

# Comparative Study of structural, vibrational, electronic properties of pentanoic acid (Valeric acid) and its derivative 4-oxopentanoic acid (Levulinic acid) by Density Functional Theory

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This work deals with the theoretical study on the molecular structure and vibrational spectra of two well known acids: Valeric acid & Levulinic acid. The spectra were interpreted with the aid of normal mode analysis following full structure optimization carried out with the (B3LYP/LANL2DZ) basis set combination. A detailed interpretation of the infrared spectra of Valeric acid & Levulinic acid is also reported in the present work. The similarities and differences between the vibrational spectra of the two molecules studied have been highlighted. In the absence of FTIR spectra, these calculated frequencies are very helpful for experimental research. The thermodynamic calculations related to the title compounds were also performed at same level of theory. Quantum chemical calculations have been carried out to understand the dynamical behavior of the bioactive molecules Valeric acid & Levulinic acid.

## Introduction

Valeric acid, or pentanoic acid, is a straight-chain alkyl carboxylic acid with the chemical formula  $C_5H_{10}O_2$ . Like other low-molecular-weight carboxylic acids, it has a very unpleasant odor. It is found naturally in the perennial flowering plant valerian (*Valeriana officinalis*), from which it gets its name. Its primary use is in the synthesis of its esters. Volatile esters of valeric acid tend to have pleasant odors and are used in perfumes and cosmetics. Ethyl valerate and pentyl valerate are used as food additives because of their fruity flavors. Valeric acid appears similar in structure to GHB and the neurotransmitter GABA in that it is a short-chain carboxylic acid, although it lacks the alcohol and amine functional groups that contribute to the biological activities of GHB and GABA, respectively. It differs from valproic acid simply by lacking a 3-carbon side-chain [1].

Levulinic acid, or 4-oxopentanoic acid, is an organic compound with the formula  $CH_3C(O)CH_2CH_2CO_2H$ . It is classified as a keto acid. This white crystalline is soluble in water and polar organic solvents. It is derived from degradation of cellulose and is a potential precursor to biofuels [2, 3]. Levulinic acid is the precursor to pharmaceuticals, plasticizers, and various other additives [4].

Potential biofuels can be prepared from levulinic acid including methyltetrahydrofuran, valerolactone, and ethyl levulinate. Dehydration of levulinic acid gives angelica lactone [5]. Levulinic acid is used in cigarettes to increase nicotine delivery in smoke and binding of nicotine to neural receptors [6].

As a part of our ongoing research work [7-18], here, the main objective of the present study is to investigate in detail the vibrational spectra of the important industrial and biological molecule i.e. Valeric acid & Levulinic acid.

## Computational Details

The entire calculations were performed on a Pentium IV/1.66 GHZ personal computer using the Gaussian 09W [19] program package, invoking gradient geometry optimization [20]. The initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface at the B3LYP level, adopting the standard LANL2DZ basis set. The optimized structural parameters were used in the vibrational frequency calculations to characterize all stationary points as minima. We have utilized the gradient corrected density functional theory (DFT) [21] with the three-parameter hybrid functional (B3LYP) [22] for the exchange part, and the Lee-Yang-Parr (LYP) correlation function [23] for the computation of the molecular structure, vibrational frequencies, and energies of the optimized structures. Vibrational frequencies calculated at the B3LYP/LANL2DZ level were scaled by a factor of 0.96 above 800 and by 1.0013 below 800 [24]. Finally, the calculated normal mode vibrational frequencies also provided the thermodynamic properties through the principles of statistical mechanics.

## Results and Discussion

### Geometry Optimization

The optimized structural parameters of Valeric acid & Levulinic acid calculated by DFT, B3LYP method with the LANL2DZ basis set are listed in Table 1 in accordance with the atom numbering scheme given in Fig-1 and Fig-2. In Valeric acid, the optimized bond lengths of C-C in chain structure falls in the range from 1.513 Å to 1.542 Å. The optimized bond lengths of C=O and C-O in chain structure are 1.239 Å and 1.394 Å respectively. The optimized bond lengths of O-H in chain structure are 0.984 Å. The optimized bond lengths of C-H in chain structure falls in the range from 1.097 Å to 1.101 Å. In Levulinic acid, the optimized bond lengths of C-C in chain structure falls in the range from 1.511 Å to 1.534 Å. The

optimized bond lengths of C=O are 1.241 Å & 1.249 Å but C-O in chain structure is 1.389 Å respectively. The optimized bond lengths of O-H in chain structure are 0.984 Å. The optimized bond lengths of C-H in chain structure falls in the range from 1.093 Å to 1.100 Å. All calculated bond lengths and bond angles also shown an excellent agreement with experimental data.

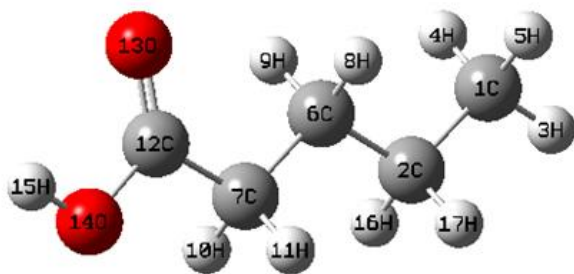


Fig. 1 Model Molecular structure of Valeric acid

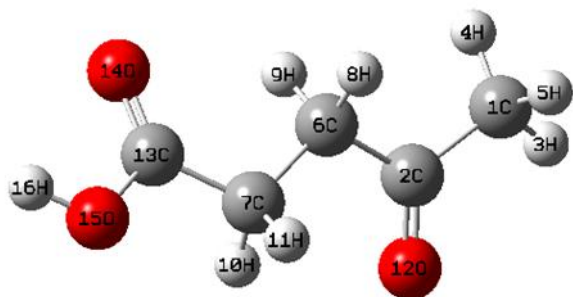


Fig. 2 Model Molecular structure of Levulinic acid

### Dipole moment, Thermo-dynamical and electrical properties

The frontier orbitals, HOMO and LUMO determine the way the molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gap is more polarized having more reactive part as far as reaction is concerned [25]. According to the present calculations, the frontier orbital gap in case of the given molecules is 5.9103 and 3.7479 eV respectively for Valeric acid & Levulinic acid given in Table 3. The plots of the HOMO, LUMO and electrostatic potential for both the molecules are shown in Fig. 3-6.

For Valeric acid, HOMO is located over left hand side of molecule. LUMO are located at same place as HOMO i.e. left hand side of chain. For Levulinic acid, HOMO is located over right hand side of chain. LUMO is located over whole molecule differing from valeric acid (Fig.3 & 4). Potential Energy Surface (PES) pictures of Valeric acid (left) and Levulinic acid are given in figure 5.

The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading (shown in Fig. 6) and is very useful in investigation of molecular structure with its physiochemical property relationship [26-30].

The total dipole moment a Cartesian frame is defined by

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

The calculated dipole moments for Valeric acid & Levulinic acid are 1.65 and 2.17 Debye respectively. Comparison of the calculated dipole moment of given compounds with water show that it is than higher for Levulinic acid and lower for Valeric acid. [A dipole moment value for water is 2.16 Debye, at the same level of calculations i.e., B3LYP/LANL2DZ]. Thermodynamic properties of the Valeric acid & Levulinic acids were calculated by B3LYP/LANL2DZ levels and are given in Table 2.

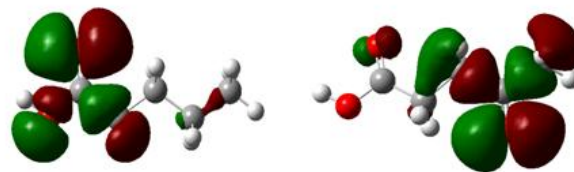


Fig. 3 HOMO pictures of Valeric acid (left) and Levulinic acid (right)

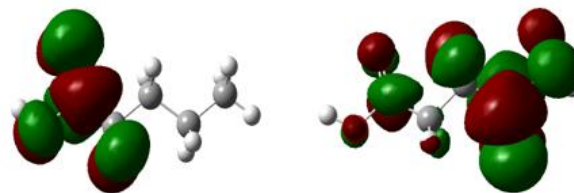


Fig. 4 LUMO pictures of Valeric acid (left) and Levulinic acid (right)

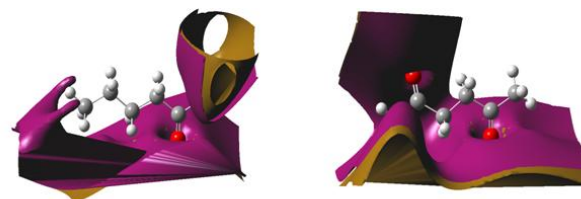


Fig. 5 Potential Energy Surface (PES) pictures of Valeric acid (left) and Levulinic acid (right)

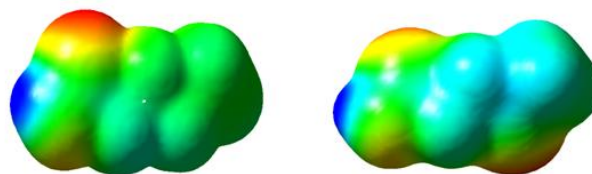


Fig. 6 MESP pictures of Valeric acid (left) and Levulinic acid (right)

### Vibrational Assignments

The molecules Valeric acid & Levulinic acid contains 17 and 16 atoms and they have 45 and 42 normal modes of vibration respectively. All the fundamental vibrations are active IR. The harmonic-vibrational frequencies are calculated for both the molecules at B3LYP/LANL2DZ level and are listed in Tables 4

and 5 for Valeric acid & Levulinic acid respectively. Table 3 and 4 also includes the vibrational assignments of the normal modes. Vibrational assignments are based on the observation of the animated modes in *GaussView* [31] and assignments reported in literature.

**Table 1** Comparison of Bond-lengths and Bond-angles of Valeric acid & Levulinic acid

Valeric acid			Levulinic acid		
Bond Length	Exp.	Cal.	Bond Length	Exp.	Cal.
R(1,2)	1.57	1.54	R(1,2)	1.50	1.52
R(1,3)	-	1.09	R(1,3)	0.98	1.09
R(1,4)	-	1.09	R(1,4)	0.98	1.09
R(1,5)	-	1.09	R(1,5)	0.98	1.09
R(2,6)	1.57	1.54	R(2,6)	1.50	1.52
R(2,16)	-	1.10	R(2,12)	1.22	1.24
R(2,17)	-	1.10	R(6,7)	1.52	1.53
R(6,7)	1.53	1.53	R(6,8)	0.99	1.09
R(6,8)	-	1.09	R(6,9)	0.99	1.10
R(6,9)	-	1.09	R(7,10)	0.99	1.09
R(7,10)	-	1.09	R(7,11)	0.99	1.09
R(7,11)	-	1.09	R(7,13)	1.50	1.51
R(7,12)	1.53	1.51	R(13,14)	1.20	1.24
R(12,13)	1.26	1.23	R(13,15)	1.33	1.38
R(12,14)	1.35	1.39	R(15,16)	0.83	0.98
R(14,15)	-	0.98			
Bond Angles	Exp.	Cal.	Bond Angles	Exp.	Cal.
A(2,1,3)	-	111.34	A(2,1,3)	109.5	110.20
A(2,1,4)	-	110.97	A(2,1,4)	109.5	111.26
A(2,1,5)	-	110.97	A(2,1,5)	109.5	109.42
A(3,1,4)	-	107.86	A(3,1,4)	109.5	110.02
A(3,1,5)	-	107.86	A(3,1,5)	109.5	108.58
A(4,1,5)	-	107.66	A(4,1,5)	109.5	107.19
A(1,2,6)	111.18	112.50	A(1,2,6)	116.57	116.53
A(1,2,16)	-	109.41	A(1,2,12)	122.14	121.69
A(1,2,17)	-	109.41	A(6,2,12)	121.30	121.76
A(6,2,16)	-	109.45	A(2,6,7)	114.68	112.99
A(6,2,17)	-	109.45	A(2,6,8)	108.6	109.22
A(16,2,17)	-	106.41	A(2,6,9)	108.6	107.92
A(2,6,7)	107.31	112.03	A(7,6,8)	108.6	111.41
A(2,6,8)	-	109.76	A(7,6,9)	108.6	109.71
A(2,6,9)	-	109.76	A(8,6,9)	107.6	105.23
A(7,6,8)	-	109.49	A(6,7,10)	109.4	109.68
A(7,6,9)	-	109.49	A(6,7,11)	109.4	111.94
A(8,6,9)	-	106.11	A(6,7,13)	111.32	112.35
A(6,7,10)	-	111.07	A(10,7,11)	108.0	105.42
A(6,7,11)	-	111.08	A(10,7,13)	109.4	108.29
A(6,7,12)	111.34	113.41	A(11,7,13)	109.4	108.83
A(10,7,11)	-	105.69	A(7,13,14)	124.51	126.95
A(10,7,12)	-	107.59	A(7,13,15)	112.48	111.42
A(11,7,12)	-	107.59	A(14,13,15)	123.01	121.61
A(7,12,13)	127.14	127.40	A(13,15,16)	106.3	110.76
A(7,12,14)	115.56	111.23			
A(13,12,14)	116.49	121.35			
A(12,14,15)	-	110.54			

<sup>a</sup> Bond-lengths (in Å) and bond-angles in degrees.

**Table 2** Calculated Thermodynamic Properties<sup>a</sup> of Valeric acid and Levulinic acid by B3LYP/LANL2DZ method

	E (Thermal) (kcalmol <sup>-1</sup> )		C <sub>v</sub> (cal K <sup>-1</sup> mol <sup>-1</sup> )		S (cal K <sup>-1</sup> mol <sup>-1</sup> )	
	Valeric	Levulinic	Valeric	Levulinic	Valeric	Levulinic
Total	97.787	85.822	28.952	30.762	91.344	97.215
Translational	0.889	0.889	2.981	2.981	39.779	40.162
Rotational	0.889	0.889	2.981	2.981	28.178	28.874
Vibrational	96.009	84.045	22.990	24.800	23.387	28.180

<sup>a</sup>At 298 K

5

**Table 3** Lowest Energy, HOMO- LUMO Gap (Frontier orbital energy gap) and Dipole Moment of Valeric acid and Levulinic acid by B3LYP/LANL2DZ methods.

Parameters	Valeric acid	Levulinic acid
Energy (in au)	-346.9747	-420.9794
HOMO (in eV)	-7.8336	-7.0203
LUMO (in eV)	-1.9233	-3.2724
Frontier orbital energy gap (in eV)	5.9103	3.7479
Dipole moment (in Debye)	1.651	2.175

#### <sup>10</sup> Spectral region over 2800 cm<sup>-1</sup>

The bands located in the high frequency region of the spectra of Valeric acid are easy to identify and belong to O–H and C–H stretching modes. The band due to O–H stretching vibration attached to the base ring is calculated at 3511 cm<sup>-1</sup> having good IR intensity. The corresponding bands at 2946 and 3010 cm<sup>-1</sup> are assigned to the C–H stretching mode having good IR intensity. For Levulinic acid, the band due to O–H stretching vibration is calculated at 3513 cm<sup>-1</sup> having good IR intensity. The corresponding bands at 2937 and 3007 cm<sup>-1</sup> are assigned to the C–H stretching mode. These are usual range of appearance for O–H and C–H stretching vibrations.

**Table 4** Vibrational frequencies and assignments of Valeric acid.

B3LYP (Calc)	IR (Int.)	Vibrational Assignments [P.E.D.]
39	0.0964	Twist CH2 in whole molecule
76	0.0997	Whole molecule twist from center
117	0.1425	Twist CH2
120	1.4675	Torsion in whole molecule
220	0	Rock CH3
285	2.0574	τ (C–C–C–H) whole molecule
316	4.7926	τ (C–C–C–C) whole molecule
475	23.389	τ (C–C–C–C) whole molecule
496	35.662	τ (O13–C12–O14–H15)
580	24.252	β (O14–C12–O13)
618	142.16	γ (H15–O14–C12)
720	16.545	Rock CH2
788	1.2623	Rock CH2
838	2.3885	Whole molecule bend
889	12.501	Rock CH3
917	5.4172	Twist CH2
1002	62.561	Whole molecule bend
1043	189.98	β (C12–O14–H15) + Rock CH2
1056	12.722	β (C–C–C) whole molecule
1107	51.404	β (C–C–C) whole molecule

1109	0.3928	Twist CH2
1200	0.3136	Twist CH2
1229	0.0082	$\beta$ (C12-O14-H15) + Rock CH2
1265	0.3979	Rock CH2 group
1277	30.876	Twist CH2 group
1280	0.0956	Rock CH2 group
1338	29.518	Twist CH2 group
1366	18.888	$\beta$ (C-C-H) in whole molecule
1386	16.93	Bending in CH3 group
1433	26.588	$\beta$ (H10-C7-H11)
1460	1.2481	$\beta$ (C-C-H) in whole molecule
1465	11.982	Twist CH3
1466	1.5679	S (H9-C6-H8) + S (H16-C2-H17) + S (H4-C1-H5)
1478	19.562	S (H9-C6-H8) + S (H16-C2-H17) + S (H4-C1-H5)
1654	234.58	$\nu$ (C12-O13)
2913	39.750	$\nu$ (C2-H16) + $\nu$ (C2-H17)
2922	28.111	$\nu$ (C1-H3) + $\nu$ (C1-H4) + $\nu$ (C1-H5)
2938	2.0294	$\nu$ (C-H) at C6, C7
2946	43.085	$\nu$ (C-H) at C6, C7
2951	11.934	$\nu$ (C-H) at C2, C6
2978	0.0308	$\nu$ (C-H) at C6, C7
3001	0.4318	$\nu$ (C-H) at C1, C6, C7
3010	56.445	$\nu$ (C1-H3) + $\nu$ (C1-H4) + $\nu$ (C1-H5)
3013	131.30	$\nu$ (C-H) whole molecule
3511	32.262	$\nu$ (O14-H15)

<sup>a</sup>  $\nu$  - Stretching,  $\beta$ : - bending; S- scissoring,  $\tau$  - torsion.

**Table 5** Vibrational frequencies and assignments of Levulinic acid.

B3LYP (Calc)	IR (Int.)	Vibrational Assignments [P.E.D.]
26	8.117	Twist in whole molecule
54	0.0895	Twist in whole molecule
79	0.9032	Twist in whole molecule
99	0.2025	Rock CH3
137	10.319	Twist in whole molecule
248	0.245	Torsion in whole molecule
315	1.9616	Torsion in whole molecule
445	9.7905	Rocking in whole molecule
469	28.554	Torsion in whole molecule
501	55.925	$\tau$ (H11-C7-C13-O14)
563	23.655	$\tau$ (C-C-C-C) whole molecule
587	9.9247	$\tau$ (H16-O15-C13-O14)
628	138.14	w (O-H)
754	12.410	Twist CH2
796	4.208	whole molecule bend
873	0.2827	$\beta$ (C-C-C) whole molecule
925	12.014	Twist CH2
955	1.6811	Twist CH3
1039	184.92	$\beta$ (C13-O15-H16)
1058	2.6141	$\beta$ (C-C-C) whole molecule
1083	122.84	$\beta$ (C-C-C) whole molecule
1154	5.1233	Rock CH2
1170	30.920	Twist CH2 + Twist CH3

1235	23.706	Twist CH2 + Twist OH
1249	28.779	Twist CH2
1314	130.16	$\beta$ (C-C-H) whole molecule
1370	59.690	$\beta$ CH3
1373	12.576	$\gamma$ CH2
1432	0.1396	S (H8-C6-H9) + S (H10-C7-H11)
1435	15.960	Rock CH2
1439	76.431	S (H9-C6-H8) + S (H16-C2-H17)
1447	17.332	Twist CH3
1628	162.35	$\nu$ (C2-O12)
1649	185.72	$\nu$ (C13-O14)
2929	1.0716	$\nu$ (C1-H3) + $\nu$ (C1-H4) + $\nu$ (C1-H5)
2937	14.641	$\nu$ (C6-H8) + $\nu$ (C6-H9)
2961	13.680	$\nu$ (C7-H10) + $\nu$ (C7-H11)
2980	9.0914	$\nu$ (C6-H8) + $\nu$ (C6-H9)
3007	14.855	$\nu$ (C1-H4) + $\nu$ (C1-H5)
3020	11.516	$\nu$ (C7-H11) + $\nu$ (C7-H10)
3060	14.276	$\nu$ (C1-H3) + $\nu$ (C1-H4)
3513	39.074	$\nu$ (O15-H16)

<sup>a</sup>  $\nu$  - Stretching,  $\beta$ : - bending; S- scissoring, w – wagging,  $\tau$  - torsion.

### Spectral region 1750–1000 $\text{cm}^{-1}$

For Valeric acid, in middle region, the H-C-H scissoring predicted at 1478  $\text{cm}^{-1}$  having good IR intensity. The strong stretching vibration of the C-O band is calculated at 1654  $\text{cm}^{-1}$ , having highest IR intensity. For Levulinic acid, in middle region, the H-C-H scissoring predicted at 1439  $\text{cm}^{-1}$  having good IR intensity. The strong stretching vibrations of the C-O bands are calculated at 1628 and 1649  $\text{cm}^{-1}$  having appropriate IR intensity.

### Spectral region 1000–450 $\text{cm}^{-1}$

For codeine, as expected, the ring torsion modes along with out of plane bending modes appear in the observed low frequency range. The ring torsion and out of plane ring bend; all of them appear in the 1000-450  $\text{cm}^{-1}$  frequency range. The ring torsion is calculated at 475  $\text{cm}^{-1}$ , having good IR intensity. For Levulinic acid, the torsion is calculated at 501 and 563  $\text{cm}^{-1}$ . In plane bending is calculated at 1039  $\text{cm}^{-1}$  having high IR intensity.

In the absence of experimental data, these calculated frequencies are very helpful for experimental researchers.

### Conclusion

Attempts have been made in the present work for the proper frequency assignments for Valeric acid & Levulinic acid from calculated frequencies. The equilibrium geometries and harmonic frequencies of Valeric acid & Levulinic acid were determined and analyzed at DFT level of theory utilizing LANL2DZ as the basis set. The vibrational frequency calculation proved that both structures are stable (no imaginary frequency). Experimental FTIR is not available so we have done calculated frequency assignments. The advantage of calculated frequencies over FTIR spectra is due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. So these calculated frequencies are very helpful for experimental researchers.

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### Notes and References

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