	9.89	1026	1.97	22.29	1028	1031	δCH
1025	2.13	18.43	1000	9.54	8.70	1021	1021	νPy
1017	0.53	0.53	997	0.25	7.72			γCH
999	9.76	13.68	967	0.06	0.66			γCH
976	1.08	0.01	939	1.03	1.13			$\nu\text{C-C}$
966	0.15	1.51	928	0.03	2.65			γCH
809	55.29	10.79	814	43.32	10.60	828	828	γCH
803	21.97	0.84	782	17.90	1.81	800	800	$\delta\text{C=O}$
690	38.28	0.26	692	22.13	0.24	700	703	γPy
649	40.75	3.21	652	26.31	4.41	663	663	$\gamma\text{C=O}$
603	3.68	3.78	605	2.46	3.57	621	621	δPy
441	0.03	0.91	435	0.18	6.23	442	435	$\delta\text{Py(X)}$
432	0.39	4.71	429	0.59	1.59			$\gamma\text{Py(X)}$
409	5.30	0.09	393	3.58	0.01			γPy
225	5.64	1.86	225	2.94	1.45			$\delta\text{CC(X)}$
210	7.55	0.43	207	5.63	0.33			$\gamma\text{CC(X)}$
113	8.03	1.77	117	4.38	2.38			$\gamma\text{C(=O)H}$

ν -stretching; δ -in-plane deformation; γ -out-of-plane deformation; Py-pyridine ring; X-Substituent sensitive; IR and Raman spectral data are taken from reference 6.

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