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## VIBRATIONAL AND ELECTRONIC SPECTRAL STUDIES OF *Cis- and trans-PYRAZINECARBOXYLIC ACID*

MANDRU V. S. PRASAD & NEREDIMELLI UDAYA SRI

Molecular Spectroscopy Laboratory, Department of Physics, D.N.R.College BHIMAVARAM, W.G.DT.,  
A.P. INDIA-534202

Email: prasad2008mandru@gmail.com

### 1. Introduction

Crystal engineering of coordination polymers is of intense interest as they may afford new materials with useful properties such as electrical conductivity, non-linear optical activity, micro-porosity, co-operative magnetic behavior etc., [1–4]. Pyrazine is one of the *bridging ligands*. Pyrazine is a weak diacid base due to the induction effect of the second nitrogen. Its inherent bifunctionality and the low lying unoccupied molecular orbital permit pyrazine to form coordination polymers having unusual electrical and magnetic properties [5]. Pyrazines are found mainly in processed food, where they are formed during dry heating processes *via* Maillard reactions [6]. Pyrazine is a much weaker diacid base ( $pK_1 = 0.57$ ) than pyridine ( $pK_2 = -5.51$ ) due to the induction effect of the second nitrogen. Thus it might seem unlikely that the carboxylic acid groups of (*cis* and *trans*) Pyrazinecarboxylic acid (PCA) would be able to transfer a hydrogen to nitrogen to create a zwitterionic form in the solid state. However, no information was available on the possible effect of the carboxyl substituents on the base strength of the ring nitrogens of pyrazine, but, such groups decrease the base strength of pyridine, but increase the base strength of imidazoles. This ambiguity may be solved by the vibrational and electronic spectral analysis of such compounds. Hence, using these powerful spectroscopic techniques one can investigate the structural and molecular properties of biological systems as the spectra produced in these methods has fingerprint information about the molecule. Now-a-days NIR-FT-Raman spectroscopy combined with quantum chemical computations has been recently used as an effective tool in the vibrational analysis of drug molecules, biological compounds and natural products.

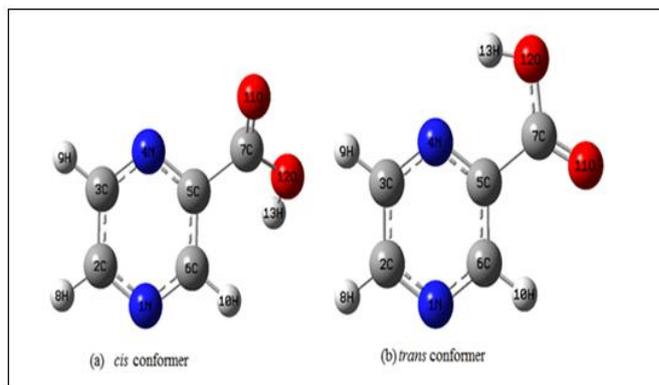
Literature survey reveals that, vibrational and electronic spectra, molecular structure and density functional theoretical studies of pyrazine carboxylic acid are not carried out. In view of this, the present investigation to study the electronic and vibrational spectra is taken up.

### 2. Results and Discussion

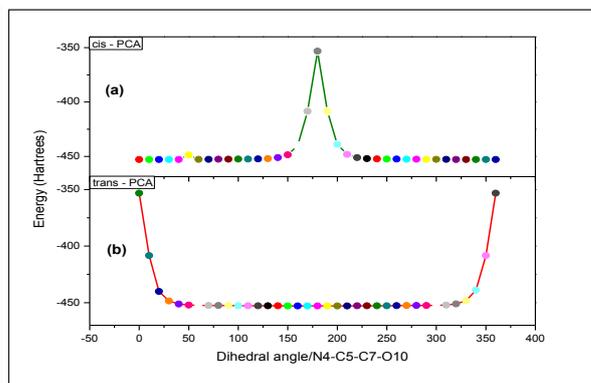
#### 2.1 Molecular geometry

The optimized structures of *cis*-, and *trans*-pyrazine carboxylic acid obtained using B3LYP/6-31G(d,p) basis set are shown in Fig.1. The Cartesian representation of the theoretical force constants has been computed at optimized geometry by assuming  $C_1$  point group symmetry. The optimized structural parameters of both conformers calculated with the same basis set are shown in Table 1 along with the available experimental data [7]. The calculated geometric parameters can be used as foundation to calculate the other parameters for the compound. Since the exact crystal structure of the title compound is not available till now, the optimized structure can only be compared with the other similar system for which the crystal structure has been solved. These molecules have a single phenyl ring with two nitrogen atoms at 1 and 4 positions. The X-

ray data [7,8] shows that the C-C bond lengths are observed in the range 1.38–1.51 Å. For the *cis*-conformer, the optimized C-C bond lengths are calculated to be in the range 1.400–1.512 Å, whereas it is 1.398–1.508 Å in case of *trans*-conformer. The optimized bond lengths of C-N in *cis*-, and *trans*-conformers of the ring are observed between 1.324–1.341 and 1.335–1.340 Å respectively.



**Figure 1. Molecular structure of (a) *cis* and (b) *trans*-pyrazinecarboxylic acid along with numbering of atoms.**



**Figure 2. Potential energy surface scan for dihedral angle N4-C5-C7-O11. of *cis* and (b) *trans*-pyrazinecarboxylic acid**

Several authors have explained the changes in frequency or bond length of the C-H bond on the substitution due to a change in charge distribution on the carbon atom of the aromatic ring [9,10]. In the molecule under study, introduction of carboxylic acid group to the 1, 4-Diazine ring causes some changes in the ring C-C bond distances. The substituents may play a very important role on the structural and electronic properties of the molecules.

Carboxylic group interacts with systems. In general, the interaction can affect regular hexagonal structure, but in present case there is no such effect on the structure due to substitution. The other values show that our calculated results are consistent with the experimental data [7,8]. In order to describe conformational stability of pyrazinecarboxylic acid (PCA), the energy profile as a function of N4-C5-C7-O11 torsion angle is achieved with B3LYP/6-31G(d,p) method for both the conformers. The results are quite complementary. The energy obtained at 180° of dihedral angle for the conformer-1 (*cis*) is maximum (see Fig. 2(a)), whereas the energy obtained for the same dihedral angle of the conformer-2 (*trans*) is minimum (see Fig. 2(b)), which is the global minima for of pyrazinecarboxylic acid (PCA). This reveals that the *trans*-conformer is the most stable conformer.

The energy barrier may be due to the steric interactions (due to closely occupation or overlap of atoms) between the  $\pi$  electrons. It is clear from Fig 4.2, there are two local minima observed at 0° and 360° for conformer-1, but it is only one in case of conformer-2. The minimum energy values for conformer-1 and conformer-2 are -452.85436570 (at 0°) and -452.8696471 (at 180°) Hartrees respectively.

Table 1: Optimized geometrical parameters of *cis*- and *trans*-pyrazinecarboxylic acid obtained by DFT /B3LYP/6-31G(d,p) method.

	Bond length (Å) <sup>a</sup>				Bond angle (°) <sup>a</sup>				
	Cis	Trans	Exp <sup>b</sup>	Exp <sup>c</sup>	Cis	Trans	Exp <sup>b</sup>	Exp <sup>c</sup>	
N1-C2	1.334	1.338	1.32	1.33	C2-N1-C6	117.7	116.3	116.5	120.1
N1-C6	1.338	1.337	1.34	1.34	N1-C2-C3	120.4	122.3	122.9	119.0
C2-C3	1.400	1.398	1.37	1.38	N1-C2-H8	118.2	117.0	-	120.4

C2-H8	1.088	1.088	0.93	0.94	N1-C6-C5	120.4	121.6	122.9	118.7
C3-N4	1.324	1.335	1.33	1.32	N1-C6-H10	118.2	118.2	-	120.5
C3-H9	1.088	1.087	0.93	0.95	C3-C2-H8	121.5	120.7	-	120.4
N4-C5	1.341	1.340	1.34	1.34	C2-C3-N4	122.7	121.2	120.4	122.6
C5-C6	1.400	1.398	1.39	1.37	C2-C3-H9	119.7	121.4	-	118.6
C5-C7	1.512	1.508	1.51	1.50	N4-C3-H9	117.7	117.4	-	118.6
C6-H10	1.089	1.086	0.93	-	C3-N4-C5	116.2	116.8	117.7	116.7
C7-O11	1.201	1.209	1.26	1.19	N4-C5-C6	122.7	120.6	120.5	122.5
C7-O12	1.362	1.343	-	1.32	N4-C5-C7	117.7	121.9	115.9	116.6

Table 2: Definition of internal coordinates of cis and trans-pyrazinecarboxylic acid.

NO. (i)	Symbol	Type	Definition
<b>STRETCHING</b>			
1 to 4	$R_i$	NC	N1-C2, C3-N4, N4-C5, C6-N1.
5 to 7	$R_i$	CC	C2-C3, C5-C6, C5-C7.
8 to 10	$R_i$	CH	C6-H10, C2-H8, C3-H9.
11 to 12	$R_i$	CO	C7-O11, C7-O12.
13	$R_i$	OH	O12-H13
<b>IN PLANE BENDING</b>			
14 to 19	$\gamma_i$	Ring	N1-C2-C3, C2-C3-N4, C3-N4-C5, N4-C5-C6, C5-C6-C1, C6-C1-C2,
20 to 25	$\gamma_i$	CH	N1-C6-H10, C5-C6-H10, C2-C3-H9, N4-C3-H9, N1-C2-H8, C3-C2-H8,
26 to 27	$\gamma_i$	CC	C6-C5-C7, N4-C5-C7,
28 to 30	$\gamma_i$	CO	O12-C7-O11, C5-C7-O11, C5-C7-O12
31		OH	C7-O12-H13
<b>OUT-OF-PLANE BENDING</b>			
32 to 34	$\omega_i$	CH	H8-C2-C3-N1, H9-C3-C2-N4, H10-C6-C5-N1
35	$\omega_i$	CC	C7-C5-C6-N4
36	$\omega_i$	CO	C5-C7-O11-O12
<b>TORSION</b>			
37 to 42	$\omega_i$	Ring	N1-C2-C3-N4, C2-C3-N4-C5, C3-N4-C5-C6, N4-C5-C6-N1, C5-C6-N1-C2, C6-N1-C2-C3,
43 to 44	$\tau_i$	CO	C6-C5-C7-O11, N4-C5-C7-O12
45 to 46	$\tau_i$	CH	C5-C7-O12-H13, O11-C7-O12-H13

## 2.2 Assignments of spectra

The molecule belongs to  $C_1$  point group of symmetry. The 33 modes of PCA span the representations as 23 in-plane and 10 out-of-plane vibrations. All vibrations are active in both the Raman and infrared absorption. A detailed description of vibrational modes is given by means of normal coordinate analysis (NCA). For this purpose, the full set of standard internal coordinates for PCA, are defined as given in Table 2. A non redundant set of local symmetry coordinates are constructed by suitable linear combinations of internal coordinates, which are summarized in Table 3.

### C-H vibrations

Aromatic compounds commonly exhibit multiple weak bands in the region of  $3100 - 3000 \text{ cm}^{-1}$  due to aromatic C-H stretching vibration [11]. In the FT-IR spectrum of pyrazinecarboxylic acid (PCA), there are three medium strong to strong bands observed at  $3093, 3060$  and  $3031 \text{ cm}^{-1}$ . And in the FT-Raman spectrum, only

two bands with weak to very strong intensity are observed at 3095 and 3068  $\text{cm}^{-1}$  which are assigned to C-H stretching of PCA.

The calculated three modes of C-H stretching vibrations are assigned at 3087, 3071 and 3058  $\text{cm}^{-1}$  respectively for conformer-1 and conformer-2 with an exception of the mode 3052  $\text{cm}^{-1}$  and as shown in Table 4.4 with a PED contribution of ~99% indicating that the modes are purely due to stretching vibrations. The bands, due to C-H in-plane bending vibrations, coupled with C-C stretching vibrations, are observed as a number of bands in the region 1500–1100  $\text{cm}^{-1}$ . The C-H out-of-plane bending vibrations occur in the region 1000–800  $\text{cm}^{-1}$ . In this region; the bands are not affected appreciably by the nature of the substituents.

For pyrazinecarboxylic acid (PCA), the C-H in-plane bending vibrations are observed at 1444, 1394 and 1309  $\text{cm}^{-1}$  in FT-IR; and at 1463, 1398 and 1282  $\text{cm}^{-1}$  in FT-Raman spectra respectively. The frequencies calculated by DFT method in the ranges 1463–1282  $\text{cm}^{-1}$  (three modes) and 1448–1316  $\text{cm}^{-1}$  (three modes) are assigned to C-H in-plane bending vibration for conformer-1 and conformer-2 respectively, which are well correlated with the experimental frequencies. The C-H out-of-plane bending vibrations are predicted in the regions 954–850  $\text{cm}^{-1}$  and 995–880  $\text{cm}^{-1}$  for conformer-1 and conformer-2 respectively, which are coinciding well with the observed frequencies of FT-IR spectrum at 956 and 821  $\text{cm}^{-1}$ . Their counterparts in FT-Raman spectrum are observed at 962 and 827  $\text{cm}^{-1}$ . The PED contribution of C-H out-of-plane bending is ~90% for pure modes and ~60% for mixed modes (with ring torsion).

#### **C-C vibrations**

The C–C stretching modes of the phenyl group are expected in the range from 1625–1430  $\text{cm}^{-1}$  [12]. In pyrazinecarboxylic acid (PCA), there are two C-C stretching modes in pyrazine ring and one mode outside the ring, consequently there will be three stretching modes. The strong mode observed in FT-Raman spectrum at 1594  $\text{cm}^{-1}$  (mode no. 6) and very strong modes (mode nos. 9 and 11) appearing at 1398 and 1272  $\text{cm}^{-1}$  in FT-IR spectrum and 1394  $\text{cm}^{-1}$  in FT-Raman spectrum were assigned to C-C stretching vibration mode. The calculated modes observed at 1558, 1388 and 1261  $\text{cm}^{-1}$  (mode nos. 6, 9 and 11) in conformer-1 which are mixed with  $\beta\text{CH}$  and  $\beta\text{COH}$  are assigned to the C–C stretching frequency. The same vibrations at mode no. 9, 12 and 13 at 1560, 1244 and 1199  $\text{cm}^{-1}$  are assigned for conformer-2. The C-C in-plane and out-of-plane vibrations are observed at lower frequency range.

#### **C=O vibrations**

Owing to the electronegativity differences between the carbonyl carbon and nitrogen atom of pyrazine ring, the C=O bond has a large dipole moment. The C=O stretching vibration band can be easily identified from the IR and Raman spectra, and because of the degree of conjugation, the strength and polarizations are increasing. The carbonyl stretching vibrations in carboxyl group are expected in the region 1715–1680  $\text{cm}^{-1}$  [13]. For the PCA molecule, the C=O stretching band with strong intensity is observed at 1710  $\text{cm}^{-1}$  in both FT-IR and FT-Raman spectra. The calculated C=O stretching mode is assigned at 1724, and 1717  $\text{cm}^{-1}$  for conformer-1 and conformer-2 respectively. Since the C=O group is a terminal group, only the carbon is involved in a second chemical bond. This reduces the number of force constants determining the spectral position of the vibrations. The carbon–oxygen double bond is formed by  $\pi$ – $\pi$  bonding between carbon and oxygen. Because of the different electronegativities of the carbon and oxygen atoms, the bonding electrons are not equally distributed between the two atoms. The conjugation of C=O bond with C-O may increase its single bond character resulting in lowered values of carbonyl stretching wavenumbers. In the present study, we can expect one C-O stretching vibration observed at 1054  $\text{cm}^{-1}$  in both FT-IR and FT-Raman spectra. The bond associated with the C=O stretching mode is found to be strongly and simultaneously active in both IR and Raman spectra. Computed wavenumbers by B3LYP/6-31G(d,p) method at 1046 and 1070  $\text{cm}^{-1}$  are assigned to conformer-1 and conformer-2 respectively.  $\text{CO}_2$  scissoring mode vibrations in conformer-1 and conformer-2 are assigned at 631 and 556  $\text{cm}^{-1}$  respectively. The rocking mode of  $\text{CO}_2$  was assigned at 129 and 178  $\text{cm}^{-1}$ .

respectively for conformer-1 and conformer-2. The CO<sub>2</sub> torsion vibration of conformer-1 and conformer-2 are assigned at 65 cm<sup>-1</sup>.

Table 3: Definition of local-symmetry coordinates and the values of corresponding scale factors used to correct the B3LYP/6-31G(d,p) (refined) force field of *cis* and *trans*-pyrazinecarboxylic acid.

No.(i)	Symbol <sup>a</sup>	Definition <sup>b</sup>	Scale factors	
			CIS	TRANS
<b>STRETCHING</b>				
1-4	vNC	R <sub>1</sub> , R <sub>2</sub> , R <sub>3</sub> , R <sub>4</sub>	0.902	0.922
5-7	vCC	R <sub>5</sub> , R <sub>6</sub> , R <sub>7</sub>	0.902	0.022
8-10	vCH	R <sub>8</sub> , R <sub>9</sub> , R <sub>10</sub>	0.922	0.912
11-12	vCO	(R <sub>11</sub> + R <sub>12</sub> )/√2, (R <sub>11</sub> - R <sub>12</sub> )/√2	0.880	0.890
13	vOH	R <sub>13</sub>	0.922	0.912
<b>IN PLANE BENDING</b>				
14-16	βRtri	(Y <sub>14</sub> - Y <sub>15</sub> + Y <sub>16</sub> - Y <sub>17</sub> + Y <sub>18</sub> - Y <sub>19</sub> )/√6	0.985	0.935
	βRsym	(Y <sub>15</sub> - Y <sub>16</sub> + Y <sub>18</sub> - Y <sub>19</sub> )/2	0.985	0.935
	βRasy	(2 Y <sub>14</sub> - Y <sub>15</sub> - Y <sub>16</sub> +2 Y <sub>17</sub> - Y <sub>18</sub> - Y <sub>19</sub> )/√12	0.985	0.935
17-19	βCH	(Y <sub>20</sub> - Y <sub>21</sub> )/√2, (Y <sub>22</sub> - Y <sub>23</sub> )/√2, (Y <sub>24</sub> - Y <sub>25</sub> )/√2	0.940	0.950
20	βCC	(Y <sub>26</sub> - Y <sub>27</sub> )/√2	0.940	0.950
21	CO2sci	(2Y <sub>28</sub> -Y <sub>29</sub> -Y <sub>30</sub> )/√6,	0.890	0.930
22	CO2roc	(Y <sub>29</sub> -Y <sub>30</sub> )/√2	0.890	0.930
23	bCOH	Y <sub>31</sub>	0.940	0.950
<b>OUT-OF-PLANE BENDING</b>				
24-26	ω CH	ω <sub>32</sub> , ω <sub>33</sub> , ω <sub>34</sub>	0.930	0.970
27	ω CC	ω <sub>35</sub>	0.930	0.970
28	CO2wag	ω <sub>36</sub>	0.980	0.950
<b>TORSION</b>				
29-31	τ Rtri	(τ <sub>37</sub> - τ <sub>38</sub> + τ <sub>39</sub> - τ <sub>40</sub> + τ <sub>41</sub> - τ <sub>42</sub> )/√6	0.940	0.960
	τ Rsym	(τ <sub>37</sub> - τ <sub>39</sub> + τ <sub>40</sub> - τ <sub>42</sub> )/2	0.940	0.960
	τ Rasy	(- τ <sub>37</sub> + 2 τ <sub>38</sub> - τ <sub>39</sub> - τ <sub>40</sub> +2 τ <sub>41</sub> - τ <sub>42</sub> )/√12	0.940	0.960
32	tCO2	(τ <sub>43</sub> + τ <sub>44</sub> )/2	0.955	0.935
33	tCH	(τ <sub>45</sub> + τ <sub>46</sub> )/2	0.800	0.850

<sup>a</sup> These symbols are used for description of the normal modes by PED in Table 4

<sup>b</sup> The internal coordinates used here are defined in Table 2

### O-H Vibrations

The O–H stretching vibrations are sensitive to hydrogen bonding. The non-hydrogen bonded or free hydroxyl group absorbs strongly in the 3600–3550 cm<sup>-1</sup> region. The existence of an intermolecular hydrogen bond can lower the O–H stretching wavenumber to 3550–3200 cm<sup>-1</sup> region with the increase in IR intensity [13,14]. The lone pair of nitrogen atoms in pyrazine ring can possibly point towards the adjacent hydroxyl group, forming intramolecular chelation. The computed results suggest the possibility of intramolecular effects. The O–H (O12–H13) bond distance in the *cis*- and *trans*-conformers of the present compound is observed as 0.971 and 0.982 Å respectively. The O–H···N bond (N4–H13) distance observed only in *trans*-conformer as 2.024 Å. The band due to the O–H stretching is of weak intensity in the infrared spectrum, although it may be broad. In Raman spectra no band is observed in the expected region. Unassociated hydroxyl group absorb strongly in the region 3670–3580 cm<sup>-1</sup>. The band due to the free hydroxyl group is

sharp and its intensity increases. For solids, a broad band of less intensity is normally observed [15,16]. In this case, the broad band observed in FT-IR spectrum at  $3440\text{ cm}^{-1}$  is assigned to O–H stretching vibrations. A comparison of this band with that of the calculated value of  $3599\text{ cm}^{-1}$  by B3LYP method deviating approximately by  $\sim 160\text{ cm}^{-1}$  for *cis*-conformer may be due to intramolecular hydrogen bond. The same band in *trans*-conformer was observed at  $3405\text{ cm}^{-1}$ . The PED corresponding to this vibration suggests that it is a pure mode and exactly contributing to 100%.

The O–H in-plane bending vibration for phenyl, in general lies in the region  $1150\text{--}1250\text{ cm}^{-1}$  and it is not much affected due to hydrogen bonding unlike that of stretching and out-of-plane bending wavenumber [17]. For pyrazinecarboxylic acid (PCA), the O–H in-plane bending vibration appears as a weak band in FT-IR spectrum at  $1272\text{ cm}^{-1}$ . The theoretically computed wavenumbers by B3LYP/6-31G(d,p) method show good agreement with experimental observation at 1261 and  $1263\text{ cm}^{-1}$  respectively for *cis*- and *trans*-conformers. As revealed by PED, the O-H in-plane bending vibration has  $\sim 67\%$  contribution to the band predicted at  $1272\text{ cm}^{-1}$  as shown in Table 4.4.

Table 4: Detailed assignments of fundamental vibrations of *cis* and *trans*-pyrazinecarboxylic acid by normal mode analysis based on SQM force field calculations using B3LYP/6-31G(d,p)

S.No	Experiment al( $\text{cm}^{-1}$ )		Cis-PCA			Trans-PCA			Characterization of normal modes with PED(%) <sup>d</sup>	
	FT-IR	FT-Raman	Scaled freq. ( $\text{cm}^{-1}$ )	Intensity	$I_{IR}^b$	$I_{RA}^c$	Scaled freq. ( $\text{cm}^{-1}$ )	Intensity		$I_{IR}^b$
1	3440w	-	3599	0.114	13.7	vOHsub(100)	3405	0.244	5.23	vOHsub(100)
2	3093ms	3095w	3087	0.116	99.5	vCH(99)	3087	0.006	18.5	vCH(99)
3	3060s	3068vs	3071	0.034	48	vCH(99)	3071	0.061	32.5	vCH(99)
4	3031ms	-	3058	0.084	41.2	vCH(99)	3052	0.008	16.4	vCH(99)
5	1710s	1710s	1724	1	96.8	CO2(56),CO1(22)	1717	0.442	30.3	CO2(63), CO1(19)
6	-	1594s	1558	0.009	68.4	vCC(36),βCH(27)	1560	0.009	21.6	vCC(45), vNC(27), βCH(20)
7	1531ms	1533vs	1534	0.013	47.1	vNC(70),βCH(12)	1526	0.004	16.6	vNC(81)
8	1444w	1463vw	1457	0.016	2.36	βCH(58),vNC(28)	1448	0.013	1.84	βCH(52), vNC(35)
9	1394vs	1398vw	1388	0.068	4.34	βCH(68),vCC(18),vNC(11)	1389	0.124	4.68	βCH(42), vCC(34), vNC(11)
10	1309vs	1282s	1291	0.277	22.6	βCH(52),vNC(20),vCC(11)	1316	1	10	βCOH(63), CO2(15)
11	1272vs	-	1261	0.991	34.8	βCOH(25),vCC(24),βCH(15)	1263	0.019	8.77	βCH(67), vNC(24)
12	-	-	1206	0.472	18.9	vNC(51),Rtri(20)	1244	0.021	1.89	vNC(70), vCC(26)
13	1174vs	1174ms	1175	0.087	4.62	βCOH(75),vCC(20)	1199	0.005	42.5	vCC(29), vNC(22), βCH(20)
14	1155vs	1159ms	1152	0.07	33.4	vNC(43),vCC(25),βCH(23)	1150	0.053	5.72	βCH(44), vNC(35), vCC(12)
15	1054vs	1054ms	1046	0.49	86.4	CO1(27),vCC(23),CO2(16)	1070	0.053	8.29	CO1(42), CO2(20), βCH(14)
16	1018vs	1020vs	1043	0.411	66.4	Rtri(49),vNC(23),vCC(12)	1038	0.041	15	vCC(29), vNC(29), CO1(20)
17	-	-	1004	0.165	51.8	CO1(30),vNC(23),CO2(17)	995	0.002	1.69	ωCH(91)
18	956ms	962vw	954	0.004	4.75	ωCH(90)	976	0.002	4.52	ωCH(86), τRtri(12)
19	-	-	928	0.037	16.8	ωCH(91)	909	0.088	9.39	Rtri(66), vNC(12), vCC(11)
20	821vs	827ms	850	0.021	4.98	ωCH(61),τRtri(16)	880	0.017	1.49	ωCH(75)
21	784vs	788vw	801	0.047	65	Rasy(41),vCC(18),CO1(14)	786	0.014	6.36	CO2wag(37), τRtri(21), ωCH(21)
22	-	-	772	0.078	15.4	ωCH(31),CO2wag(27),τRtri(24)	732	0.011	18.3	Rasy(30), vCC(30), Rtri(20)
23	723ms	711vw	721	0.014	3.34	τRtri(70),CO2wag(14)	712	0.003	2.73	τRtri(76), CO2wag(11)
24	659vw	646w	658	0.036	29.3	Rsym(50),CO2sci(21)	641	0.027	0.69	τCH(96)
25	617vw	-	631	0.036	20.2	CO2sci(29),Rsym(26),Rasy(22)	556	0.015	16.5	Rsym(57), CO2sci(18)
26	501s	507vw	507	0.008	9.66	CO2roc(25),ωCC(20),τRsym(19)	498	0.014	6.97	Rasy(37), CO2sci(23), Rsym(23)
27	441s	-	451	0.396	28.8	τCH(88)	437	0.046	1.05	τRsym(33), τRasy(29), ωCC(23)
28	406ms	406ms	406	0.14	9.32	τRasy(71),ωCH(13)	408	0.021	7.75	CO2roc(45), βCC(33)
29	-	-	363	0.011	74	vCC(32),CO2sci(30),Rasy(15)	378	0.003	0.75	τRasy(48), τRsym(23), ωCC(18)
30	-	-	349	0.027	21.2	τRsym(37),ωCC(20),τRasy(14)	323	0.002	29	CO2sci(67), Rasy(13), vCC(10)
31	-	194s	200	0.342	39.9	βCC(57),CO2roc(19)	178	0.035	17.1	βCC(44), CO2roc(40)
32	-	129s	133	0.015	50.2	τRsym(37),ωCC(32),CO2roc(14)	154	0.005	99.2	τRsym(46), ωCC(32)
33	-	-	65	0.017	89.5	τCO2(82)	65	0.002	34.2	τCO2(71), τCH(24)

<sup>b</sup> Relative absorption intensities normalized with highest peak absorption equal to 1.

<sup>c</sup> Relative Raman intensities calculated ( by Eq. 2.51 in Ch.2) and normalized to 100.

<sup>d</sup> Only PED contributions  $\geq 10\%$  are listed

The ring vibrations of PCA are mixed modes which are difficult to predict the exact wave number. In pyrazinecarboxylic acid (PCA) ring trigonal deformation mode is observed 723 and 711 in FT-IR and FT-Raman respectively. The ring symmetrical and asymmetrical bending vibrations are observed at 659, 406  $\text{cm}^{-1}$  in FT-IR and at 646 and 406  $\text{cm}^{-1}$  in FT-Raman spectra respectively. The calculated modes are correlated with these modes of recorded spectra.

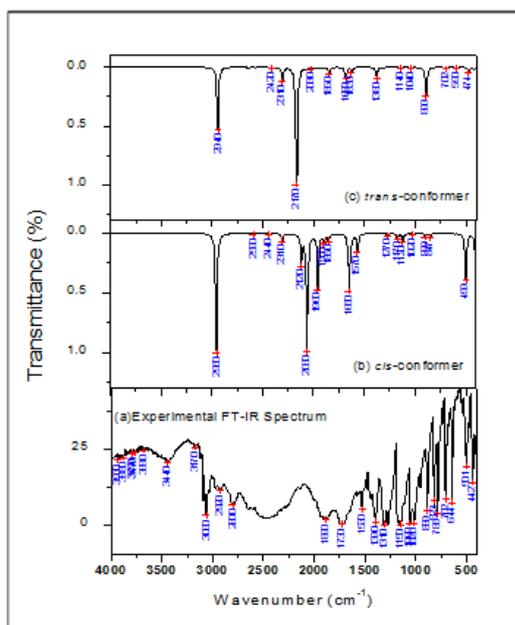


Fig 3 (a) Experimental FT-IR spectra and simulated FT-IR spectra of (b) *cis*- and (c) *trans*- pyrazinecarboxylic acid

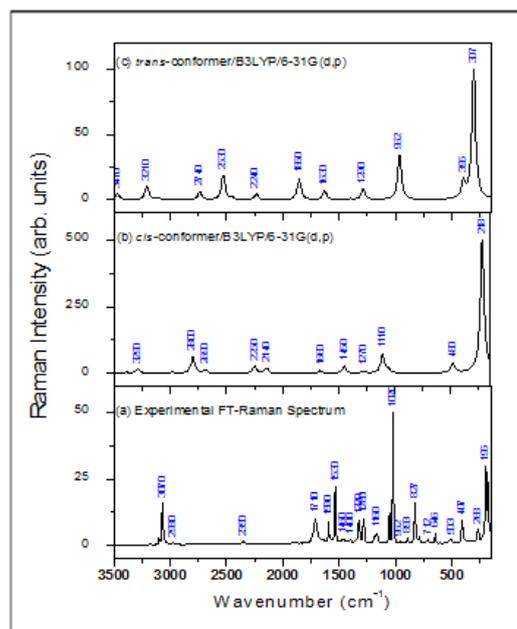


Fig 4 (a) Experimental FT-Raman spectra and simulated FT-Raman spectra of (b) *cis*- and (c) *trans*- pyrazinecarboxylic acid

We know that the DFT potentials systematically overestimate the vibrational wave numbers. These discrepancies are corrected by scaling the wavenumber with the proper scaling factor. After scaling, the deviation from experimental values has been reduced systematically. Theoretical and experimental results of FT-IR and FT-Raman spectra of the compounds under study are compared and we found that very few wavenumbers are missing or slightly different in the calculated spectra. In order to obtain the correct theoretical spectra we may have to follow two important steps. The first one is choosing a large basis set than the one preferred at present and the second one is to go for another set of scaling factors. We are planning to execute these two steps in our future extension study.

### 3. Nonlinear Optical (NLO) Properties

The second-order NLO properties of both the conformers are estimated by calculating their molecular hyperpolarizabilities using the Hartree-Fock (HF) method implemented at the Gaussian 03W software packages. The theoretical calculation of the hyperpolarizabilities of the *cis*- and *trans*-PCA are carried out using the HF/6-31G(d,p) level. Data thus obtained (Table 4.6) showed that *trans*-conformer had higher hyperpolarizabilities than *cis*-conformer. Since there are not any reported experimental values for the first hyperpolarizability of the title compound in the literature, it is difficult to conclude which basis set computes reliable values of  $\beta_{tot}$ . Furthermore, a closer analysis of the structure-property relationship suggests that, when the system possesses an electron-withdrawing group attached to C2 and an electron releasing group on the C5 atom, hyperpolarizability acquires higher values. In the present case, the hyperpolarizability of conformer-1 is  $\sim 4$  times and conformer-2 is  $\sim 6$  times that of urea which reveals that the compound exhibits good NLO properties in *trans* position than the *cis* position. The dipole moment ( $\mu_{tot}$ ) values of the present

molecules are calculated to be 1.93589 and 1.87960 Debye respectively in *cis* and *trans* conformations, and polarizability ( $\alpha_{tot}$ ) is calculated to be  $20.395 \times 10^{-24}$  and  $22.502 \times 10^{-24}$  *esu* respectively for the two conformers.

Table 6: The electric dipole moment  $\mu$  (D), the average polarizability  $\alpha_{tot}$  and the first hyperpolarizability  $\beta_{tot}$  of pyrazinecarboxylic acid by HF/6-31G(d,p) method.

$\mu$ and $\alpha$ components	HF/6-31G (d,p)		$\beta$ components	HF/6-31G (d,p)	
	<i>cis</i>	<i>Trans</i>		<i>cis</i>	<i>trans</i>
$\mu_x$	-1.8098280	-0.9536395	$\beta_{xxx}$	-29.662313	27.6492106
$\mu_y$	0.6796247	-0.0014072	$\beta_{xyy}$	13.158145	0.00982
$\mu_z$	0.1016195	1.6197151	$\beta_{yyy}$	-8.880102	-0.16471
$\mu_{tot}$	1.9358960	1.8796029	$\beta_{yyy}$	9.070963	-0.00188
$\alpha_{xx}$	75.5086338	81.6888441	$\beta_{xxz}$	-15.801979	-17.783286
$\alpha_{xy}$	-2.2117716	0.0689729	$\beta_{xyz}$	-1.920222	-0.034421
$\alpha_{yy}$	30.6225426	27.0964860	$\beta_{yyz}$	-3.472283	1.620265
$\alpha_{xz}$	-7.5176354	-10.7034490	$\beta_{xzz}$	-16.4673385	-35.5815245
$\alpha_{yz}$	2.5857286	0.0008563	$\beta_{yzz}$	4.464596	-0.029091
$\alpha_{zz}$	71.0810004	82.6772712	$\beta_{zzz}$	32.575205	97.3664423
$\alpha_{tot}(esu)$	$20.395 \times 10^{-24}$	$22.502 \times 10^{-24}$	$\beta_{total}(esu)$	$0.540 \times 10^{-30}$	$0.704 \times 10^{-30}$

#### 4. Electronic absorption spectra and HOMO-LUMO analysis

A further inspection of the frontier molecular orbitals of the present compounds reveals that their HOMOs are mainly located over the C-N-C heterocyclic framework while the corresponding LUMO topologies are determined by the position and electronic nature of carboxylic groups linked to the C5 atom as well as C-C heterocyclic framework. Thus, the LUMO largely concentrates on the carboxylic group and the pictures of both frontier orbitals (Fig 5) make it possible to imagine the charge transfer taking place between such orbitals when the material is stimulated with a strong electric field. This charge transfer, in which the C2 carbon atom acts as the overlapping path of transition, will induce a change in the polarization that is oriented in the direction of the electron attracting group (carboxylic acid). In fact it is a necessary condition for a large nonlinear response to occur [19,20]. Moreover, the charge distribution of the HOMO and LUMO for conformer-1 and conformer-2 are complementary to each other which is quite interesting as shown in Fig 5. The HOMO and LUMO energies of the both the conformers are shown in the Table 7. The energy difference between HOMO and LUMO is calculated to be 5.04421 eV and 4.5849 eV respectively, for conformer-1 and conformer-2. The energy difference between HOMO and LUMO orbitals is also an important factor in the search for molecular candidates with nonlinear optical responses. It is generally accepted that there is an inverse relationship between the first hyperpolarizability and the HOMO-LUMO energy gap, thereby enabling the overlap of orbitals and charge transfers from the donor to acceptor groups. As inferred from Table 4.6, the HOMO-LUMO energy gaps (in eV) calculated by the B3LYP/6-31G(d,p) for both the conformers is similar to that of the compounds which have good nonlinear responses.

Table 7: The calculated HOMO, LUMO energies and HOMO-LUMO-energy gap for *cis*- and *trans*-pyrazinecarboxylic acid obtained by using B3LYP/6-31 G(d,p)

Property	<i>cis</i> -PCA	<i>trans</i> -PCA
$E_{HOMO}$ (eV)	-7.290259	-7.377064
$E_{LUMO}$ (eV)	-2.246045	-2.418567
$\Delta E = E_{HOMO} - E_{LUMO}$ (eV)	5.044214	4.958497

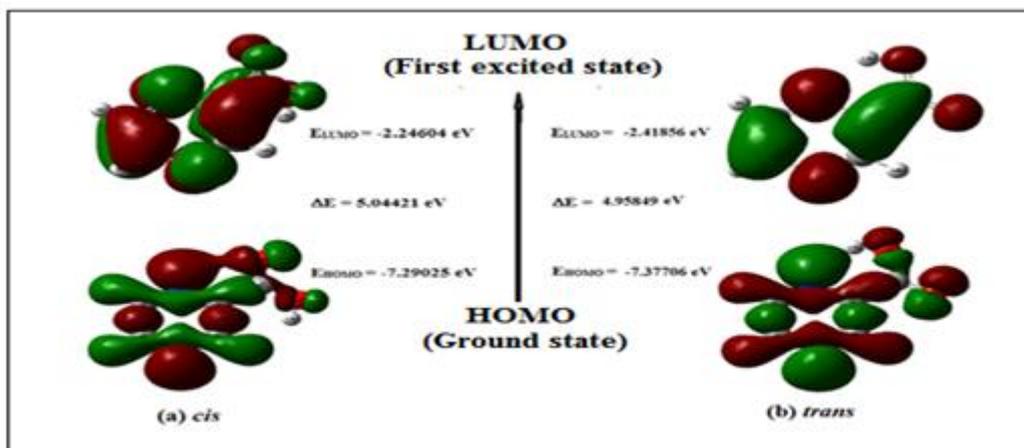


Fig. 5 The atomic orbital components of the frontier molecular orbital of pyrazinecarboxylic acid.

The electronic absorption spectra of the title compound in ethanol solvent is recorded within the 200–500 nm range and a representative spectrum is shown in Fig 6. As can be seen from the Fig 6, electronic absorption spectra showed four bands at 342, 285, 258 and 227 nm. On the basis of fully optimized ground-state structure, TD-DFT/B3LYP/6-31G(d,p) calculations are performed to determine the low-lying excited states of PCA. The calculated result involving the vertical excitation energies, oscillator strengths ( $f$ ) and wavelengths are compared with measured experimental values and listed in Table 8. Typically, according to Frank–Condon principle, the maximum absorption peak  $\lambda_{\max}$  corresponds in an UV–vis spectrum to vertical excitation. TD-DFT/B3LYP/6-31G(d,p) method predicts  $\lambda_{\max}$  at 364 nm with an oscillator strength  $f = 0.0024$  along with two intense electronic transitions at 239 nm and 206 nm with oscillator strength  $f = 0.0987, 0.1313$  respectively. They are compared with the measured experimental data as shown in Fig. 6. The majority contributions of molecular orbitals are also shown in the Table 8. All the structures allow strong  $\pi-\pi^*$  and  $\sigma-\sigma^*$  transition in the UV–vis region with high extinction co-efficient. The  $\pi-\pi^*$  transitions are expected to occur relatively at lower wavelength, due to the consequence of the extended aromaticity of the benzene ring. Natural bond orbital analysis also indicates that molecular orbitals are mainly composed of  $\pi$  atomic orbitals, so that the above electronic transitions are mainly derived from the contribution of  $\pi-\pi^*$  bonds.

Table 8: The UV-vis excitation wavelength ( $\lambda$ ), energy (E) and oscillator strength ( $f$ ) calculated by TDDFT/B3LYP/6-31G(d,p) method for pyrazinecarboxylic acid.

No.	Exp.	TDDFT/6-31G(d,p)			Symmetry	Major contributions
	$\lambda$ (nm)	$\lambda$ (nm)	E ( $\text{cm}^{-1}$ )	$f$		
1	342	364.89	27405.2	0.0024	Singlet-A	HOMO->LUMO (93%)
2	285	315.64	31680.8	0.0003	Singlet-A	HOMO-1->LUMO (72%)
3	276	307.39	32531.7	0.0011	Singlet-A	HOMO->LUMO+1 (75%)
4	258	259.20	38579.3	0.0001	Singlet-A	HOMO-3->LUMO (53%)
5	237	248.84	40185.2	0.0001	Singlet-A	HOMO-1->LUMO+1 (54%)

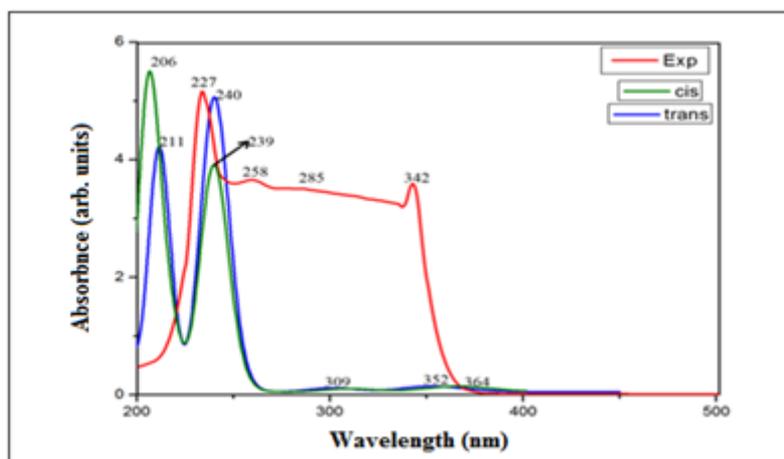


Fig. 6 Experimental and calculated (TDDFT) UV-visible spectra of pyrazinecarboxylic acid.

Presently, there are many functionals which are considered for excited state calculations of organic molecules in LDA, GGA, meta-GGA, global hybrid (GH) and long range corrected hybrids (LCH) etc., methods. They are identified by the symbols such as BLYP, BP86, PBE, B3LYP, X3LYP, PBE0, BHHLYP etc. TDDFT is the most widely applied ab initio tool for modeling the electronic spectra of organic molecules. Despite its successes, TDDFT is limited and suffers an important drawback i.e., the quality of obtained results is profoundly functional dependant. The approximate selection of the exchange correlation functional form is often crucial to achieve accuracy in calculations. For most excited states, hybrid functionals that incorporate a fraction of exact exchange tend to provide more accurate estimates than pure functionals. We find many TDDFT studies using global hybrid or long range corrected hybrids but often specific to a specific class of molecules. In addition, we also observe that the choice of basis set is also contributing to the accuracy in the results. Consequently, for an arbitrary molecule we have to find which functional is most adequate to evaluate the electronic spectra. We have to choose either GH or LCH with a proper basis set. In our study, after careful observations of different combinations of hybrid functionals and basis sets, we have chosen the B3LYP functional with 6-31G(d,p) basis set keeping the past success of this combination for organic molecules and the limited computational facilities available in our laboratory. However, from our study, we could find that this combination is inadequate. Hence, we need to change the correlation functional and the basis set on trial and error basis and choose the most accurate combination for the molecules under study. We are planning to undertake this work as part of our future extension.

## 5. Conclusions

In this chapter we have reported complete structural, vibrational and electronic properties of the title compound by using experimental techniques (FT-IR, FT-Raman and UV-Vis absorption spectra) and theoretical method (DFT/B3LYP/6-31G(d,p)). The fully optimized molecular structure is compared with available compounds having similar structure and the crystal structure of which are determined by X-ray diffraction. Better agreement between the predicted bond lengths and bond angles and the corresponding experimental values is obtained as an increasingly larger basis set is used. The scaled vibrational frequencies are in good agreement with the experimental data. The vibrational modes of the experimental wavenumbers are assigned on the basis of potential energy distribution (PED). The calculated first hyperpolarizability of title compound is about 6 times greater than that of urea. The above results show that the title compound is a good material for NLO applications. In the UV-vis absorption spectrum one intense electronic transition  $\pi \rightarrow \pi^*$  is observed at  $\lambda_{\max} = 342$  nm.

**References**

- [1]. S. R. Batten and R. Robson, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 1460.
- [2]. J. A. Whiteford, E.M. Rachlin and P. J. Stang, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2524.
- [3]. Y. B. Dong, M. D. Smith, R.C. Layland and H. C. Zur Loye, *Chem. Mater.* 12 (2000) 1156
- [4]. M. A. Withersby, A. J. Blake, N. R. Champness, P. Hubbertsey, W. S. Li and M. Schroder, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2327.
- [5]. C. J. Brown III, J. M. Knaust, *Acta Cryst. Sect. E65* 12 (2009) o3052
- [6]. L. C. Maillard, *Compt. Rend.* 154 (1912) 66.
- [7]. Guang-Shan Zhu, *Acta. Cryst.* Section C, 63 (2007) m159.
- [8]. Ezzatollah Najafi, Mostafa M. Amini, Seik Weng Ng, *Acta. Cryst.* E67 (2011) m238
- [9]. J. V. Prasad, S. B. Rai, S. N Thakur, *Chem Phys Lett.* 164 (1989) 629.
- [10]. M. K. Ahmed, B. R. Henry, *J. Phys. Chem.* 90 (1986) 629.
- [11]. G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*, Vol. 1 and 2, Academic Kiado: Budapest, 1973.
- [12]. George Socrates, *Infrared and Raman Characteristic Group wavenumbers – Tables and Charts* (3rd edn), John Wiley and Sons: New York. 2001.
- [13]. R.M. Silverstein, F.X. Webster, *Spectrometric Identification of Organic Compounds*, 6th edition, Wiley, New York, 1998, p. 102.
- [14]. N.B. Colthup, L.H. Daly, S.E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1990.
- [15]. B.C. Smith, *Infrared Spectral Interpretation*, CRC Press, Boca Raton, FL, 1996.
- [16]. J. Marshal, *Ind. J. Phys.* 72B (1998) 661.
- [17]. E.T.G. Lutz, J.H.V. Mass, *Spectrochim. Acta* 42A (1986) 749.
- [18]. D. Michalska, D.C. Bienko, A.J.A. Bienko, Z. Latajaka, *J. Phys. Chem.* 100 (1996) 1186.
- [19]. D. R. Kanis, M. A. Ratner and T. J. Marks, *Chem. Rev.* 94 (1994) 195
- [20]. T. Vijayakumar, I. H. Joe, C. P. R. Nair and V. S. Jayakumar, *Proceedings of the 2nd International Conference on Perspectives in Vibrational Spectroscopy* (ICOPVS 2008), AIP Conf. Proc., 85 (2008) 1075.