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IR, Raman, NMR, IVP & DFT Studies of Dipicolinic and Quinolinic Acids

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Abstract: Theoretical (DFT) and spectroscopic (IR, Raman, NMR) properties of with 2,3-pyridinedicarboxylic acid (P23DICA) and 2,6-pyridinedicarboxylic acid (P26DICA) were studied. The FTIR and FT-Raman spectra of were recorded in the range 4000-450 cm^{-1} and 4000-50 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra of analyzed compounds have been recorded. A normal coordinate analysis was carried out for all the vibrations using 74-parameter modified valence force field by solving inverse vibration problem (IVP) employing overlay least-squares techniqueThe optimized geometry and vibrational frequencies were computed using density functional theory (DFT) employing B3LYP functional with 6-311++G(d,p) basis set. A study on NLO, HOMO and LUMO energies are performed.

Keywords: P23DICA, P26DICA, IR, RAMAN, NMR

I. 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). In our earlier paper, we reported the results of experimental and theoretical study of 2,4-, 2,5-, 3,5,- and 3,4-pyridine dicarboxylic acids [1]; and evaluated their optimized geometries and valence force field. In continuation of this work, we now investigated 2,3-pyridinedicarboxylic acid and 2,6-pyridinedicarboxylic acid. In pharmaceuticals and medicines, PDA is found to be suitable ligand to develop more effective HIV agents [2-4].Quinolinic acid is a downstream product of Kynurenine pathway, which metabolizes the amino acid tryptophan. It acts as an NMDA receptor agonist. Quinolinic acid is involved in many psychiatric disorders, neurodegenerative processes in the brain as well as other disorders. Within the brain quinolinic acid is only produced by activated microglia and macrophages. Dipicolinic acid and its salts are major constituents of bacterial spores. Hence, pyridine-dicarboxylic acids have huge applications in the chemical field that way, we thought it is useful to take up experimental and theoretical spectroscopic investigations of the pyridine-dicarboxylic acids.

A. The objectives of this investigation namely

To record Fourier Transform Infrared (FTIR) and Fourier Transform Raman (FTR) spectrum of pyridine-2, 3-dicarboxylic acid (P23DICA), P26DICA, in order to get information on its vibrational frequencies.

1) To calculate vibrational spectra, IR and Raman, NMR using the method of Density Functional Theory (DFT) approach for P23DICA and P26DICA.
2) To obtain the values of first order hyper polarizability for P23DICA and P26DICA.
3) To evaluate HOMO and LUMO energies for P23DICA and P26DICA.

II. EXPERIMENTAL DETAILS

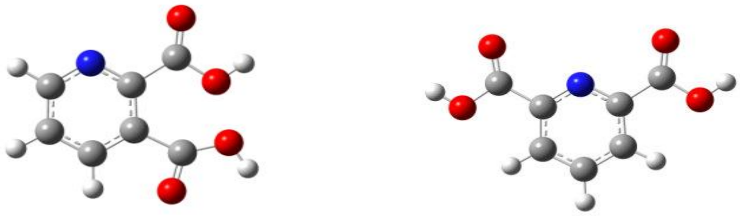
The Chosen molecule is obtained from TCI Chemical Company, Japan and used as such for the spectra measurements. The room temperature FTIR spectra of this molecule is recorded using Bruker IFS 66V spectrometer employing KBr optics in the spectral range 4000-450 cm^{-1} with a scanning speed of 30 cm^{-1} min^{-1} with spectral width 2.0 cm^{-1}. The FT-Raman spectra is recorded in the range 4000-50cm^{-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.

III. COMPUTATIONAL DETAILS

A. The Quantum Chemical Calculations – Molecular geometry

The starting point for calculations is to determine the most stable conformer for the molecule under investigation. The molecule, PDA, was submitted to a rigorous conformational analysis around free rotation bonds using Gaussian 09w software package [5] implemented on Pentium-V (3.2 GHz) workstation. The computations were established by employing the standard density functional triply-parameter hybrid model DFT/B3LYP [6, 7] using 6-311++G(d,p) basis set. These computations yielded six stable rotational conformersamong these we got the lowest global minimum energy at -625.6076 and -625.6078 Hartree. Hence, this is accepted asthe most stable conformer for optimizing the geometry of this molecule. Subsequent calculations were performed with these optimized structures as shown in figure 1.

Figure1. Optimized structures of P23DICA and P26DICA with energy in Hartree



P23DICA: -625.6076P26DICA: -625.6078

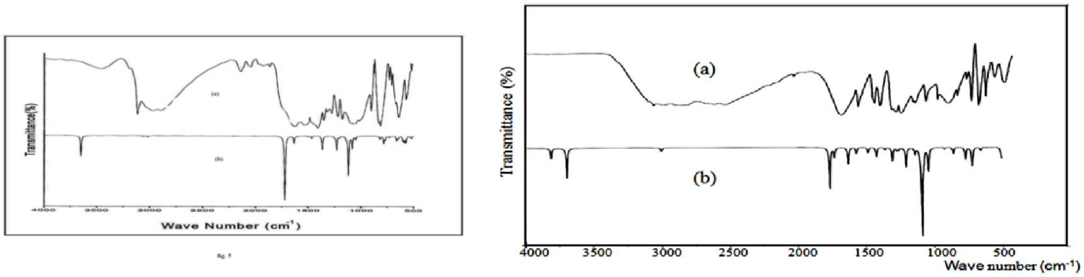


Figure 2. FTIR spectrum of PDA: (a) Observed, (b) Simulated DFT/B3LYP/6-311++G(d,p)

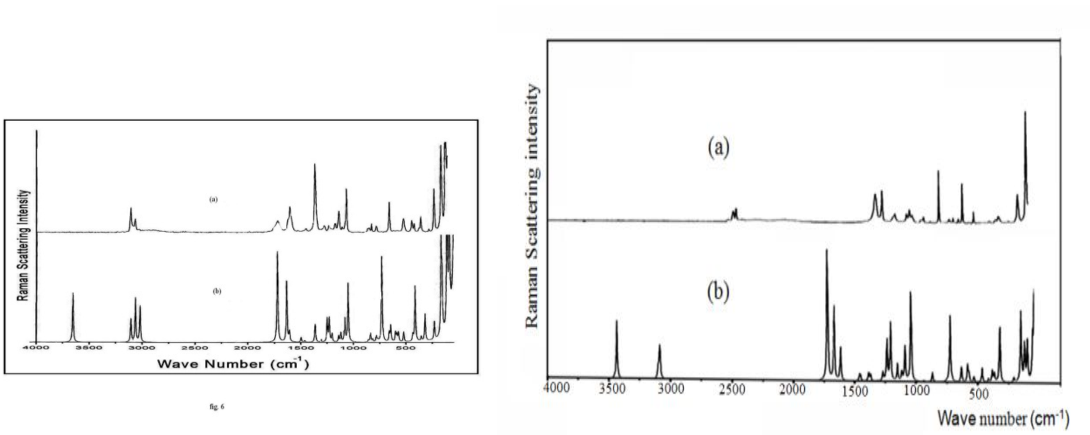


Figure 3. FT-Raman spectrum of PDA: (a) Observed, (b) Simulated DFT/B3LYP/6-311++G(d,p)

The experimental and simulated FTIR and FT-Raman spectra are presented in figures 2 and 3. The optimized structure parameters namely bond lengths, bond angles and dihedral angles of PDA in its most stable conformation are presented in Table 1. Scaling of the force constants was made according to scaled quantum mechanical (SQM) procedure [8, 9] employing selective scaling in the natural coordinate representation [10, 11]. Transformation of the force field, normal coordinate analysis, least-square refinement of scale factors and calculation of potential energy distribution (PED) were established with the MOLVIB program (version 7.0) written by Suindius [12, 13].

Table 1.Optimized geometrical parameters of P23DICA and P26DICA.

P23DICA						P26DICA					
Bond	Bond length (Å)	Bond angle	Value (in °)	Torsional angle	Value (in °)	Bond	length	Bond angle	Value (in °)	Torsional angle	Value (in °)
N1-C2	1.334	N1-C2-C3	123.03	N1-C2-C3-C4	0.0	N1-C2	1.331	N1-C2-C3	123.136	N1-C2-C3-C4	0.0
C2-C3	1.404	C2-C3-C4	117.68	C2-C3-C4-C5	0.0	C2-C3	1.400	C2-C3-C4	118.293	C2-C3-C4-C5	0.0
C3-C4	1.397	C3-C4-C5	119.46	C3-C4-C5-C6	0.0	C3-C4	1.389	C3-C4-C5	118.934	C3-C4-C5-C6	0.0
C4-C5	1.386	C4-C5-C6	118.19	C6-N1-C2-C7	173.87	C4-C5	1.389	C4-C5-C6	118.293	C6-N1-C2-C7	-180.0
C5-C6	1.392	N1-C2-C7	113.31	N1-C2-C3-C8	-180.0	C5-C6	1.400	N1-C2-C7	115.527	N1-C2-C3-H8	180.0
C6-N1	1.334	C2-C3-C8	125.01	C2-C3-C4-H9	180.0	C6-N1	1.335	C2-C3-H8	120.216	C2-C3-C4-H9	180.0
C2-C7	1.513	C3-C4-H9	118.74	C3-C4-C5-H10	180.0	C2-C7	1.507	C3-C4-H9	120.532	C3-C4-C5-H10	180.0
C3-C8	1.491	C4-C5-H10	121.21	C4-C5-C6-H11	180.0	C3-H8	1.081	C4-C5-H10	121.490	C4-C5-C6-C11	-180.0
C4-H9	1.083	C5-C6-H11	120.78	N1-C2-C7-O12	-104.56	C4-H9	1.083	C5-C6-C11	121.336	N1-C2-C7-O12	0.0
C5-H10	1.082	C2-C7-O12	123.45	N1-C2-C7-O13	72.25	C5-H10	1.081	C2-C7-O12	125.754	N1-C2-C7-O13	180.0
C6-H11	1.085	C2-C7-O13	112.10	C2-C7-O13-H14	-176.43	C6-C11	1.507	C2-C7-O13	111.393	C2-C7-O13-H14	180.0
C7-O12	1.202	C7-O13-H14	107.36	C2-C3-C8-O15	-162.57	C7-O12	1.199	C7-O13-H14	106.792	N1-C6-C11-O15	0.0
C7-O13	1.343	C3-C8-O15	124.05	C2-C3-C8-O16	19.14	C7-O13	1.361	C6-C11-O15	125.754	N1-C6-C11-O16	180.0
O13-H14	0.969	C3-C8-O16	112.95	C3-C8-O16-H17	-180.00	O13-H14	0.968	C6-C11-O16	111.393	C6-C11-O16-H17	-180.0
C8-O15	1.207	C8-O16-H17	107.61			C11-O15	1.199	C11-O16-H17	106.792		
C8-O16	1.349					C11-O16	1.361				
O16-H17	0.968					O16-H17	0.968				

B. Solving inverse vibrational problem

This section deals with the solution of inverse vibrational problem (IVP), wherein Wilson’s GF-matrix method was employed for the normal coordinate analysis [14]. The computations were carried out using the structure parameters (Table 1) obtained from DFT computations; internal coordinates and symmetry coordinates presented in our earlier work [1]. Thus, a 74-element valence force field was chosen for solving inverse vibrational problem using normal coordinate analysis of all the vibrations of the molecule under investigation. The initial set of force constants was transferred from our earlier work on pyridines [15] for the pyridine ring, whereas those of acid group were taken from the literature [16, 17]. This set could at best be an approximation to the final set. Hence, it needs to be refined. The refinement was carried out using Schachtschneider’s program [18]. Initially, the force constants were refined through several cycles with a damping factor of 0.10 without fixing any of the force constants In the final refinement, 49 force constants were fixed either because they were correlated or could be determined inadequately with the available data. Thus, 39 frequencies (unknown frequencies were given a zero weight) of this molecule were used to refine 25 valence force constants by reducing the damping factor to zero. The refinement converged in four cycles with an average error of 09.21 cm^{-1} between the observed and calculated frequencies. The final force constants are presented in our earlier work [1]. The vibrational modes along with calculated frequencies (DFT and IVP) of this molecule are presented in Table 2.

IV. VIBRATIONAL ASSIGNMENTS

The observed and calculated (NCA and DFT) frequencies of P23DICA, P26DICA are presented in Table-2 respectively, along with vibrational assignments. The vibrations are represented in Wilson’s notation**[19]** **[51]** following the suggestions made by Varsanyi for 1,2,3-tri light and 1,2,4-tri light and 1,3,5-tri light substituted benzenes [See Ref. **57**, pp. 298, 323 and 280], respectively. It can be understood in table-2 that the calculated frequencies obtained by normal coordinate analysis method are in good agreement with experimental frequencies and DFT. The assignments presented in these tables are self-explanatory and the discussion is confined to some of the important vibrational modes only.

A. C-C and C-N stretching vibrations

The modes 1, 8a, 8b, 14, 19a and 19b (Wilson’s notation is used for benzene ring modes, see Ref. 4) are known as C-C stretching vibrations in benzene and its derivatives. The molecules under investigation consist one nitrogen atom and five carbon atoms in aromatic nucleus. Hence, we get four C-C and one C-N stretching vibrations for the molecules under investigation. The modes 8a, 14, 19a and 19b designate the C-C stretching vibrations, whereas, the modes 1 and 8b represent C-N stretching vibrations in these molecules. Mode 1 is highly sensitive to the nature of the substituent and hence classified as ring vibration. Further, mode 14 is observed to have considerable mixing with C-H in-plane bending vibration 3. For the molecules P23DICA and P26DICA the modes 8a and 8b are expected around 1600 cm^{-1}. Hence, the absorptions near 1603 and 1642R, cm^{-1} are assigned to C-C stretching vibration 8a and bands near 1583 and 1574 cm^{-1} are ascribed to C-N stretching vibration 8b in P23DICA and P26DICA respectively. Modes 19a and 19b are expected in the spectral range 1400-1500 cm^{-1} in benzene and its derivatives. The frequencies near 1528C and 1455cm^{-1} are assigned to mode 19a and the absorptions around 1494 and 1415cm^{-1} are attributed to mode 19b P23DICA and P26DICA respectively. C-C and C-N stretching vibrations of above molecules are good agreements in the literature of P. Koczon and his co-workers [20].

B. Mode 14 and C-H in-plane bending vibrations

The assignment of mode 14 (the Kekule mode) in which alternate C-C bonds either increase or decrease, is usually difficult as the highest C-H in-plane bending vibration 3 appears in its vicinity around 1000-1300 cm^{-1} [21-24]. According to the DFT and IVP calculations, the bands observed at 1277 and 1240C cm^{-1} in P23DICA and P26DICA, respectively, exhibit strong mixing between the modes 14 and 3. The bands near 1277 and 1264cm^{-1},it seems reasonable as these frequencies fall in the range 1230-1330 cm^{-1} proposed for mode 14 by Varsanyi in 1,2,3-tri-substituted benzenes [see Ref. **[25]**, pp 298]. The C-H in-plane bending vibrations are designated as mode 3, 9b and 18a in P23DICA, P26DICA. In aromatic compounds, they generally appear in the spectral region 1000-1300 cm^{-1}. Based on the calculations, the bands near 1232 and 1238C cm^{-1},are assigned as mode 3, respectively in these molecules. The absorptions near 1130 and 1173; 1162 and 1175 cm^{-1} are assigned to modes 9b and 18a in P23DICA and P26DICA.

C. Vibrations of C-C_α (bond between pyridine and acid groups)

Modes 7b and 20a in P23DICA and P26DICA designate the two C-C_α stretching vibrations, whereas the modes 9a and 18b in P23DICA and P26DICA represent the corresponding in-plane bending vibrations. The pair of frequencies near 1037 and 1307 cm^{-1}; 996 and 1299 cm^{-1}; are assigned to C-C_α stretching vibrations in P23DICA and P26DICArespectively based on the results of DFT and NCA calculations. The pair of frequencies near 101R and 227R cm^{-1}; 210R and 310R cm^{-1}are assigned to C-C_α in-plane bending modes, respectively in P23DICA and P26DICA. The two out-of-plane bending vibrations associated with C-C_α bonds are designated as modes 10b and 17b in P23DICA and P26DICA. The frequencies near 160R and 122R cm^{-1}; 169C and 129C cm^{-1}are assigned to the modes 10b and 17b in P23DCA and P26DCA.

D. Ring vibrations

The four ring vibrations 1, 6a, 6b and 12 are sensitive to the position and the nature of the substituent, which makes their correlation with corresponding benzene modes very difficult. Hence, they were identified and assigned from careful consideration of their characteristic eigen vector distribution following Patel et al [26].

According to normal coordinate analysis, the absorptions near 353R and 460 cm^{-1}; 395R and 441cm^{-1} are assigned to modes 6a and 6b, in P23DICA and P26DICA, respectively. According to the calculations, the ir absorptions near 768, 752 and 771 cm^{-1} are assigned to mode 12 in these molecules. These frequencies retain the essential CCC bending nature despite their mixing with several other vibrational frequencies. In benzene, mode 1 at 990 cm^{-1} is a pure C-C stretching vibration as it is totally symmetric and widely separated from C-H stretching modes. Hence, the band near 823 and 800Rcm^{-1}are ascribed to mode 1 in P23DICA and P26DICA, respectively.

E. Ring torsions

The frequencies near 741C and 701cm^{-1} are assigned as mode 4 in P23DICA and P26DICA, respectively.The ir absorptions near 612 and 647cm^{-1} are attributed mode 16a, whereas, the frequencies around 414R and 480R cm^{-1} are assigned to mode 16b in P23DICA and P26DICA, respectively.

F. Vibrations of the acid groups

There are six in-plane and three out-of-plane vibrations for each of two acid groups in the molecules under study. These are, $\nu(C_\alpha{=}O)$, $\nu(C_\alpha\text{-}O)$, $\delta(OH)$, $\nu(O\text{-}H)$, $\delta(C_\alpha{=}O)$, $\gamma(C_\alpha\text{-}O)$, $\omega(OH)$, $\omega(C_\alpha{=}O)$ and $\tau(CC_\alpha)$. The bands near 1714R and 1695, cm^{-1} are assigned to $C_\alpha{=}O$ stretching vibration in P23DICA and P26DICA, respectively. The stretching and in-plane bending vibrations, $\nu(C_\alpha\text{-}O)$ and $\delta(OH)$, of the acid group generally appear in the range 1200-1450 cm^{-1} depending on whether monomeric, dimeric or other hydrogen bonded species are present. Usually, $\delta(OH)$ appears at higher frequency than that of $\nu(C_\alpha\text{-}O)$. Moreover, these bands overlap with other bands that are due to aromatic nucleus or aliphatic chain vibrations making unambiguous assignment difficult. Based on the results of computations, the ir absorptions near 1363 and 1378Rcm^{-1} are in P23DICA and P26DICA,respectively and hence, they are attributed to $\delta(OH)$ vibration. The frequencies near 1329C, and 1328cm^{-1} are assigned to mode $\nu(C_\alpha\text{-}O)$ in these molecules. The ir absorptions identified near 3453 and 3568cm^{-1} are assigned to mode ν(O-H) in P23DICA and P26DICA, respectively. Vibrations of the acid groups like $\nu(C_\alpha=O)$, $\nu(C_\alpha\text{-}O)$, δ(OH), ν(O-H), $\delta(C_\alpha=O)$, $\gamma(C_\alpha\text{-}O)$, ω(OH), and $\omega(C_\alpha=O)$ are good agreements in the assignments of K. McCan, and J. Laane **[27]**.

Table 2: Observed, calculated frequencies with DFT and IVP; and vibrational modes of PDA

S. No.	Mode^a	Obs. freq		Cal. freq. (cm^{-1})			Obs. freq. (cm^{-1})		Cal. freq. (cm^{-1})		
		IR	Raman	DFT		IVP	IR	Raman	DFT		IVP
				Unscaled	Scaled				Unscaled	Scaled	
a_1 – species											
1	ν(C-H)2	-	3097	3198	3084	3091	-	3063	3074	3063	3069
2	ν(C-H)7a	3068	3069	3188	3064	3072	-	-	3080	3091	3094
3	$\nu(C\text{-} C_{\alpha})_{20a}C_{\alpha})20a$	1299	1295	1324	1304	1308	1307	-	1358	1312	1304
4	ν(C-N)1	-	800	814	801	8011	823	821	815	819	816
5	ν(C-C)8a	-	1642	1632	1638	1644	1603	1598	1631	1630	1621
6	ν(C-C)19a	1455	1444	1460	1452	1459	-	-	1560	1530	1528
7	β(CH)18a	1175	1178	1190	1181	1175	1173	1165	1144	1154	1160
8	$\beta(C\text{-}C_\alpha)9a$	-	201	187	191	203	-	101	95	102	99
9	β(CCC)6a	-	395	423	410	409	-	353	342	353	352
10	β(CCC)12	752	760	786	753	754	768	-	753	767	751
11	$\nu(C_\alpha=O)_1$	1695	-	1720	1706	1710	-	1714	1792	1721	1722
12	$\nu(C_\alpha\text{-}O)_1$	1328	1324	1345	1327	1320	-	-	1342	1329	1324
13	$\delta(OH)_1$	-	1378	1381	1369	1378	1363	1359	1372	1363	1350
14	$\nu(OH)_1$	-	-	3691	3561	3568	3453	-	3748	3452	3463
15	$\delta(C_\alpha=O)_1$	-	681	691	685	682	651	652	648	642	661
16	$\gamma(C_\alpha\text{-}O)_1$	581	-	577	562	571	587	-	581	562	571
b_2 – species											
17	ν(C-H)20b	3003	-	3211	3010	3008	3103	3105	3123	3105	3111
18	$\nu(C\text{-}C_\alpha)7b$	996	997	1002	991	993	1037	1058	1069	1052	1048
19	ν(C-N)8b	1574	1574	1591	1578	1571	1583	-	1602	1607	1610
20	ν(C-C)14	1264	1270	1258	1268	1265	1277	1273	1262	1248	1268
21	ν(C-C)19b	1415	-	1430	1411	1419	1494	-	1478	1498	1503
22	β(CH)3	-	-	1257	1237	1238	1232	1230	1228	1227	1222
23	β(CH)9b	1162	1153	1160	1165	1149	1130	1131	1136	1139	1134
24	β(C-	-	310	323	303	307					
25	β(CCC)6b	441	-	461	440	439	460	-	439	441	452
26	$\nu(C_\alpha=O)_2$	1695	-	1724	1709	1710	-	1714	1815	1718	1724
27	$\nu(C_\alpha\text{-}O)_2$	1328	1324	1345	1324	1328	-	-	1328	1324	1320
28	$\nu(OH)_2$	-	-	3691	3567	3564	3453	-	3766	3452	3461
29	$\nu(C_\alpha\text{-}O)_2$	1328	1324	1345	1324	1328	-	-	1328	1324	1320
30	$\gamma(C_\alpha\text{-}O)_2$	581	-	574	581	567	-	-	318	319	317
31	$\delta(OH)_2$	-	1378	1385	1361	1371	3453	-	3766	3452	3461
a_1 – species											
32	π(CH)11	782	-	768	785	796	777	779	776	780	787
33	π(CH)17a	918	-	930	921	912	-	-	871`	885	897
34	τ(cccc)16a	647	646	657	640	639	612	-	581	598	604
35	$\tau(c\text{-}c_\alpha)_1$	-	74	99	87	73	-	114	109	99	98
36	$\omega(O\text{-}H)_1$	515	-	519	510	517	515	516	513	509	510
37	$\omega(C_\alpha=O)_1$	854	853	897	869	861	852	-	848	857	868
b_1 – species											
38	π(CH)5	-	893	881	890	870	967	-	988	986	979
39	$\pi(C\text{-} C_{\alpha)10b}C_{\alpha})10b$	-	-	187	167	169	-	160	181	165	163
40	$\pi(C\text{-} C_{\alpha})_1C_{\alpha})17b$	-	-	135	121	129	-	122	123	137	128
41	τ(cccc)4	701	-	721	702	706	-	-	752	741	741
42	τ(cccc)16b	-	480	478	481	489	-	414	408	411	424
43	$\tau(C\text{-}C_\alpha)_2$	-	113	127	109	111	-	75	72	68	66
44	$\omega(O\text{-}H)_2$	-	-	430	438	431	-	438	415	428	424
45	$\omega_2(C_\alpha=O)_2$	854	853	891	857	850	852	-	836	858	853

[a] Mode in Wilson's notation [14]. C_α – 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

V. POLARIZABILITY AND FIRST ORDER HYPERPOLARIZABILITY

The theoretical and experimental study of NLO properties is required for the development of organic materials for device applications in the fields of chemistry, physics, and engineering. The electronic polarization in the molecular NLO process and the establishment of structure-property relationship can be understood from Quantum chemical calculations [28,29].The response of a molecular system in the applied electric field can be characterized by the polarizability and hyperpolarizability [30-32]. Polarizabilities and hyperpolarizabilities of the systems help to study not only the strength of the molecular interactions, the cross sections of different scattering and collision process, but also the NLO property [33].

The non-linear optical response of an isolated molecule in an electric field can be expressed as a Taylor series expansion of the total dipole moment, μ_t, induced by the field:

$$\mu_t = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \cdots$$

where, μ_0 is the permanent dipole moment,

$\alpha_{ij}$are the components of polarizability,

β_{ijk} are the components of the first order hyperpolarizability.

The first order hyperpolarizability is a third rank tensor. Hence, it contains 27 components represented by a 3 x 3 x 3 matrix. Due to Klienman symmetry [34], the 27 components get reduced to 10 components ($\beta_{xyy}= \beta_{yxy}= \beta_{yyx}= \beta_{yyz}= \beta_{yzy}= \beta_{zyy}$;….. Similarly, other permutations of x, y, z subscripts also take same value). These components are:

$$\beta_{xxx}, \beta_{xxy}, \beta_{xyy}, \beta_{yyy}, \beta_{xxz}, \beta_{xyz}, \beta_{yyz}, \beta_{xzz}, \beta_{yzz}, \beta_{zzz}$$

They can be calculated using the following equation [35]:

$$\beta_i = \beta_{iii} + (1/3) \sum_{i\neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

The total static dipole moment μ_t,the isotropic (or average) linear polarizabilityα_t and the mean first order hyperpolarizabilityβ_t, using the x, y, z components are defined as:

$$\mu_t = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_t = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$$

$$\beta_t = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

Where, $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$

$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$

$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$

The first order hyperpolarizability is a measure of non-linear optical (NLO) effects. NLO effects arise due to interaction of incident electromagnetic fields with media (NLO materials). The effect is manifested as generation of new fields that differ in phase, frequency, amplitude or other propagation characteristics that differ from those of the incident fields **[36]**. NLO effects are important in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in the area of telecommunications, signal processing and optical inter-connections [37-40]. Hence, DFT has been extensively used to investigate the organic NLO materials [41-45].

The total molecular dipole moment (μ_t) and its components; total molecular polarizability (α_t) and its components; and first order hyperpolarizability (β_t) and its components of P23DCA and P26DCA are computed with DFT employing B3LYP/6-33++G(d,p) basis set using Gaussian 09 program. The results are summarized in Table 3.

Urea is a prototypical molecule used in the NLO properties of molecular systems. The total molecular dipole moment (μ_t) 1.3732 Debye and the mean first order hyperpolarizability (β_t) 0.3728 x 10^{-30} cm^5/esu of Urea are used frequently as threshold values for the purpose of comparison. The total molecular dipole moment (μ_t) values are calculated as 2.2059 and 5.5578Debye and the mean first order hyperpolarizability (β_t) values are obtained as 0.989 x 10^{-30} and 1.859 x 10^{-30} cm^5/esu for P23DICA and P26DICA, respectively. Thus, we find that the dipole moment value (μ_t) of these molecules is greater than the threshold value corresponding to Urea. The computation of hyperpolarizability (β_t) and its components is very useful to describe charge delocalization. The large value of hyperpolarizability, which is a measure of the non-linear optical activity of the molecular system, is associated with the intermolecular charge transfer, resulting from the electron cloud movement, through π-conjugated framework of electron [46].Based on the magnitude of the first order hyperpolarizability value, the compounds P23DICA and P26DICA may be considered as the potential applicants in the development of NLO materials.

Table 3: Polarizabiltiy and Hyperpolarizability of Pyridine dicarboxylic acids

Component	P23DICA	P26DICA
μ_x	-1.2237	5.5578
μ_y	0.0485	0.0000
μz	-1.8347	0.0000
μ_{total}	2.2059	5.5578
α_{XX}	123.4699	115.6755
α_{XY}	3.3030	0.0000
α_{YY}	112.2718	134.6755
α_{XZ}	0.3697	0.0000
α_{YZ}	2.5374	0.0000
α_{ZZ}	63.8663	53.2219
$<\alpha>$	79.426	101.1909
β_{xxx}	-56.9189	94.2980
β_{xxy}	48.3698	-0.0005
β_{xyy}	109.7473	-207.9840
β_{yyy}	47.6848	-0.0012
β_{xxy}	-29.8391	0.0000
β_{xyz}	-2.6759	0.0000
β_{yyz}	-15.7251	0.0000
β_{xzz}	-58.3718	58.0462
β_{yzz}	2.3598	0.0003
β_{zzz}	-12.8292	0.0000
β_{total}	0.989×10^{-30}	1.859×10^{-30}

VI. FRONTIER MOLECULAR ORBITALS

Frontier molecular orbitals (HOMO and LUMO) and their energies are very useful parameters for spectroscopists in the field of quantum chemistry. This is also used by frontier electron density for predicting the most reactive position in π-electron systems and explains several types of reaction in conjugated system [47]. The conjugated molecules are characterized by a small separation between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), which is the result of a significant degree of intermolecular charge transfer from the end-capping electron-donor groups to the efficient electron-accepter groups through π-conjugated path [48].A molecule having a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity and low kinetic stability [49-51].The HOMO represents the ability to donate an electron, whereas, the LUMO represents the ability to accept an electron and the gap between HOMO and LUMO characterizes the molecular chemical stability. On the other hand, LUMO energy is directly related to electron affinity [52,53].For understanding the various aspects of pharmacological sciences including drug design and the possible ecotoxicological characteristics of the drug molecules, several new chemical reactivity descriptors have been proposed. Conceptual DFT based descriptors have helped in many ways to understand the structure of the molecules and their reactivity by calculating the chemical potential, global hardness and electrophilicity. Using, the HOMO and LUMO orbital energies, the ionization energy (I), electron affinity (A), Global hardness (η), chemical potential (μ) [54] and global electrophilicity power (ω)[55] of a compound can be calculated as:

$I = -E_{HOMO}$; $A = -E_{LUMO}$; $\eta = (-E_{HOMO}+ E_{LUMO})/2$; $\mu = (E_{HOMO}+E_{LUMO})/2$; and $\omega = \mu^2/2\eta$.

The HOMO and LUMO computed at B3LYP/6-311++G(d,p) level for P23DCA and P26DCA are illustrated in Fig. The energy values of HOMO, LUMO and difference between them are calculated as -0.35715 eV, -0.20978 eV and 0.14737 eV for P23DCA, -0.37121 eV, -0.21092 eV and 0.16029 for P26DCA, respectively. It is seen from the HOMO-LUMO energy values (Table: 4). that the chemical potential of the molecules under investigation are negative and hence, the compounds are stable.

Table: 4. HOMO-LUMO

Energy	**P23DCA**	**P26DCA**
E_{HOMO}	-0.35715	-0.37121
E_{LUMO}	-0.20978	-0.21092
$\Delta E = \lvert E_{HOMO} - E_{LUMO} \rvert$	0.1473	0.16029

VII. THERMODYNAMIC PARAMETERS

On the basis of vibrational analysis and DFT studies at B3LYP/6-311++G(d,p) level, several thermodynamic parameters and rotational constants are calculated for P23DICA and P26DICAand presented in Table **5**. The zero point energy (E_0), SCF energy, total energy (E_{total}), entropy (S) and heat capacity (C_v) of the above molecules have been computed from the frequency.

Table-5 : Thermodynamics properties of Pyridine dicarboxylic acids

S.No	Thermodynamic parameter	P23DICA	P26DICA
01	SCF Energy (Hartrees)	-625.6075	-625.6109
02	Total energy (thermal),E_{total}(Kcal mol^{-1}	80.098	80.071
03	Heat capacity at const.volume,c_v(cal mol^{-1} k^{-1})	36.906	36.929
04	Entropy,S (cal mol^{-1} k^{-1})	101.626	101.690
05	Vibrational energy,Evib(kcal mol^{-1})	78.321	78.293
06	Zero-point Vibrational energy,E_0(kcal mol^{-1})	73.766	73.780
	Rotational constants (GHz)		
07	A	1.1417	1.8856
08	B	1.0595	0.6046
09	C	0.6041	0.4578

VIII. NMR SPECTRA

Chemical shifts of the signals coming from protons in the ^1H NMR spectra of P23DICA and P26DICA (Fig (4.1 & 4.2)take lower values than the corresponding ones for acids. An aromatic pyridine ring is disturbed, resulting in a change in the electron density around the protons of the aromatic ring. The values for the chemical shifts of aromatic protons labeled H3, H4 and H5 in the spectra of acid shown in table. For P23DICAacid give its spectral image of three clearly separated signals. Decreases in proton chemical shifts for H4 and H5 in P23DICAacid are small, and the decreases in proton chemical shifts for H3 are much larger and similar in size as those in P26DICA. The values are shown in Table (6).

Table (6): Chemical shift values in 1H and 13C NMR spectra of 23PDA and 26PDA

		P23DICA			P26DICA	
1*H NMR*		Experimental	Theoretical	1*H NMR*	Experimental	Theoretical
1	H_4	8.12	8.45	H_3	8.52	8.21
2	H_5	7.56	7.30	H_4	8.61	8.03
3	H_6	8.85	8.78	H_5	8.77	8.16
13*C NMR*				13*C NMR*		
4	C_2	151.56	181.23	C_2	151.23	161.23
5	C_3	149.45	136.52	C_3	139.65	125.21
6	C_4	149.10	136.20	C_4	136.25	154.23
7	C_5	139.40	131.9	C_5	149.66	130.29
8	C_6	156.20	169.25	C_6	159.00	164.59
9	C_7	184.23	178.9	C_7	169.87	163.21
10	C_8	159.32	147.5	C_8	189.23	175.11

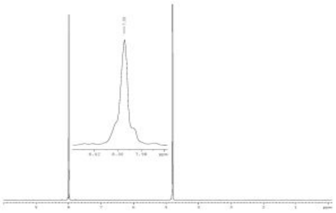


Fig.4.1:^{1}HNMR spectra for P23DICA(solvent: D2O)

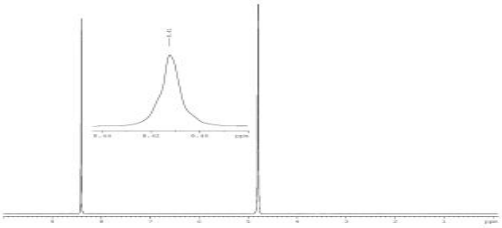


Fig.4.2: ^{1}HNMR spectra for P26DICA (solvent: D2O)

IX. CONCLUSION

The calculated frequencies using scaled DFT and classical IVP methods employing normal coordinate analysis are in good agreement with the corresponding observed frequencies for 23PDA and 26PDA. On the basis of calculated potential energy distribution result, assignments of the fundamental vibrational frequencies have been made unambiguously. There is a close agreement between the vibrational assignments arrived at on the basis of DFT and IVP results. . ^{1}H NMR and ^{13}C NMR spectra of analyzed compounds have been studied. A study on NLO, HOMO and LUMO energies are performed. The HOMO-LUMO energy gap and other related molecular properties were discussed and reported. The value of energy gap indicates that it is a good chemical reactive molecule. The values of dipole moment (μ_{tot}), linear polarizability (α_{tot}) and first-order hyperpolarizability (β_{tot}) of the molecule were calculated. It has been found that the value of first-order hyper-polarizability, which shows that the molecule is a good NLO material.

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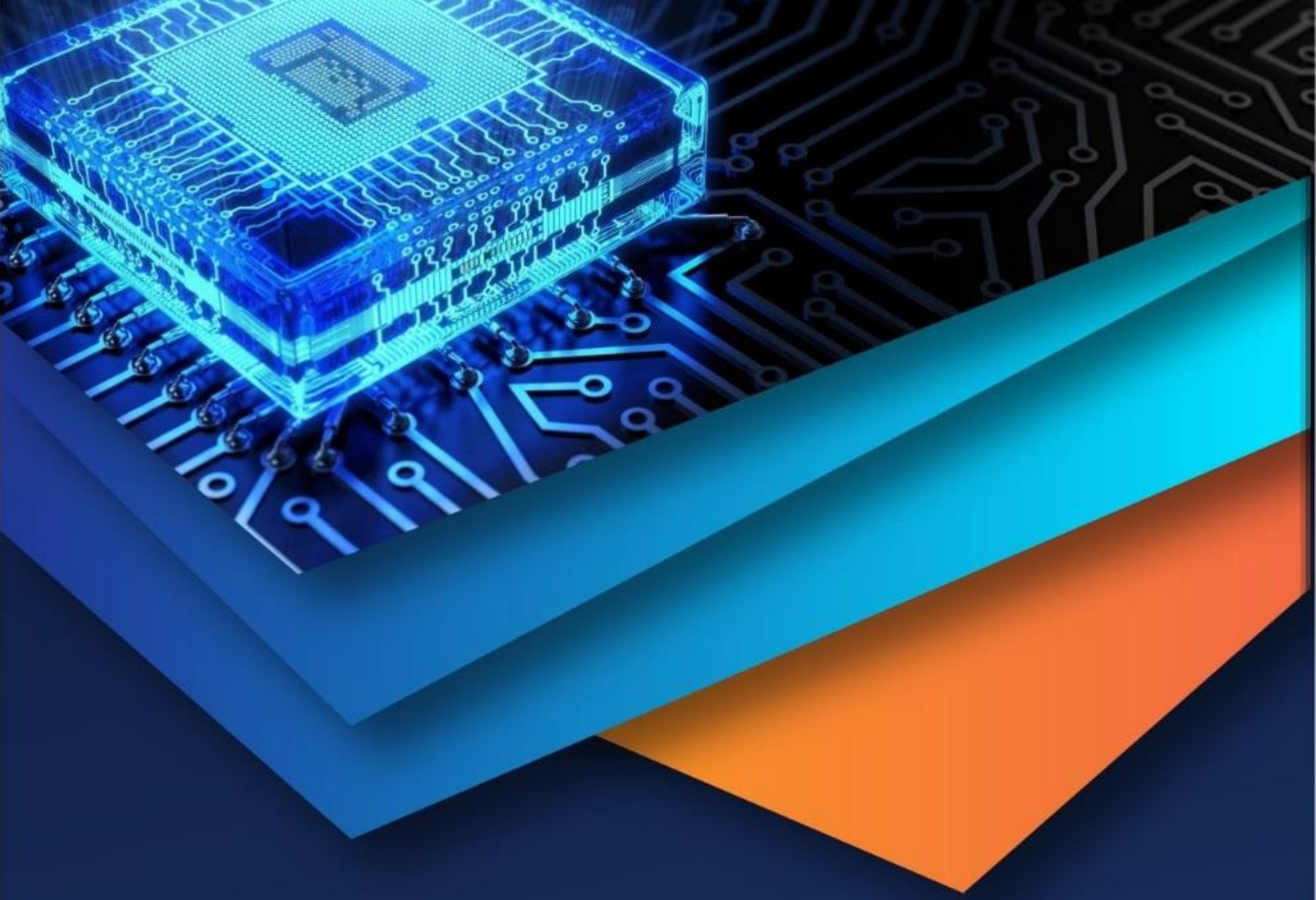

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