Chapter 10
Theoretical Investigation of the Conformational Stabilities, Internal Rotations, and Vibrational Infrared Spectra of 2-Formylpyridine, 3-Formylpyridine, and 4-Formylpyridine

Yunusa Umar and Jimoh Tijani

Abstract The molecular structures, conformational stabilities, and infrared vibrational wave numbers of 2-formylpyridine, 3-formylpyridine, and 4-formylpyridine have been computed using Becke-3-Lee-Yang-Parr (B3LYP) density functional theory (DFT) method with 6-31+G* basis set. From the computations, 2-formylpyridine and 3-formylpyridine were predicted to exist predominantly in *cis* conformation both in gas and solution phases. The infrared vibrational wave numbers of the molecules in C_s symmetry were computed and compared with the observed infrared vibrational wave numbers. The effect of solvents on the conformational stability of the molecules in nine different solvents was investigated. The Integral Equation Formalism in the Polarizable Continuum Model (IEF-PCM) was used for all solution phase computations.

Keywords Density functional theory · Conformational stability · Vibrational wave numbers · Solvent effect · Formylpyridine

10.1 Introduction

The molecules 2-formylpyridine (picolinaldehyde), 3-formylpyridine (nicotinaldehyde), and 4-formylpyridine (isonicotinaldehyde) are pyridine derivatives that contain an aldehyde (CHO) group, substituted ortho, meta, or para to the nitrogen of a

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Y. Umar (✉)
Department of Chemical and Process Engineering Technology,
Jubail Industrial College, Jubail, Saudi Arabia
e-mail: umar_y@jic.edu.sa; uyunusa@gmail.com

J. Tijani
Department of General Studies, Jubail Industrial College, Jubail, Saudi Arabia
e-mail: jimoht@yahoo.com

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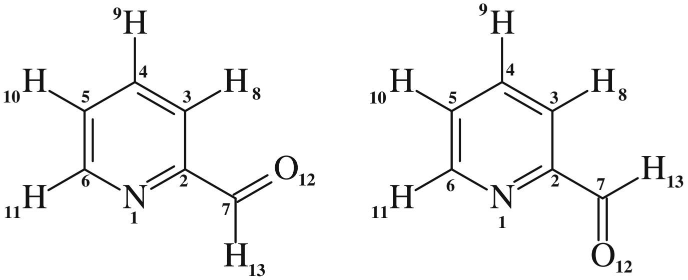
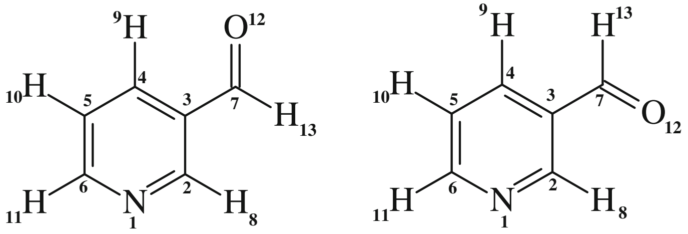


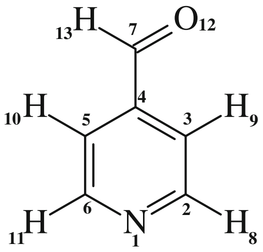
Cis 2-formylpyridine
(ON-*trans*)

Trans 2-formylpyridine
(ON-*cis*)



Cis 3-formylpyridine
(ON-*trans*)

Trans 3-formylpyridine
(ON-*cis*)



4-formylpyridine

Fig. 10.1 Structures and atomic numbering of 2-formylpyridine, 3-formylpyridine, and 4-formylpyridine

pyridine ring. The rotation of the aldehyde group on the pyridine rings of both 2-formylpyridine and 3-formylpyridine leads to two equilibrium configurations. As such, both 2-formylpyridine and 3-formylpyridine can exist in two asymmetric planar rotational conformers whereby the nitrogen and oxygen can be either ON-*cis* or ON-*trans*. On the other hand, 4-formylpyridine has only one conformer as illustrated in Fig. 10.1. Several experimental and theoretical studies examined the conformational preference and vibrational spectra of these molecules [1–4]. A brief summary of the experimental and theoretical studies on conformational preference of the aldehyde group on 2-formylpyridine and 3-formylpyridine has been reported [2, 3].

It is well known that the position of equilibrium between alternative rotational isomers of a particular molecule can be remarkably medium dependent and to the best of our knowledge, computational studies about the effect of solvent on the conformational preference of these molecules have not been reported. The ability to predict the conformational preference and the rotational barrier reliably are of great interest for systems where experimental conformational preference is not clear and is strongly solvent dependent. Such study will contribute to a better understanding of many controversial aspects of their molecular structures, structural stabilities, and vibrational spectra. Thus, the aim of this work is to take advantage of the quantum mechanics to carry out calculations that will aid in clarifying experimental data and contribute to better understanding of the molecular structures and conformational stabilities of the studied molecules. In this study, molecular geometry, potential energy surface, and infrared vibrational spectra of 2-formylpyridine, 3-formylpyridine, and 4-formylpyridine are investigated using the Gaussian 03 program package [5]. Computations were performed at DFT/B3LYP level of theory, which had been previously used successfully in a variety of conformational studies [6–11].

10.2 Computational Methods

GAUSSIAN 03 program package was used to optimize the structures, predict energies, and calculate infrared vibrational wave numbers for 2-formylpyridine, 3-formylpyridine, and 4-formylpyridine in their possible conformations (Fig. 10.1). The *trans* and *cis* conformers of the studied molecules are defined by the position of the carbonyl oxygen atom with respect to the adjacent C–C bond in pyridine ring (Fig. 10.1).

The energies of the possible conformers of the molecules were optimized by Becke's three-parameter exchange functional [12] combined with Lee-Yang-Parr [13] correlation functional (B3LYP) method using the standard 6-31+G* basis set. From the data, the relative conformational stability and the barrier to internal rotation were determined. The infrared vibrational wave numbers were computed and then scaled by 0.955 and 0.967 for wave numbers above 1800 cm^{-1} and below 1800 cm^{-1} respectively [14]. The effect of solvents on the conformational stability of 2-formylpyridine and 3-formylpyridine was investigated using solvents with different polarities. Dielectric constants of 1.92, 4.90, 7.58, 10.36, 20.70, 24.55, 32.63, 46.70, and 78.39 were used as the values for heptane, chloroform, tetrahydrofuran, dichloroethane, acetone, ethanol, methanol, dimethylsulfoxide and water, respectively. The integral equation formalism in the Polarizable Continuum Model (IEF-PCM) [15–17] was used for all solution phase computations.

10.3 Results and Discussion

Generation of potential energy functions from the experimental data is a difficult task, since only conformations near the minima are appreciably populated. The alternative is to carry out accurate computation for appropriate numbers of rotational angles. Therefore, to study the different conformations of the molecules, potential energy scan (PES) for the internal rotation of the aldehyde group about the C–C single bond was performed at B3LYP/6-31+G* level of theory. The rotational energy profiles were obtained by optimizing the total energy at a fixed dihedral angle, and the other parameters were relaxed to their equilibrium values. The torsional angle ϕ(OC-CC) was varied in steps of 15° between $\phi = 0^o$ (*cis* position, where C=O bond eclipses the adjacent C–C bond) to $\phi = 180^o$ (*trans* position, where the C=O bond is anti to the adjacent C–C bond). The adjacent C–C bond refers to C_2–C_3, C_3–C_4, and C_4–C_5 (atoms numbering are given in Fig. 10.1) in 2-formylpyridine, 3-formylpyridine and 4-formylpyridine, respectively. The *cis* and *trans* correspond to ON-*trans* and ON-*cis,* respectively. The saddle points were determined, and full geometry optimization was carried out at the transition state. Figure 10.2 shows the potential energy surface of the three molecules as a function of the dihedral angle (ϕ). All the reported minima along the potential energy surface were subjected to full geometry optimization, and the minimum was verified by calculating the vibrational wave numbers that result in the absence of imaginary

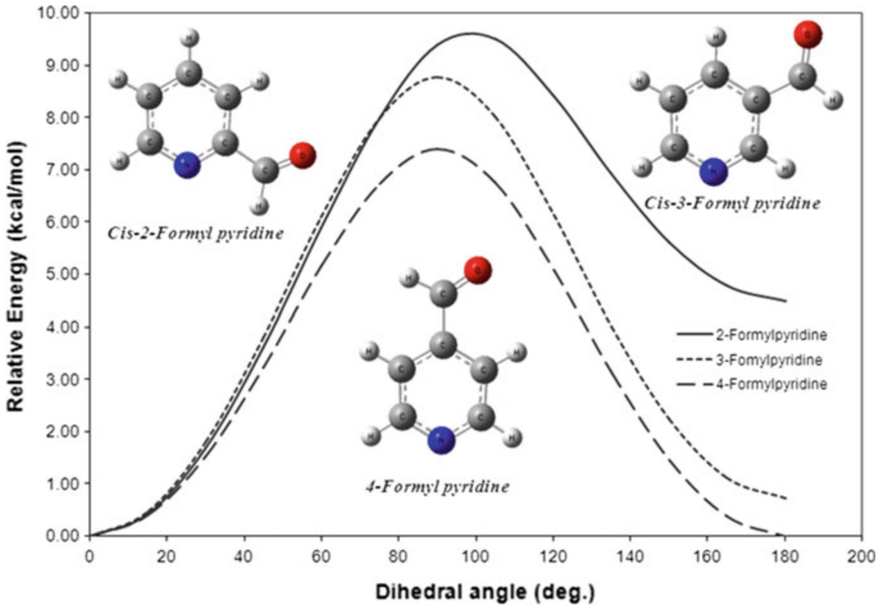


Fig. 10.2 Computed internal rotational potential energy profiles for 2-formylpyridine, 3-formylpyridine and 4-formylpyridine

wave numbers. The lowest energy structure for 2-formylpyridine and 3-formylpyridine was found to be the planar conformer with dihedral angle of zero degree. On the other hand, both conformers of 4-formylpyridine have equal energy due to the symmetry of the molecule. The highest energy structure for the three molecules occurs at dihedral angle close to 90° (referred to as perpendicular structure) which is the transition state with one imaginary infrared vibrational wave number corresponding to the rotation of the aldehyde (CHO) group. The transition states for 2-formylpyridine, 3-formylpyridine, and 4-formylpyridine are located at a dihedral angle (ϕ) of 81.7°, 89.9° and 90.2°, respectively. The trend of the internal rotational barriers is 2-formylpyridine > 3-formylpyridine > 4-formylpyridine. The same trend was observed experimentally [19].

Table 10.1 shows the gas phase computed total energies (hartree), relative energy (kcal/mol), rotational barriers (kcal/mol), and relative stabilization energy of the stable conformers of the studied molecules. The *cis* conformers of 2-formylpyridine and 3-formylpyridine are more stable than their *trans* conformer but the relative energy between the *cis* and *trans* conformer of 2-formylpyridine (4.42 kcal/mol) is higher than the *cis-trans* relative energy of 3-formylpyridine (0.73 kcal/mol). The energies of the conformers have been used to calculate the relative energy ($\Delta E = E_{trans} - E_{cis}$). The *cis-trans* and *trans-cis* rotational barriers of the three pyridine derivatives are presented in Table 10.1.

The relative stabilization energy which is the energy differences between the stable conformers (*cis*) shows that 3-formylpyridine has the smallest energy, followed by 4-formylpyridine and then 2-formylpyridine having the highest energy. These relative stabilization energies of the stable conformers (*cis*) of the studied molecules can be explained in terms of the resonance structures shown in Fig. 10.3.

The conjugations of both 2-formylpyridine (Fig. 10.3a) and 4-formylpyridine (Fig. 10.3c) show destabilizing contributions. In addition, steric effect could

Table 10.1 Computed total energies (hartree), relative energy (kcal/mol), rotational barriers (kcal/mol) and relative stabilization energy of the stable conformers of 2-formylpyridine (2-FP), 3-formylpyridine (3-FP) and 4-formylpyridine (4-FP)

	2-FP	3-FP	4-FP
Cis	−361.7091876	−361.7074841	–361.7055214
Trans	−361.7021433	−361.7063198	–361.7055088
Transition state	−361.6942465	−361.6938526	–361.6940739
Relative energy	4.42	0.73	0.0
Cis-trans barrier	9.38	8.55	7.18
Trans-cis barrier	4.96	7.82	7.18
Relative stabilization energy of the stable conformers	2.62	0.00	0.51
Experimental energy barrier[a]	7.50	7.19	5.90

[a] Taken from Ref. [18]

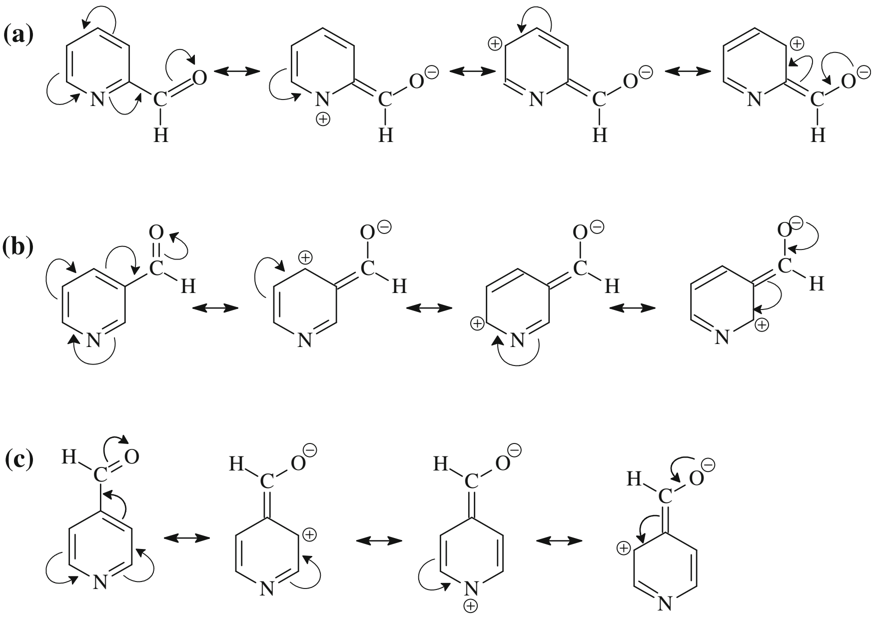


Fig. 10.3 Conjugation in 2-formylpyridine (**a**), 3-formylpyridine (**b**), and 4-formylpyridine (**c**)

contribute to the high energy of 2-formylpyridine. In general, the higher energy of 4-formylpyridine could be due to electronic effect and the higher energy of 2-formylpyridine could be due to both electronic and steric effects.

It is well known that the position of equilibrium between alternative rotational isomers of a particular molecule can be remarkably medium dependent. In order to establish the preferred conformations in solution, IEF-PCM model implemented at the B3LYP/6-31+G* level of theory was used to investigate the conformational preference of 2-formylpyridine and 3-formylpyridine in nine different solvents. Figure 10.4 shows the variation of *cis-trans* relative energy with dielectric constant of solvent obtained from IEF-PCM optimization at B3LYP/6-31+G* level of theory. The relative energy of both molecules decreases with the increase in dielectric constant of solvents. Thus, the *cis* conformer of both 2-formylpyridine and 3-formylpyridine which are more stable in gas phase remained the more stable comformers in solution, but the stability decreases as the dielectric constant of the solvent increases (Fig. 10.4).

The decrease in relative energy of the conformers with solvent dielectric constant may be due to the increase in stability of the *trans* conformer in different solvents, because conformers of higher dipole moment are usually more favored in media of high dielectric constant [19]. The dipole moments of the *trans* conformers of both 2-formylpyridine and 3-formylpyridine are generally higher than the dipole moments of the *cis* conformers and the dipole moments of the *cis* and the *trans*

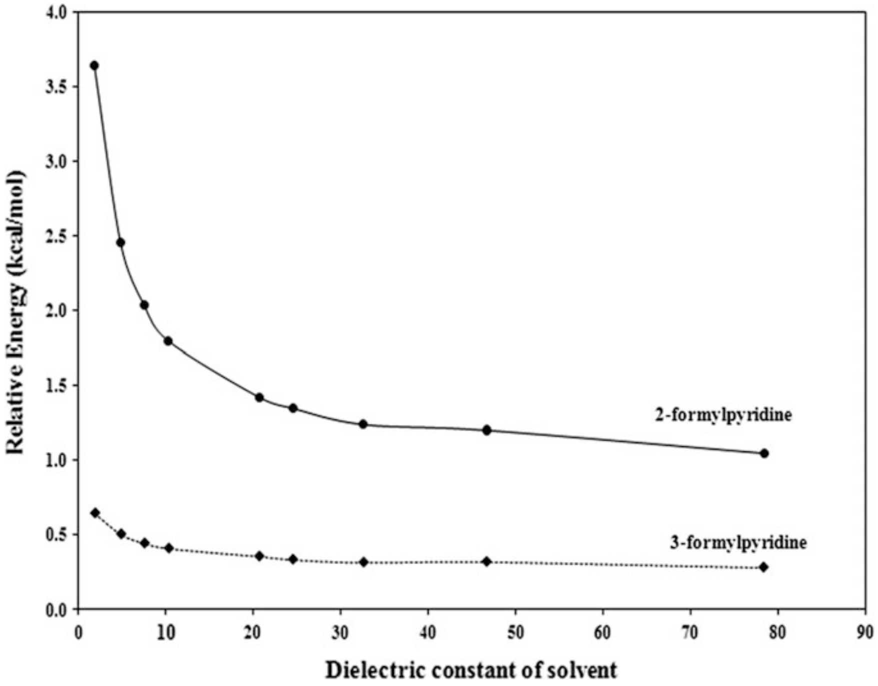


Fig. 10.4 Variation of relative energy with dielectric constant of the solvent

conformers increase with the increase in dielectric constant of the solvent. The variations of the dipole moment as a function of solvent dielectric constant for the *cis* and *trans* conformers of 2-formylpyridine and 3-formylpyridine are presented in Fig. 10.5.

The computed relative energies (kcal/mol) of 2-formylpyridine and 3-formylpyridine in gas and solution phases are provided in Table 10.2. It is interesting to note that the gas phase relative energy for all the molecules are in good agreement with literature values computed at HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory [2]. The percentage of the cis conformers at 298.15 K for 2-formylpyridine and 3-formylpyridine are given in Table 10.2.

Some of the geometry parameters optimized at DFT/B3LYP level of theory for the *cis* 2-formylpyridine in gas phase and different solvents are presented in Table 10.3. There are no systematic and significant changes in the structures of both 2-formylpyridine and 3-formylpyridine in different solvents. The mean absolute deviations (MAD) from the gas phase for the nine solvents are 0.0028 Å for the bond lengths and 0.160° for the bond angles. The individual MAD values for the nine solvents are given in Table 10.3.

The optimized structural parameters were used to compute the infrared vibrational wave numbers and the resulting scaled infrared vibrational wave numbers and

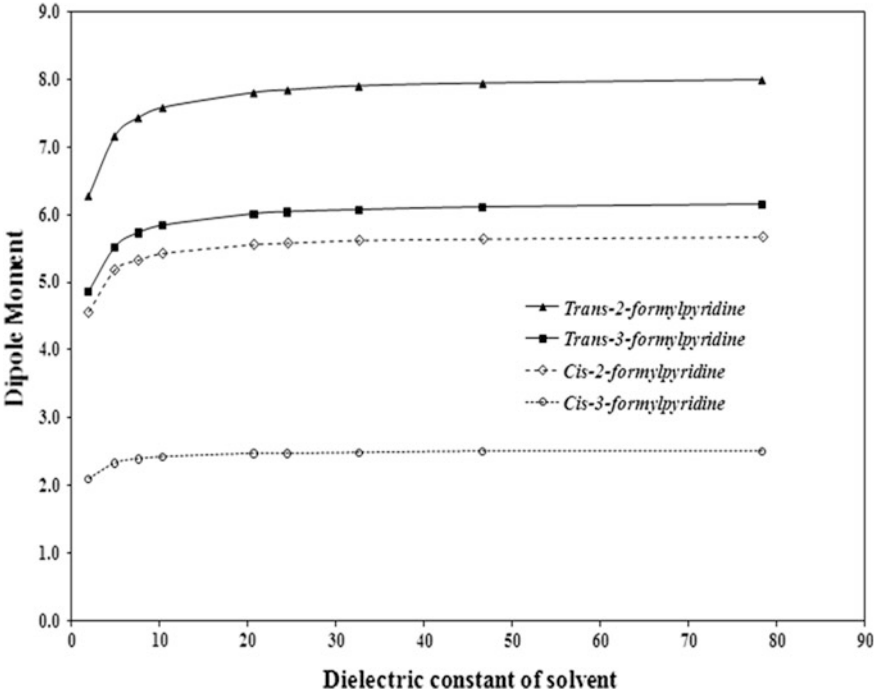


Fig. 10.5 Variation of dipole moment with dielectric constant of the solvent

Table 10.2 Computed relative energy (kcal/mol) of 2-formylpyridine and 3-formylpyridine in gas phase and different solvents

Solvent	Dielectric constant	2-formylpyridine		3-formylpyridine	
		ΔE	% *cis* at 298.15 K	ΔE	% *cis* at 298.15 K
Gas phase	–	4.42	99.9	0.73	77.5
Heptane	1.92	3.64	99.8	0.65	77.0
Chloroform	4.90	2.45	98.4	0.51	70.3
Tetrahydrofuran	7.58	2.04	95.5	0.44	67.8
Dichloroethane	10.36	1.80	91.8	0.41	66.7
Acetone	20.70	1.43	90.8	0.36	64.8
Ethanol	24.55	1.35	89.1	0.34	64.0
Methanol	32.63	1.24	88.4	0.32	63.2
Dimethylsulfoxide	46.70	1.20	88.4	0.32	63.2
Water	78.39	1.05	85.6	0.28	61.6

their intensities are given in Tables 10.4, 10.5 and 10.6. Complete assignments of the vibrational modes of the studied molecules have been reported [2, 3, 20]. Both conformers of the studied molecules belong to C_s symmetry and the 33 vibration modes are accounted by the irreducible representations $\Gamma_{vib} = 23\ A' + 10\ A''$

Table 10.3 Optimized bond lengths (Å), bond angles (°) and dipole moments (μ_t) for *cis* 2-formylpyridine in gas and solution phases

	Gas phase	C_7H_{16}	$CHCl_3$	THF	$C_2H_4Cl_2$	CH_3COCH_3	C_2H_5OH	CH_3OH	DMSO	H_2O
Bond lengths										
N_1–C_2	1.345	1.346	1.347	1.348	1.348	1.349	1.349	1.349	1.349	1.349
C_2–C_3	1.401	1.400	1.400	1.400	1.400	1.400	1.400	1.400	1.400	1.400
C_3–C_4	1.394	1.394	1.395	1.395	1.395	1.395	1.395	1.395	1.395	1.395
C_4–C_5	1.397	1.397	1.397	1.397	1.397	1.397	1.397	1.396	1.396	1.396
C_5–C_6	1.400	1.400	1.401	1.401	1.401	1.401	1.401	1.401	1.401	1.401
C_6–N_1	1.336	1.337	1.337	1.338	1.338	1.338	1.338	1.338	1.338	1.338
C_3–H_8	1.086	1.087	1.088	1.088	1.088	1.087	1.089	1.089	1.089	1.089
C_4–H_9	1.087	1.088	1.089	1.089	1.089	1.090	1.090	1.090	1.090	1.090
C_5–H_{10}	1.086	1.087	1.088	1.089	1.090	1.089	1.089	1.089	1.089	1.090
C_6–H_{11}	1.086	1.090	1.090	1.090	1.090	1.091	1.091	1.091	1.091	1.091
C_2–C_7	1.495	1.490	1.488	1.487	1.487	1.486	1.486	1.486	1.486	1.486
C_7=O_{12}	1.217	1.212	1.222	1.223	1.223	1.224	1.224	1.224	1.224	1.224
MAD		0.0017	0.0023	0.0028	0.0028	0.0031	0.0033	0.0033	0.0033	0.0034
Bond angles										
$N_1C_2C_3$	123.6	123.6	123.5	123.5	123.5	123.5	123.5	123.5	123.5	123.5
$C_2C_3C_4$	118.2	118.3	118.3	118.3	118.3	118.3	118.3	118.3	118.3	118.3
$C_3C_4C_5$	118.6	118.6	118.6	118.6	118.6	118.6	118.6	118.6	118.6	118.6
$C_4C_5C_6$	118.7	118.8	118.8	118.8	118.8	118.9	118.9	118.9	118.9	118.7
$C_5C_6N_1$	123.3	123.2	123.2	123.1	123.2	123.5	123.1	123.1	123.1	123.1
$C_6N_1C_2$	117.5	117.5	117.6	117.6	117.6	117.6	117.6	117.6	117.6	117.6
$C_2C_7O_{12}$	124.1	124.5	124.4	124.5	124.5	124.5	124.5	124.5	124.5	124.5
$C_2C_7H_{13}$	114.0	114.1	114.2	114.3	114.3	114.3	114.3	114.3	114.3	114.4
MAD		0.100	0.162	0.150	0.175	0.175	0.175	0.175	0.163	0.163
Dipole moment										
	4.01	4.56	5.18	5.23	5.42	5.55	5.57	5.61	5.63	5.66

Table 10.4 Calculated infrared vibrational wave numbers (cm^{-1}) of *cis* and *trans* 2-formylpyridine computed at B3LYP/6-31+G* level

Mode	Symmetry	Experiment[a]	*Cis*		*Trans*	
			ν[b]	I_{IR}[c]	ν[b]	I_{IR}[c]
ν_1	A′	3069	3080	3.60	3071	14.21
ν_2	A′	3053	3054	9.93	3046	1.26
ν_3	A′	–	3068	14.74	3059	16.31
ν_4	A′	3009	3038	13.43	3034	16.82
ν_5	A′	2840	2848	7.10	2779	118.41
ν_6	A′	1714	1726	243.88	1744	246.78
ν_7	A′	1584	1577	14.53	1575	6.66
ν_8	A′	1569	1569	10.02	1572	15.65
ν_9	A′	1469	1459	2.14	1462	0.72
ν_{10}	A′	1437	1427	5.61	1426	10.56
ν_{11}	A′	1365	1354	7.48	1389	5.15
ν_{12}	A′	1299	1291	6.13	1295	14.36
ν_{13}	A′	1259	1271	1.90	1277	13.67
ν_{14}	A′	1213	1207	52.5	1180	27.82
ν_{15}	A′	1150	1141	0.51	1144	2.83
ν_{16}	A′	1089	1081	4.80	1089	8.10
ν_{17}	A′	1040	1031	3.58	1034	5.53
ν_{18}	A′	995	980	6.93	984	0.03
ν_{19}	A′	833	817	33.48	828	38.07
ν_{20}	A′	662	655	26.17	663	29.26
ν_{21}	A′	613	604	13.76	610	3.51
ν_{22}	A′	–	450	3.42	428	0.48
ν_{23}	A′	225	214	9.01	216	9.42
ν_{24}	A″	1006	998	2.11	988	1.96
ν_{25}	A″	985	988	0.00	978	7.76
ν_{26}	A″	974	953	0.07	951	0.01
ν_{27}	A″	905	895	0.28	887	0.24
ν_{28}	A″	765	754	55.76	750	55.05
ν_{29}	A″	735	724	0.79	725	4.15
ν_{30}	A″	450	450	1.03	454	1.85
ν_{31}	A″	408	407	7.22	398	3.50
ν_{32}	A″	225	216	10.51	218	3.99
ν_{33}	A″	130	114	4.62	94	2.41
MAD			9.63		13.68	

[a] Taken from Ref. [21]

[b] Scaled IR vibrational wave numbers (scaled with 0.955 above 1800 cm^{-1} and 0.967 under 1800 cm^{-1})

[c] I_{IR}, calculated infrared intensities in km mol^{-1}

Table 10.5 Calculated infrared vibrational wave numbers (cm^{-1}) of *cis* and *trans* 3-formylpyridine computed at B3LYP/6-31+G* level

Mode	Symmetry	Experiment[a]	*Cis*		*Trans*	
			ν[b]	I_{IR}[c]	ν[b]	I_{IR}[c]
ν_1	A′	3085	3075	8.32	3069	14.66
ν_2	A′	3053	3063	7.45	3062	2.71
ν_3	A′	3032	3040	10.51	3042	16.87
ν_4	A′	3000	3024	17.50	3037	3.40
ν_5	A′	2836	2806	101.76	2788	119.76
ν_6	A′	1712	1718	272.81	1723	272.53
ν_7	A′	1587	1586	91.99	1586	77.16
ν_8	A′	1571	1566	18.32	1566	4.86
ν_9	A′	1470	1470	1.48	1464	3.21
ν_{10}	A′	1422	1420	22.64	1423	16.80
ν_{11}	A′	1382	1380	16.69	1380	17.58
ν_{12}	A′	1325	1320	16.89	1322	10.25
ν_{13}	A′	1235	1274	7.63	1267	7.86
ν_{14}	A′	1213	1206	65.16	1191	50.79
ν_{15}	A′	1186	1183	7.88	1189	23.53
ν_{16}	A′	1109	1099	9.13	1108	8.50
ν_{17}	A′	1033	1026	1.92	1028	1.34
ν_{18}	A′	958	981	0.05	978	0.04
ν_{19}	A′	830	818	35.39	815	42.77
ν_{20}	A′	665	660	18.74	654	28.47
ν_{21}	A′	616	608	2.73	607	2.26
ν_{22}	A′	450	440	0.06	436	0.20
ν_{23}	A′	218	207	13.96	206	4.67
ν_{24}	A″	1022	1005	9.73	1004	8.23
ν_{25}	A″	1005	999	1.78	998	1.59
ν_{26}	A″	934	954	0.23	944	0.45
ν_{27}	A″	887	920	0.56	933	0.18
ν_{28}	A″	794	788	25.80	782	26.97
ν_{29}	A″	700	690	27.23	689	28.75
ν_{30}	A″	439	428	0.71	427	0.27
ν_{31}	A″	396	383	1.85	391	4.52
ν_{32}	A″	238	227	8.66	221	3.83
ν_{33}	A″	130	115	10.84	110	5.35
MAD			11.47		13.62	

[a] Taken from Ref. [21]

[b] Scaled IR vibrational wave numbers (scaled with 0.955 above 1800 cm^{-1} and 0.967 under 1800 cm^{-1})

[c] I_{IR}, calculated infrared intensities in km mol^{-1}

Table 10.6 Calculated infrared vibrational wave numbers (cm^{-1}) of 4-formylpyridine computed at B3LYP/6-31+G* level

Mode	Symmetry	Experiment[a]	ν^b	I_{IR}^c
ν_1	A′	3090	3078	3.74
ν_2	A′	3070	3053	16.24
ν_3	A′	3033	3045	22.14
ν_4	A′	–	3037	7.08
ν_5	A′	2835	2805	105.68
ν_6	A′	1712	1728	243.72
ν_7	A′	1591	1587	0.69
ν_8	A′	1565	1562	23.95
ν_9	A′	1489	1480	3.82
ν_{10}	A′	1412	1407	18.75
ν_{11}	A′	1388	1380	9.18
ν_{12}	A′	1321	1312	15.83
ν_{13}	A′	1265	1257	11.39
ν_{14}	A′	1224	1209	18.32
ν_{15}	A′	1190	1180	61.26
ν_{16}	A′	1087	1074	0.76
ν_{17}	A′	1059	1052	5.38
ν_{18}	A′	962	973	0.00
ν_{19}	A′	836	818	15.99
ν_{20}	A′	665	658	1.10
ν_{21}	A′	646	634	37.30
ν_{22}	A′	468	466	17.99
ν_{23}	A′	217	208	9.74
ν_{24}	A″	1005	997	2.07
ν_{25}	A″	962	977	3.32
ν_{26}	A″	907	952	0.06
ν_{27}	A″	876	868	0.15
ν_{28}	A″	805	794	42.86
ν_{29}	A″	726	717	1.32
ν_{30}	A″	431	421	1.75
ν_{31}	A″	377	376	0.03
ν_{32}	A″	–	219	1.30
ν_{33}	A″	126	108	12.43
MAD			11.66	

[a] Taken from Ref. [21]

[b] Scaled IR vibrational wave numbers (scaled with 0.955 above 1800 cm^{-1} and 0.967 under 1800 cm^{-1})

[c] I_{IR}, calculated infrared intensities in km mol^{-1}

of C_s point group. As seen in Tables 10.4 and 10.5, the experimental vibrations are in good agreement with the calculated values of both the *cis* and *trans* conformers of 2-formylpyridine and 3-formylpyridine. The *cis/trans* mean absolute deviation (MAD) between the experimental infrared vibrational wave numbers and the corresponding scaled vibrational wave numbers are found to be 9.63 cm^{-1}/13.68 cm^{-1} and 11.47 cm^{-1}/13.62 cm^{-1} for the 2-formylpyridine and 3-formylpyridine respectively. The vibrational deviations for the *cis* conformers are better than those of *trans* conformers. Thus, the preferential conformers for the 2-formylpyridine and 3-formylpyridine are the *cis* conformers which are in agreement with the calculated relative energies. For 4-formylpyridine, both conformers are equally energetic due to the symmetry of the molecule and the observed vibrations correspond to the average of the conformers. The MAD value of calculated infrared vibrational wave numbers from the experimental wave numbers for 4-formylpyridine is about 11.66 cm^{-1}.

The correlation graphs between computed vibrational [3] and observed wave numbers of the most stable conformers (*cis*) of the studied molecules are presented in Figs. 10.6, 10.7, and 10.8. The correlations reflect a high level of conformity between the harmonic wave numbers obtained from DFT/B3LYP computations [3] and the observed fundamental wave numbers.

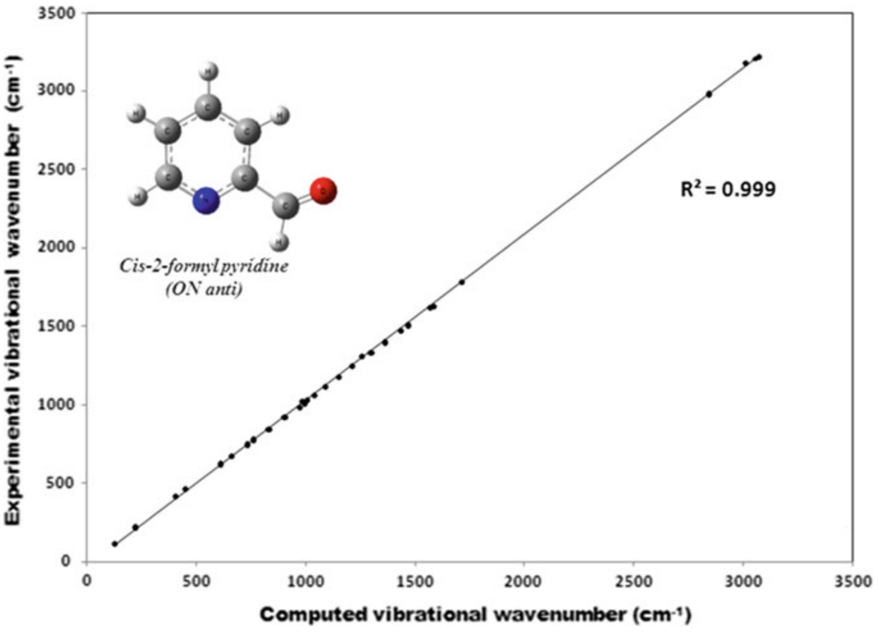


Fig. 10.6 Comparison between the observed and computed infrared vibrational wave numbers of *cis* 2-formylpyridine

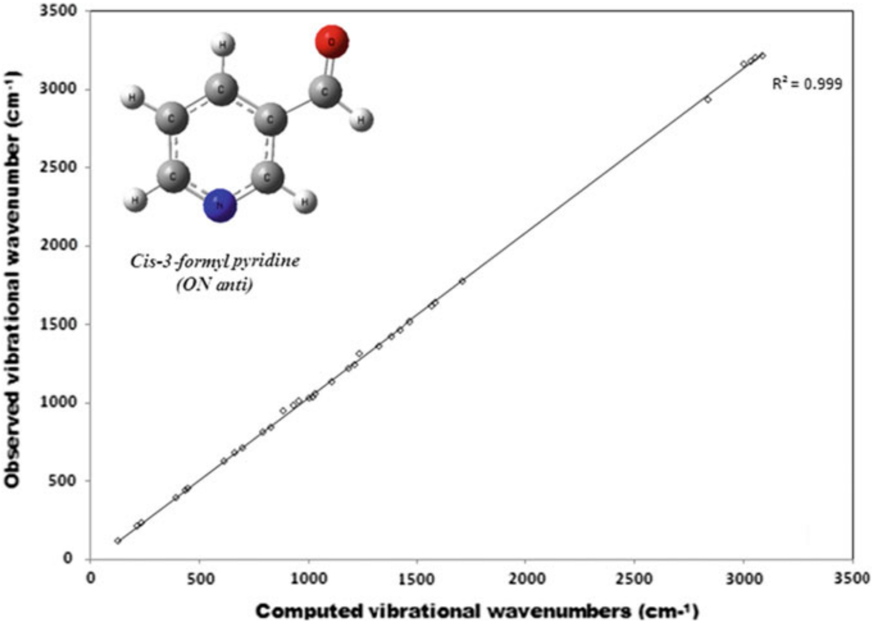


Fig. 10.7 Comparison between the observed and computed infrared vibrational wave numbers of *cis* 3-formylpyridine

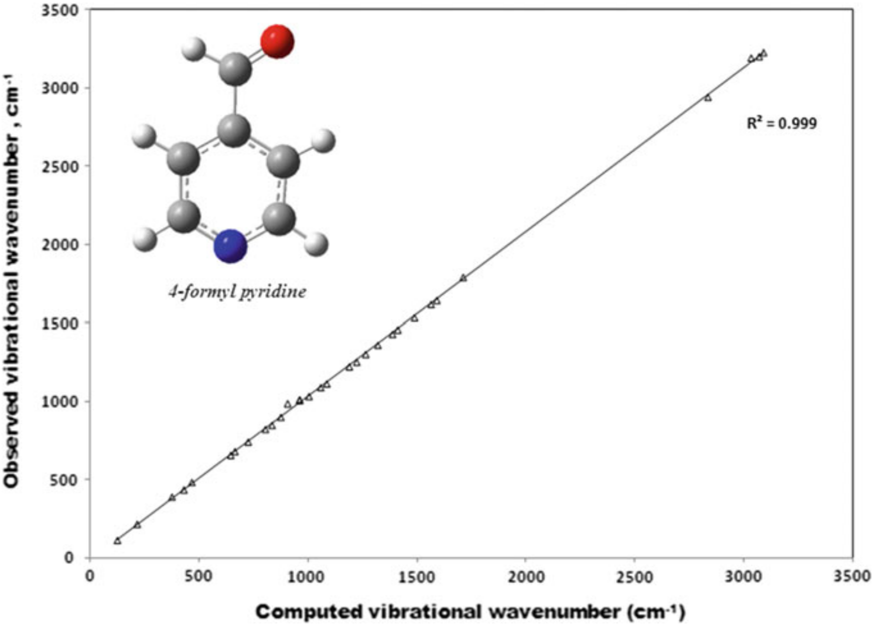


Fig. 10.8 Comparison between the observed and computed vibrational wave numbers of *cis* 4-formylpyridine

10.4 Conclusions

The B3LYP/6-31+G* computations indicate that the internal rotation potential energy profiles of 2-formylpyridine, 3-formylpyridine, and 4-formylpyridine have the same skeleton and the trend of the internal rotational barriers is 2-formylpyridine > 3-formylpyridine > 4-formylpyridine. From the computations, 2-formylpyridine and 3-formylpyridine were predicted to exist predominantly in *cis* conformation with the *cis-trans* rotational barrier of 9.38, 8.55, and 7.18 kcal/mol for 2-formylpyridine, 3-formylpyridine and 4-formylpyridine, respectively. The computations of solvent effects were performed over nine different values of dielectric constant to illustrate the effects of varying dielectric constant using IEF-PCM methods. The *cis* conformer of both 2-formylpyridine and 3-formylpyridine which are more stable in gas phase remain the more stable conformers in solution but the stability decreases as the dielectric constant of the solvent increases. The computed vibrational wave numbers at B3LYP/6-31+G* give a reasonable agreement with the observed vibrational wave numbers.

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