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FT-IR, FT-Raman, NMR and FMO Analysis of 3-(2-Furyl) Propionic Acid By Quantum Chemical Calculations

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Abstract— **In the present study 3-(2-Furyl) Propionicacid ($C_7H_8O_3$) abbreviated as 32FPA which has biological applications had been investigated with Density functional theory calculations with Gaussian 03 software package. The FT-IR, FT-Raman, NMR spectra of the title compound was recorded and analyzed. The equilibrium geometry, bonding features and harmonic vibrational wave numbers were investigated with the help of DFT method using B3LYP/6-311++G (d,p) basis set. The observed vibrational wave numbers were compared with the calculated results. The Frontier Molecular Orbital (FMO) Analysis of the title compound has also been carried out and the results were interpreted.**

Keywords- DFT; FT-IR; FT-Raman; NMR; 3-(2-Furyl) Propionic acid; FMO

I. INTRODUCTION

The Propionic acid (PA) inhibits the growth of mold and some bacteria [1]. As a result, most PA produced is used as a preservative for both animal feed and food for human consumption and the most effective use of it as growth promoter and feed additive in animal food especially poultry and pig [2,3]. For animal feed, it is used either directly or as its ammonium salt. Uses of antibiotics have a great threat as it create microbial resistance after long-term use which create a serious health problem. Antimicrobial feed additives such as PA is effective to antibiotic growth promoters for safe animal products as well as human health. Propionic acid is also useful as a chemical intermediate. It can be used to modify synthetic cellulose fibers. It is also used to make pesticides and pharmaceuticals. The esters of PA are sometimes used as solvents or artificial flavorings [4]. Other uses for Propionic acid includes preservative and flavoring agent for baked goods and cheese and as Food additives to prevent mold in bread, tortillas, and cheese (as calcium propionate and sodium propionate), Cellulose acetate propionate (CAP) production .Chemical intermediate for herbicides, pharmaceuticals, dyes, textile and rubber products, plastics, plasticizers, cosmetics, and perfumes.

In the present study 3-(2-Furyl) Propionic acid ($C_7H_8O_3$) abbreviated as 32FPA which has biological applications had been investigated with Density functional theory calculations with Gaussian 03 software package. The FT-IR, FT-Raman, NMR spectra of the title compound was recorded and analyzed. The equilibrium geometry, bonding features and harmonic vibrational wave numbers were investigated with the help of DFT method using B3LYP/6-311++G (d,p) basis set. The observed vibrational wave numbers were compared with the calculated results. The Frontier Molecular Orbital (FMO) Analysis of the title compound has also been carried out and the results were interpreted.

II. EXPERIMENTAL DETAILS

The compound under investigation namely 3-(2-Furyl) Propionic Acid (32FPA) is purchased from Sigma–Aldrich chemicals which is of spectra grade and hence used for recording the spectra as such without any further purification. The FT-IR spectrum of the compound was recorded in Bruker Tensor 27 spectrometer in the range of 4000–400 cm^{-1} with resolution of ±2 cm^{-1}. FT-Raman spectrum of the sample was recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 4000–100cm^{-1} on Bruker RFS-27 FT-Raman spectrometer. The detector is a liquid nitrogen cooled germanium detector.^1H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6 (Dimethyl Sulphoxide) using TMS (Tetramethylsilane) as an internal standard on a Bruker high-resolution NMR spectrometer at 300 MHZ.

III. COMPUTATIONAL DETAILS

The DFT calculations with a hybrid functional B3LYP (Becke's three parameter hybrid functional using the LYP correlation function) at 6-311++G (d,p) basis set were performed with the Gaussian 03W software package[5] and Gauss view visualization program[6]. The electronic properties such as HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energies were determined by time-dependent DFT (TD-DFT) approach [7, 8]. The nuclear magnetic resonance (NMR) chemical shift calculations were performed using Gauge-Independent Atomic Orbital (GIAO) method [9,10] at

B3LYP level with *6-311++G (d,p)* basis set and the ^{1}H and ^{13}C isotropic chemical shifts were referenced to the corresponding values of TMS, which was calculated at the same level of theory. The effect of solvent on the theoretical NMR parameters was included using default IEF-PCM model provided by Gaussian 03. Dimethylsulphoxide (DMSO) with relative permittivity (ε) 46.7 was used as a solvent [11]. Calculated ^{1}H and ^{13}C shielding constant for TMS in DMSO solvent at B3LYP level are 31.8 and 182.4 ppm respectively.

IV. RESULTS AND DISCUSSION

A. *Molecular Geometry*

The molecular structure of 32FPA along with numbering of atoms is obtained from Gaussian 03 and Gauss View programs and is shown in Figure 1. The global minimum energy obtained by DFT/B3LYP structure optimization using *6-311++G (d,p)* basis set for the title molecule is *-497.378097103a.u.* The most optimized structural parameters (bond length and bond angle) were calculated by *DFT/B3LYP* with *6-311++G (d,p)* basis set and the corresponding values are shown in *Table I.*

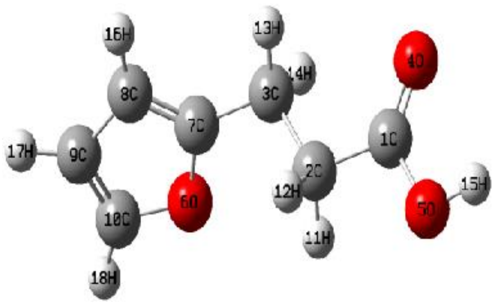

Figure 1. Optimization structure and atoms numbering of 32FPA

TABLE I. OPTIMIZED GEOMETRIC DATA FOR 32FPA USING B3LYP/6-311++G (D,P).

Bond length	**Value (Å)**	**Bond angle**	**Value (°)**	**Bond angle**	**Value (°)**
C_1-C_2	1.509	C_2-C_1-O_4	126.2	C_3-C_7-C_8	133.6
C_1-O_4	1.205	C_2-C_1-O_5	111.3	O_6-C_7-C_8	109.4
C_1-O_5	1.357	O_4-C_1-O_5	122.4	C_7-C_8-C_9	106.7
C_2-C_3	1.535	C_1-C_2-C_3	112.8	C_7-C_8-H_{16}	125.9
C_2-H_{11}	1.093	C_1-C_2-H_{11}	108.0	C_9-C_8-H_{16}	127.2
C_2-H_{12}	1.094	C_1-C_2-H_{12}	107.8	C_8-C_9-C_{10}	106.1
C_3-C_7	1.489	C_3-C_2-H_{11}	111.0	C_8-C_9-H_{17}	127.4
C_3-H_{13}	1.091	C_3-C_2-H_{12}	111.0	C_{10}-C_9-H_{17}	126.4
C_3-H_{14}	1.094	H_{11}-C_2-H_{12}	105.7	O_6-C_{10}-C_9	110.2
C_5-H_{15}	0.969	C_2-C_3-C_7	112.8	O_6-C_{10}-H_{18}	115.9
O_6-C_7	1.370	C_2-C_3-H_{13}	109.8	C_9-C_{10}-H_{18}	133.8
O_6-C_{10}	1.366	C_2-C_3-H_{14}	109.1		
C_7-C_8	1.361	C_7-C_3-H_{13}	108.4		
C_8-C_9	1.435	C_7-C_3-H_{14}	109.9		
C_8-H_{16}	1.078	H_{13}-C_3-H_{14}	106.3		
C_9-C_{10}	1.356	C_1-O_5-H_{15}	107.1		
C_9-H_{17}	1.078	C_7-O_6-C_{10}	107.4		
C_{10}-H_{18}	1.076	C_3-C_7-O_6	116.8		

B. *Vibrational Analysis*

From the structural point of view, the title molecule is assumed to have *C1* point group symmetry. The molecule consists of 18 atoms, hence undergoes $\Gamma 3N\text{-}6_{vib}=48$ normal modes of vibrations. For visual comparison, observed FT-IR and FT-Raman spectra of 32FPA are shown in *Figure 2 and 3*, respectively. The Carbon-Carbon stretching vibrations occur in the region 700-1200cm^{-1} [13]. The frequencies of the title compound observed in FT- IR spectrum at 1078, 1354, 1304cm^{-1} and the corresponding vibration appears at 1080cm^{-1} in FT-Raman vibration were assigned as C-C vibrations. In aromatic molecules, the C-H stretching vibrations appear in the range 3123-3152cm^{-1}.The asymmetric C-H stretching vibration appears from 3100-3000cm^{-1}[12]. Hence the FT- IR and FT- Raman bands at 3119, 3031, 2981, 2859, 1592, 1388cm^{-1} and 3120, 2859, 1593, 1389 cm^{-1} respectively are assigned to the C-H asymmetric bands. The symmetric C-H stretching vibrations are generally observed in the regions 2900-3000cm^{-1}[14]. In this compound FT-IR and FT-Raman modes are observed in 3144, 2924, 1505,1440,1418 cm^{-1} and 3144, 2923, 1506, 1445, 1419cm^{-1} respectively and hence assigned as C-H stretching vibrations. The absorption bands arising from the C-H in-plane and out of plane bending vibrations are usually observed in the region 850-1300cm^{-1} and 950-600cm^{-1}[15-17]. The in-plane bond vibrations of 32FPA in FT- IR and FT Raman are observed in 1354, 1304, 941, 912, 880, 597cm^{-1}and 942 cm^{-1},882cm^{-1} respectively. The C-H scissoring observed in the region 1455-1435cm^{-1}[18]. The FT- IR vibrational band at 1218, 1172, 1131cm^{-1}and the FT- Raman counterparts appeared at 32FPA vibration is 1226cm^{-1}.C-H wagging vibration is observed in the region1418-1267cm^{-1} [19, 20]. In the present case the bands observed at 1078, 1004cm^{-1} in FT-IR and at 1080cm^{-1} in Raman are assigned to the C-H wagging vibration. C-H torsion vibrations are observed in the region1295-1065cm^{-1} [20]. The torsion ring assigned to the FTIR region is 597cm^{-1}.The very weak intensity around the region 344,253cm^{-1}are assigned as torsion vibration in FT-Raman. If a compound contains a carbonyl group, the absorption caused by the C-O in plane bending vibration is observed in the region 850 cm^{-1} [21]. Consideration of these factors lead to assign the FT-IR band observed at 753cm^{-1} to C-O in plane bending vibration of the title compound. O-H stretching vibration of carboxylic acid usually appears as a very broad band and occurs in the region 3000-2400 cm^{-1} [22]. A broad band observed in the FT-IR spectrum at 3400-2400 cm^{-1} whose peaks at 3137, 2924, 2862, 2639, 2503 cm^{-1} is due to the O-H stretching of carboxylic acid.

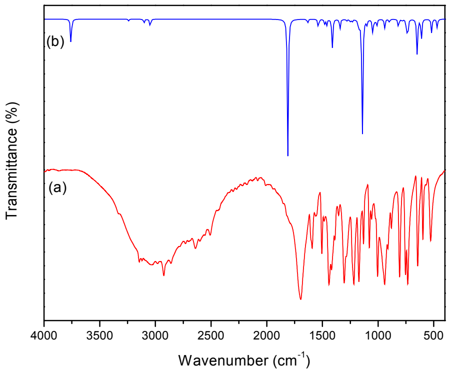

Figure 2. FT-IR spectra: (a) observed; (b) 6-311++G(d,p)

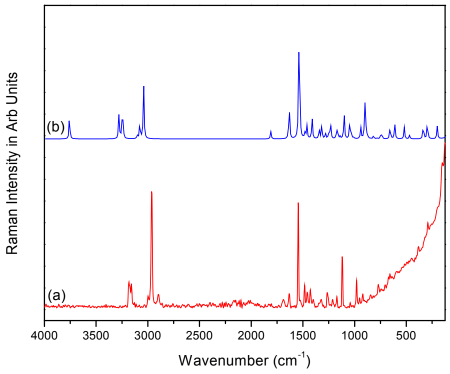

Figure 3. FT-Raman spectra: (a) observed; (b) 6- 311++G(d,p)

C. *Frontier Molecular Orbital (FMO)*

The most widely used theory by chemists is the Molecular Orbital (MO) theory. It is important that Ionization Potential (IP), Electron Affinity(EA), Electrophilicity index (ω), Chemical Potential(μ), Electro negativity(χ), Hardness(η), and First Excitation energy(τ) be put into a MO framework. On the basis of Koopman's theorem, [23] global reactivity descriptors are calculated using the energies of frontier molecular orbitals ε_{HOMO}, ε_{LUMO} and given by Equations (1) - (5) [24-29].

$$\chi = -1/2(\varepsilon_{LUMO} + \varepsilon_{HOMO}) \quad (1)$$

$$\mu = -\chi = 1/2(\varepsilon_{LUMO} + \varepsilon_{HOMO}) \quad (2)$$

$$\eta = 1/2(\varepsilon_{LUMO} - \varepsilon_{HOMO}) \quad (3)$$

$$S = 1/2\ \eta \quad (4)$$

$$\omega = \mu^2/2\ \eta \quad (5)$$

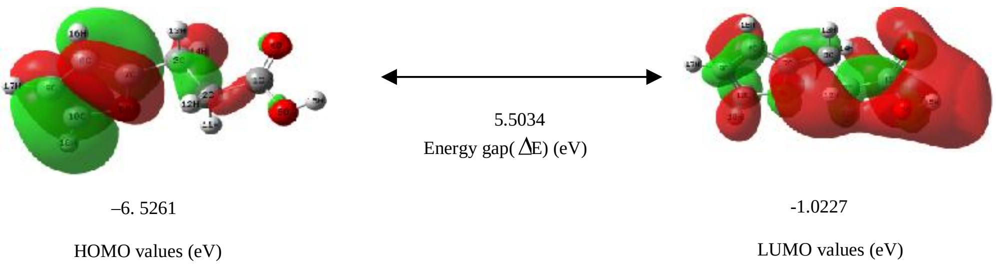

Figure 4. The atomic orbital compositions of the frontier molecular orbital of 32FPA

According to Parr et al. electrophilicity index (ω) [27] is a global reactivity index similar to the chemical hardness and chemical potential. This is a positive and definite quantity. The electronic chemical potential must be a negative quantity since it is a chemical species capable of accepting electrons and its energy must decrease upon accepting electronic charge.

The HOMO-LUMO energy gap of 32FP were calculated at the B3LYP/6-311++G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents the ability to donate an electron. The energy gap between the HOMO and LUMO molecular orbitals is a critical parameter in determining molecular electronic transport properties because it is a measure of electron conductivity [30]. The atomic orbital compositions of the frontier molecular orbital are sketched in Figure 4. The calculated Ionization Potential (IP), Electron Affinity (EA), Electrophilicity index (ω), Chemical Potential (μ), Electro negativity (χ) and Chemical Hardness (η) of the title compound are presented in Table II.

TABLE II. CALCULATED PHYSICO-CHEMICAL PROPERTIES FOR TITLE MOLECULE CORRELATED WITH MOLECULAR ORBITAL THEORY AT B3LYP METHOD.

Parameters	**Values**
HOMO energy (ε_{HOMO}) (eV)	-6.5261
LUMO energy (ε_{LUMO}) (eV)	-1.0227
HOMO-LUMO energy gap (eV)	5.5034
Ionization potential (IP) (eV)	-6.5261
Electron Affinity (EA) (eV)	-1.0227
Electrophilicity index (ω) (eV)	2.5909
Chemical Potential(μ) (eV)	-3.7744
Electro negativity(χ) (eV)	3.7744
Chemical Hardness(η) (eV)	2.7492
Softness (S) (eV^{-1})	0.1818

This large HOMO-LUMO gap automatically means high excitation energies for many of the excited states, good stability and a large chemical hardness for the title compound. The hardness has been associated with the stability of chemical system.

D. NMR Analysis

The experimental and theoretical values for ^{1}H and ^{13}C NMR of 32FPA are given in Tables III and IV. The NMR spectra were recorded in DMSO-d_6 and presented in Figures 5 and 6.In general, highly shielded protons appear downfield and vice versa.

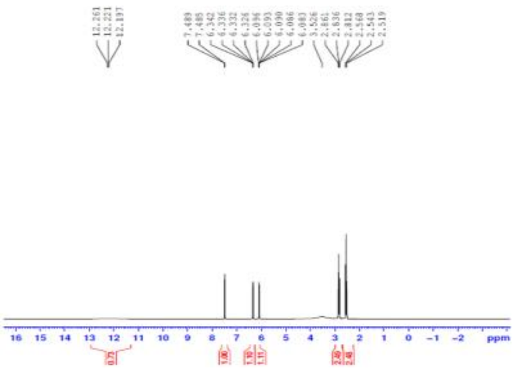

Figure 5. ^{1}H NMR spectrum of 32FPA

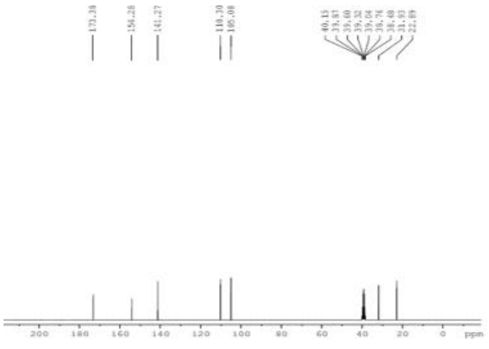

Figure 6. ^{13}C NMR spectrum of 32FPA

A singlet at 3.52 ppm mark the methylene hydrogens in the Propionic acid. Peaks at 6.5026, 6.6611, 7.7832 indicates the presence of aromatic hydrogen atoms, i.e. in the benzene ring [11]. 1C of the carboxyl group present in Propionic acid appears at higher chemical shift of 181.8 ppm due to neighbouring electronegative oxygen atoms. Peaks at 162.18 and 147.97 ppm, which belongs to 7C and 10C of the benzene ring, shows higher values when compared to 9C and 8C due to the direct attachment of electronegative oxygen atom. 15H of the Propionic acid also shows high value of 7.433 due the same reason.

TABLE III. EXPERIMENTAL AND CALCULATED ^{1}H NMR CHEMICAL SHIFTS (PPM) OF 32FPA

Proton	B3LYP/6-311++G(d,p)	Exp
11H	3.010	3.526
12H	2.501	2.543
13H	2.747	2.568
14H	2.834	2.836
15H	7.433	7.485
16H	6.502	6.336
17H	6.661	6.342
18H	7.783	7.489

TABLE IV. EXPERIMENTAL AND CALCULATED ^{13}C NMR CHEMICAL SHIFTS (PPM) OF 32FPA

Carbon	B3LYP/6-311++G(d,p)	Exp
1C	181.8	173.38
2C	34.190	38.48
3C	25.653	22.89
7C	162.185	154.28
8C	110.732	110.30
9C	115.093	105.08
10C	147.971	141.27

The calculated ^{1}H and ^{13}C NMR chemical shifts of 32FPA were compared with the experimental data. The predicted chemical shifts values were in close agreement with the experimental.

V. CONCLUSION

In this work, the compound 32FPA was experimentally characterized by means of FT-IR, FT-Raman and NMR spectroscopic techniques. The calculated geometrical parameters and vibrational frequencies obtained with density functional theory calculations B3LYP/6-311++G (d,p) method are in agreement with the experimental values obtained for the investigated molecule. In addition, the Frontier Molecular Orbital analyses of the title compound have been undergone and the result shows that the title compound having large HOMO-LUMO value is chemically stable.

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