# VIBRATIONAL ANALYSIS AND DENSITY FUNCTIONAL CALCULATION ON L-LYSINE MONOHYDROCHLORIDE DIHYDRATE

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## ABSTRACT

Semi-organic nonlinear optical single crystal of L-lysine monohydrochloride dihydrate (L-LMHCl) has been grown by slow evaporation solution growth technique. The structural analysis and internal standard calculation on the crystal L-LMHCl have been studied using Fourier transform infrared (FTIR) spectroscopy. The structural analysis of the crystal has been studied using AM1, PM3 and ab initio methods and the results have been discussed for the first time.

Keywords: L-LMHCl, FTIR, ab initio, Thermo dynamical parameters

## **1. INTRODUCTION**

The complexes of organic-inorganic give semiorganic materials, which are found to be possessing higher mechanical strength when compared to organic counterparts (Koshima H et al., 2001 and Anwar P et al., 2000). Specifically, amino acids and strong inorganic acids are good raw materials to produce semi-organic crystals because amino acid crystals are having excellent optical properties (Razzetti C et al., 2002). Also, one of the amino acids of L-lysine monohydrochloride dihydrate (L-LMHCl) is a very good semi-organic material for nonlinear optical applications (Marchewka M. K et al., 2003). In this series, a promising nonlinear optical crystals of L-Lysine monohydrochloride dehydrate (L-LMHCl) was grown by slow evaporation solution growth technique using deionised water as a solvent. The results of FTIR, FT-RAMAN, NMR, TG-DTA, UV-visible spectrum, Vicker's microhardness, SHG efficiency, high resolution X-ray diffraction, Micro-Raman, etching and dielectric studies of L-Lysine monohydrochloride dihydrate have been discussed in earlier report (Ramesh Babu and R Sethuraman K et al., 2006 and Ramesh Babu R and Vijavan N et al., 2006). In the present study, for the first time the structural analysis of L-LMHCl dihydrate crystal has been studied using AM1, PM3 and ab initio methods.

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## 2. Experimental

The saturated solution of L-LMHCl was prepared using deionised water as a solvent at room temperature and the selected seed crystals were used to grow bulk crystals using Constant Temperature Bath maintained at 303 K. A colorless bulk crystal ( $39 \times 15 \times$ 6 mm<sup>3</sup>) was harvested with in 4 weeks by slow evaporation technique. The grown crystal (Fig 1), the molecular structure and FTIR spectrum of L-LMHCl are presented in Fig. 2 and Fig. 3 respectively.

## 3. Computational details

The DFT calculations were performed on L-LMHCl using Gaussian 03 W (Frisch MJ et al., 2003) program package, invoking gradient geometry optimization (Schlegel HB, 1982). The optimized structural parameters have been used in the vibrational frequencies calculations at AM1, PM3 and ab initio methods as basis set. It has utilized the gradient corrected density functional theory (Hohenberg P et al., 1964) with three-parameter hybrid functional for exchange part and the Lee-Yang-Parr correlation function (Lee C et al., 1988) for the computation of vibrational frequencies and energies of optimized structure. The simulated IR spectra of L-LMHCl at AM1, PM3 and ab initio methods have been highlighted in Fig 4.

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Fig.1. Pure LMHCl crystal (Dimensions  $39 \times 15 \times 6 \text{ mm}^3$ )



Fig.2 Molecular structure of L-Lysine



Fig.3 FTIR spectrum of L-LMHCl





PM3 and ab initio methods

## 4. Vibrational analysis

The vibrational frequency assignments of L-LMHCl have been made on the basis of magnitude and relative intensities of the observed bands in analogy with the related compounds. The calculated vibrational wave number, IR intensities, reduced mass and force constants for L-LMHCl are summarized in Tables 2, 3 and 4 respectively for AM1, PM3 and ab initio methods. The vibrational band assignments have been summarized in Table 5. The important vibrational band assignments have been discussed below.

## O–H Stretching

Alcohols and phenols, in vapour state or in dilute solution in non-polar solvents exhibit a sharp rather weak O-H stretching absorption due to non-bonded or free OH groups. These non-bonded O-H stretching bands appear near 3650 cm<sup>-1</sup> in alcohols and near 3600 cm<sup>-1</sup> in phenols. Inter - molecular hydrogen bonding increases as the concentration of the solute in solution increases and additional bands start to appear at lower frequencies near 3550-3200 cm<sup>-1</sup> at the expense of the free hydroxyl band (Robert M Silverstein et al., 1997). In the present work the bands observed at 3463 in AM1 and 3516 cm<sup>-1</sup> in PM3 methods have been assigned to O–H Stretching vibrations.

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#### C=O/C – O Stretching

The C=O stretching vibrations of acids are considerably more intense than ketonic C=O stretching bands. The monomers of saturated aliphatic acids absorb near 1760 cm<sup>-1</sup> (Xavier Jesu Raja S et al., 1994). Based on this, in the present investigation the bands observed at 1724 in PM3, 1807 in ab initio and a very strong band at 1860 cm<sup>-1</sup> in FTIR have been assigned to C = O stretching vibrations. The absorption region for the alcohol C - O group due to its stretching vibration is 1200-1000 cm<sup>-1</sup>. Considering this point, the bands observed at 1128, 1190, 1211 in AM1 and bands at 1189, 1222 cm<sup>-1</sup> in PM3 and at 1181, 1209 in ab initio and 1215 cm<sup>-1</sup> in FTIR spectrum have been assigned to C-O stretching vibrations. These observations are in good agreement with the literature values (Gunasekaran S et al., 2004).

#### **C-N Vibrations**

The identification of C-N stretching frequency is a very difficult task since mixing of bands is possible in this region. The C-N stretching absorption of primary aliphatic amines is weak and occurs in the region 1090 -1020 cm<sup>-1</sup>, secondary aliphatic amines have two bands of medium intensity in the region 1190-1170 cm<sup>-1</sup> and 1145-1130 cm<sup>-1</sup>. For aromatic and unsaturated amines, two bands are observed at 1360-1250 cm<sup>-1</sup> and 1280-1180 cm<sup>-1</sup>. Based on this in the present investigation, the bands observed between 1274 and 1405 cm<sup>-1</sup> in all the methods have been assigned to C-N stretching vibrations.

#### Methylene group vibrations

The asymmetrical stretching and symmetrical stretching of  $CH_2$  occur, respectively near 2926 cm<sup>-1</sup> and 2853 cm<sup>-1</sup>. The frequency of methylene stretching is increased when the methylene group is part of a strained ring (Robert M Silverstein et al., 1997). Hence in the present work, the bands observed at 2980 and 2973 cm<sup>-1</sup> in AM1 method have been assigned to asymmetric stretching and symmetric stretching vibrations of  $CH_2$  respectively. Also the band observed at 2952 in PM3 method has been assigned to symmetric  $CH_2$  vibrations. In addition to these bands the other methylene bending vibrations have been assigned in the characteristic range. It is in good agreement with the literature value.

## Table 1. Vibrational wavenumbers obtained for L-LMHCl at AM1 [ harmonic frequency cm<sup>-1</sup>, IR intensities (Km mol<sup>-1</sup>), reduced masses (amu) and force constants (mdyneA<sup>-</sup>)]

		IR	Reduced	Force
No	Wavenumber	Intensity	mass	constant
1	280	1.81	3.21	0.148
2	317	6.92	3.92	0.232
3	400	5.64	3.35	0.417
4	480	19.94	3	0.41
5	487	5.95	3.19	0.44
6	542	20.09	2.41	0.42
7	557	104.46	1.3	0.24
8	623	24.32	4	0.92
9	723	11.19	5.34	1.64
10	764	5.2	1.13	0.39
11	863	1.16	1.39	0.61
12	934	17.74	1.65	0.85
13	969	48.23	1.92	1.06
14	994	183.16	1.43	0.83
15	1013	19.69	1.61	0.98
16	1060	33.63	1.58	1.04
17	1082	11.58	1.52	1.05
18	1128	6.19	1.25	0.94
19	1158	0.47	1.44	1.13
20	1190	10.54	2.15	1.79
21	1210	2.64	1.3	1.13
22	1219	0.26	1.19	1.04
23	1230	6.83	1.62	1.45
24	1239	0.23	1.26	1.14
25	1256	8.6	1.34	1.25
26	1274	2.74	1.4	1.34
27	1326	0.21	1.25	1.3
28	1338	0.91	1.29	1.36
29	1352	2.09	1.29	1.39
30	1355	2.37	1.46	1.58
31	1378	5.66	1.17	1.31
32	1398	0.14	1.55	1.79
33	1402	0.44	1.15	1.33

Table 1 continued...

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## Table 1 continued...

No	Wavenumber	IR Intensity	Reduced mass	Force constant
35	1413	46.5	1.43	1.68
36	1417	36.38	1.45	1.71
37	1440	0.2	2.78	3.4
38	1467	22	2.81	3.56
39	1472	3.71	3.24	4.13
40	1540	93.93	3.42	4.79
41	1724	4.31	1.12	1.96
42	1732	0.77	1.13	2
43	2973	13.01	1.07	5.57
44	2980	0.87	1.09	5.7
45	3008	1.13	1.09	5.8
46	3020	6.23	1.09	5.87
47	3034	2.09	1.1	5.94
48	3049	0.43	1.04	5.73
49	3079	0.68	1.04	5.83
50	3091	4.05	1.05	5.92
51	3102	1.34	1.05	5.98
52	3415	21.87	1.09	7.51
53	3418	6.42	1.09	7.51
54	3421	134.39	1.06	7.33
55	3461	17.5	1.04	7.34
56	3463	5.95	1.04	7.36

## Table 2: Vibrational wave numbers obtained for L-LMHCl at PM3 [harmonic frequency cm<sup>-1</sup>, IR intensities (Km mol-1), reduced masses (amu) and force constants (mdyneA<sup>-</sup>)]

No	Wave number	IR Intensity	Reduced mass	Force constant
1	259	4.05	3.28	0.13
2	301	4.13	3.75	0.2
3	444	19,07	4.06	0.47
4	452	10.02	3.07	0.37
5	501	0.86	2.37	0.35
6	523	115.77	1.14	0.18
7	584	12.95	4.21	0.85
8	682	18.2	6.4	1.76
9	766	1.83	1.14	0.39
10	838	1.03	0.57	1.41
11	876	0.8	1.76	0.8
12	906	6.06	2.12	1.02
13	960	3.85	1.44	0.78
14	988	1.34	1.32	0.76
15	1024	5.14	1.19	0.73

#### IR Reduced Force Intensity No Wave number constant mass 16 1035 11.51 1.83 17 1061 25.99 1.56 18 1081 5.81 1.51 19 1083 5.21 1.37 201108 6.32 1.36 21 1126 14.3 1.37 22 10.08 1136 1.37 23 1145 12.69 1.3 1152 24 6.89 1.25 25 1171 10.11 1.41 1179 26 13.06 1.37 5.04 1.23 27 1189 28 1223 48.56 1.78 29 1238 27.79 1.39 30 1243 22.01 1.4 31 1288 22.33 2.02 32 1318 6.23 1.98 33 1354 8.51 2.12 34 1380 2.48 1.19 35 1395 1.39 1.18 36 1402 0.93 1.36 37 9.52 1.63 1413 7.39 38 1414 1.76 39 1435 107.41 4.97 40 7.51 1660 1.82

Table 2 continued

1.16

1.03

1.04 0.95

0.98

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1.04

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0.98

1.13

1.12

1.06

1.57

1.26

1.27

1.97

2.03

2.29

1.33

1.36

1.57

1.92

1.49

6.03

1.12

1.86

5.17

5.59

5.62

5.63

5,66

5.06

1.05

1.05

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7.38

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7.61

1.12

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1.1

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# Table 2 continued...

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0.75

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2.29

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0.2

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7.19

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## Table 3: Vibrational wave numbers obtained for L-LMHCl at ab initio [harmonic frequency cm<sup>-1</sup>, IR intensities (Km mol<sup>-1</sup>), reduced masses (amu) and force constants (mdyneA<sup>-</sup>)]

## Table 3 continued

		IR	Reduced	Force
No	Wavenumber	Intensity	mass	constant
44	3151	24.2	1.07	6.28
45	3166	17.33	1.06	6.27
46	3174	35.84	1.07	6.36
47	3183	78.51	1.06	6.33
48	3200	25.84	1.1	6.44
49	3215	43.03	1.1	6.71
50	3220	40.28	1.08	6.63
51	3243	41.68	1.1	6.79
52	3260	47.81	1.09	6.86

Table 4: Vibrational frequency assignments of L-LMHCl

Observed frequency (cm <sup>-1</sup> )     Calculated frequency (cm <sup>-1</sup> )     Frequency Assignments       FTIR     AM1     PM3     ab initio     Frequency Assignments       -     280     259     267     C-C-Nut of plane bending (C=0 in plane bending (C=0 in plane bending)       -     317     301     306     C=0 in plane bending (C=0 in plane bending)       -     460     444     -     C-C-C out of plane bending       -     480     452     462     C-C-O out of plane bending       -     487     501     C-C-C out of plane bending       -     542     523     552     C-C-N in plane bending       555(s)     557     584     -     C-C-C out of plane bending       623     -     629     O-H out of plane bending       709(m)     723     726     713     CH <sub>2</sub> rocking       861(s)     863     876     879     C-H out of plane bending       906(m)     934     906     912     N-H wagging       97(s)     994     988     C-H in plane bending       1029(w) </th <th></th> <th></th> <th></th> <th></th> <th></th>					
FTIR     AM1     PM3     ab initio       -     280     259     267     C-C-N out of plane bending       -     317     301     306     C-NH; in plane bending       -     400     444     -     C-C-C out of plane bending       -     400     444     -     C-C-C out of plane bending       -     480     452     462     C-C-O out of plane bending       -     487     501     -     C-C-C out of plane bending       -     542     523     552     C-C-N in plane bending       555(s)     557     584     -     C-C-C out of plane bending       709(m)     723     726     713     CH2 rocking       709(m)     723     726     713     CH2 rocking       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(w)     1013     1024 <t< td=""><td>Observed frequency (cm<sup>-1</sup>)</td><td colspan="2">Calculated frequency (cm<sup>-1</sup>)</td><td>(cm<sup>-1</sup>)</td><td>Frequency Assignments</td></t<>	Observed frequency (cm <sup>-1</sup> )	Calculated frequency (cm <sup>-1</sup> )		(cm <sup>-1</sup> )	Frequency Assignments
280     259     267     C-C-N out of plane bending       .     317     301     306     C-NH2 in plane bending       .     460     444     -     C-C-C out of plane bending       .     480     452     462     C-C-C out of plane bending       .     480     452     462     C-C-C out of plane bending       .     487     501     -     C-C-C out of plane bending       .     487     501     -     C-C-C out of plane bending       .     487     501     -     C-C-C out of plane bending       .     542     523     552     C-C-N in plane bending       .     623     -     629     O-H out of plane bending       .     764     766     783     C-H out of plane bending       .     861(s)     863     876     879     C-II out of plane bending       .     966     912     N-H wagging     .     .     .       .     1013     1024     1018     C-H in plane bending     . <	FTIR	AM1	PM3	ab initio	
.     317     301     306     C-NH <sub>2</sub> in plane bending /C=O in plane bending       .     400     444     -     C-C-C out of plane bending       .     480     452     462     C-C-O out of plane bending       .     487     501     -     C-C-O out of plane bending       .     487     501     -     C-C-O out of plane bending       .     487     501     -     C-C-C out of plane bending       .     487     501     -     C-C-C out of plane bending       .     542     523     552     C-C-N in plane bending       .     623     -     629     O-H out of plane bending       .     764     766     783     C-H out of plane bending       .     861(s)     863     876     879     C-H out of plane bending       .     969     960     912     N-H wagging       .     1013     1024     1018     C-H in plane bending       .     1060     1061     1062     C-H in plane bending	-	280	259	267	C-C-N out of plane bending
·     400     444     ·     C-C-C cut of plane bending       ·     480     452     462     C-C-O out of plane bending       ·     487     501     -     C-C-C out of plane bending       ·     487     501     -     C-C-C out of plane bending       ·     542     523     552     C-C-N in plane bending       555(s)     557     584     -     C-C-C out of plane bending       623     ·     629     O-H out of plane bending       709(m)     723     726     713     CH2 rocking       764     766     783     C-H out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       1096(s)     1082     1083 <td>-</td> <td>317</td> <td>301</td> <td>306</td> <td>C-NH<sub>2</sub> in plane bending /C=O in plane bending</td>	-	317	301	306	C-NH <sub>2</sub> in plane bending /C=O in plane bending
-     480     452     462     C-C-O out of plane bending       -     487     501     -     C-C-C out of plane bending       -     542     523     552     C-C-N in plane bending       555(s)     557     584     -     C-C-C out of plane bending       623     -     629     O-H out of plane bending       709(m)     723     726     713     CH <sub>2</sub> rocking       861(s)     863     876     879     C-H out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(w)     1082     1083     1070     C-C-C in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190	-	400	444	-	C-C-C out of plane bending
•     487     501     •     C-C-C out of plane bending       -     542     523     552     C-C-N in plane bending       555(s)     557     584     -     C-C-C out of plane bending       623     -     629     O-H out of plane bending       709(m)     723     726     713     CH <sub>2</sub> rocking       709(m)     723     726     783     C-H out of plane bending       861(s)     863     876     879     C-II out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211 <td>-</td> <td>480</td> <td>452</td> <td>462</td> <td>C-C-O out of plane bending</td>	-	480	452	462	C-C-O out of plane bending
-     542     523     552     C-C-N in plane bending       555(s)     557     584     -     C-C-C out of plane bending       623     -     629     O-H out of plane bending       709(m)     723     726     713     CH2 rocking       709(m)     723     726     713     CH2 rocking       861(s)     863     876     879     C-H out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       1096(s)     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH2 wagging       -     1190     1189     1181     C-O stretching	•	487	501	-	C-C-C out of plane bending
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623     -     629     O-H out of plane bending       709(m)     723     726     713     CII <sub>2</sub> rocking       764     766     783     C-H out of plane bending       861(s)     863     876     879     C-II out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       1029(s)     1082     1083     1070     C-C-C in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	555(s)	557	584	-	C-C-C out of plane bending
709(m)     723     726     713     CH2 rocking       764     766     783     C-H out of plane bending       861(s)     863     876     879     C-II out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       -     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH2 wagging       -     1190     1189     1181     C-O stretching		623	•	629	O-H out of plane bending
764     766     783     C-H out of plane bending       861(s)     863     876     879     C-II out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching	709(m)	723	726	713	CII <sub>2</sub> rocking
861(s)     863     876     879     C-II out of plane bending       906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching		764	766	783	C-H out of plane bending
906(m)     934     906     912     N-H wagging       976(m)     969     960     949     C-H in plane bending       997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	861(s)	863	876	879	C-II out of plane bending
976(m)     969     960     949     C-H in plane bending       997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	906(m)	934	906	912	N-H wagging
997(s)     994     988     -     C-H in plane bending       1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	976( <b>m</b> )	969	960	949	C-H in plane bending
1029(w)     1013     1024     1018     C-H in plane bending       -     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	997(s)	994	988	-	C-H in plane bending
-     1060     1061     1062     C-H in plane bending       1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	1029(w)	1013	1024	1018	C-H in plane bending
1096(s)     1082     1083     1070     C-C-C in plane bending       -     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	-	1060	1061	1062	C-H in plane bending
-     1128     1126     -     C-O stretching       1142(s)     1158     1152     1150     CH <sub>2</sub> wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	1096(s)	1082	1083	1070	C-C-C in plane bending
1142(s)     1158     1152     1150     CH2 wagging       -     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	-	1128	1126	-	C-O stretching
-     1190     1189     1181     C-O stretching       1215(m)     1211     1222     1209     C-O stretching	1142(s)	1158	1152	1150	CH <sub>2</sub> wagging
1215(m) 1211 1222 1209 C-O stretching	-	1190	1189	1181	C-O stretching
	1215(m)	1211	1222	1209	C-O stretching

Table3 continued...

Table 4 continued...

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Observed frequency (cm <sup>-1</sup> )	Calculated frequency (cm <sup>-1</sup> )		Frequency Assignments	
FTIR	AMI	PM3	ab initio	-
-	1230	1238	-	C-C stretching /N-H in plane bending
-	1253	1243	1255	C-C stretching
1273 (s)	1274	1287	1299	C-N stretching
1319 (vs)	1326	1318	1310	CH <sub>2</sub> twisting
1347 (vs)	1337	-	-	C-N stretching
-	1355	1354	-	C-N stretching
-	1378	1380	-	C-N stretching
-	1398	1395	1390	C-N stretching
1406 (vs)	1405	1412	1402	C-N stretching
-	1417	1414	1417	O-H in plane bending
-	1440	1435	1444	CH <sub>2</sub> scissoring
-	1472	-	1457	CH2 scissoring
1584 (vs)	1540	-	1559	N-H scissoring
-	1724	-	-	C-O stretching
-	-	-	1807	C=O stretching
1860 (vs)	-	-	-	C=O stretching
-	2973	2952	-	CH <sub>2</sub> symmetric stretching
-	2980	-	-	CH <sub>2</sub> asymmetric stretching
3125 (vs)	3102	-	3150	N-H symmetric stretching
3333 (m)	-	3392	-	N-H asymmetric stretching
-	3463	-	-	O-H stretching
-	-	3516	-	O-H stretching

#### Table 4 continued...

(vs -very strong, s-strong, m-medium, w-weak)

#### **N-H vibrations**

As solids or liquids, in which hydrogen-bonding may occur, primary aliphatic amines absorb in the region 3450-3250 cm<sup>-1</sup>. This is a broad band of medium intensity which may show structure depending on the Hydrogen-bond polymers formed. In dilute solution in non-polar solvents, two bands are observed for primary amines due to the N-H asymmetric and symmetric vibrations. In the aliphatic case, they are in the range 3550-3250 cm<sup>-1</sup> whereas in the aromatic case they are of medium intensity one 3520-3450 and the other at 3420-3350 cm<sup>-1</sup> (Socrates G, 2000). Hence in the present case the FTIR bands observed at 3333 and 3125 cm<sup>-1</sup> have been assigned to N-H asymmetric and symmetric vibrations respectively. The same bands have also been observed in the other methods.

In addition, the N-H bending (scissoring) vibration of primary amines has been observed in the 1650-1580 cm<sup>-1</sup> region of the spectrum. The band is medium to strong in intensity and is moved to slightly higher frequencies when the compound is associated (Robert M Silverstein et al., 1997). Considering this factor in the present work, the bands observed at 1540, 1559 and 1584 cm<sup>-1</sup> in AM1, ab initio and FTIR have been assigned to N-H scissoring vibration. The N-H wagging vibrations have been observed in the present case and it agreed very well with literature value (Krishankumar P et al., 1998).

Similarly, the other stretching and bending vibrations have been observed and they have been assigned in the characteristic range.

## 5. Thermodynamical parameters

On the basis of vibrational analysis at AM1, PM3 and ab initio methods, several thermodynamic parameters have been calculated for L-LMHCl and they have been illustrated in Table 5. The zero point vibration energies (ZPVE), rotational constants, thermal energy, heat capacity and the entropy  $S_{vib}$  (T) are calculated to the extent of accuracy and the variation found in ZPVEs is insignificant.

Table 5. Zero point energy (Kcal mol<sup>-1</sup>), Rotational constants (GHz), Thermal Energy (Kcalmol<sup>-1</sup>, Heat Capacity (Cal mol<sup>-1</sup>-Kelvin Entropy (Cal mol<sup>-1</sup>-

•	· ·		1.4
		Kelvin) for L	-LMHC1

Parameters	AM1	РМ3	ab initio			
Zero point energy	134.207	129.850	142.557			
E (Thermal)-Total	141.736	137.628	149.799			
Electronic	0.000	0.000	0.000			
Translational	0.889	0,889	0.889			
Rotational	0.889	0.889	0.889			
Vibrational	139.959	135.85	148.022			
Heat Capacity	41.381	43.504	40.848			
Entropy	111.896	114.309	108.717			

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## 6. Conclusion

In the present investigation, the vibrational frequency assignments have been made for L-LMHCl using the FTIR spectrum and compared with the calculated frequencies using AM1, PM3 and ab initio methods. The vibrational band assignments have been made according to the position, shape, nature and relative intensity with the derivatives of benzene as guide lines. The optimized vibrational wave numbers, IR intensities, reduced mass, force constants, zero point energy, rotational constants, thermal energy, heat capacity and entropy had been calculated and analyzed by AM1, PM3 and ab initio methods. It has been observed that the theoretical values show slight variation with the experimental values due to the theoretical calculations belonging to isolated molecules in gaseous phase and the experimental results belong to molecules in the solid phase.

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