



International Journal of ChemTech Research CODEN (USA): IJCRGG ISSN : 0974-4290 Vol.4, No.1, pp 361-376, Jan-Mar 2012

# Experimental and theoretical investigation of spectroscopic properties of diazepam

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**Abstract:** Semi embirical Austin Model 1, Ab initio and density functional computations of the vibrational IR spectrum and Molecular geometry were carried out on diazepam. The FTIR spectrum of diazepam was recorded in the region 4000-400 cm<sup>-1</sup>. Assignments were made in accordance with the calculated and experimental spectra. The observed IR spectrum agree well with the theoretically predicted spectra. The experimental geometry and wave numbers are compared with the results of theoretical calculations. **Keywords:** FTIR, density functional theory, AM 1.

# 1. Introduction

Benzodiazepines are widely used in the clinical treatment of anxiety, insomnia and panic disorder(1). Diazepam is the most common benzodiazepine drug used as hypnotic, tranquilizer, anticonvulsant and muscle relaxant(2). Its chemical name is 7-chloro-1,3-dihydro-1methyl-5-phenyl-1,4-benzodiazepin-2-one and its molecular formula is C<sub>16</sub>H<sub>13</sub>ClN<sub>2</sub>O. It enhances the activity of gamma-aminobutyric acid, the most common inhibitory neurotransmitter in the central nervous system. It is used in the treatment of severe anxiety disorder, in the short term management of insomnia, and in the management of alcohol withdrawal syndrome. Diazepam has been determined in pharmaceuticals by high performance liquid chromatography (HPLC) micellar liquid chromatography or thin laver chromatography(3). Capillary zone electrophoresis,

voltametry and polarography have been also employed for diazepam determination in tablets. Ultraviolet spectrophotometric has been used for the diazepam determination based on zero order or first order derivation signals. Additionally, diazepam has been determined in the visible region based on the formation of an ion-association complex with bromocresol green and by flow injection fluorimetry by Moros (3). Mielcarek et al discussed the hybrid method for estimation of molecular dynamics of diazepam(4). Recent spectroscopic studies of benzene and its derivatives have been motivated, by their biological and pharmaceutical importance. The vibrational spectroscopic studies on benzene ring fused to fivemembered received considerable attention recently. The results obtained from these studies reveal that the change of simple constituents on a constant ring system produces only little changes in the spectrum. Also a

small variation in the spectral panorama follows the replacement of atom in the five membered rings(5). Melting behavior of pure polyethylene glycol 6000 and polyethylene glycol 6000 in solid dispersions containing diazepam or temazepam have been reported by Verheyen et al(6). Zayed et al(7) have reported thermogravimetric analysis along with mass spectrometric analysis of diazepam.

The present investigation has been undertaken to study the vibrational spectra of diazepam completely and to identify the various normal modes of vibration. Ab initio calculations with 6-31G(d,p) basis set were performed to support the frequency assignments. Vibrational spectra of diazepam has been studied by applying the DFT calculations based on Becke-3-Lee-Yang-Parr(B3LYP) level with 6-31G(d,p) basis set. Experimentally observed spectral data of the title compound is found to be well comparable with the data obtained by quantum mechanical methods.

# 2. Experimental

The sample of diazepam was purchased from reputed pharmaceutical firm in Chennai, India. The mid-infrared spectrum of the compound in powder form in the region 400-4000 cm<sup>-1</sup> was recorded at Indian Institute of Technology, Chennai with Bruker IFS 66V Fourier transform spectrophotometer equipped with a Globar source, KBr beam splitter and a TGS detector with 4.0 cm<sup>-1</sup> resolution.

## 3. Computational Details

The entire calculations were performed at RHF and B3LYP levels on a Pentium dual core personal computer using GAUSSIAN 03W (8) program package, invoking gradient geometry optimization. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at RHF and B3LYP levels, adapting the standard 6-31G(d,p) basis set. The optimized structural parameters were used in the vibrational frequency

calculations at the RHF and B3LYP levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of diazepam was used for harmonic vibrational frequency calculations together with intensities. Semiempirical Austin Model 1 (AM1) (9) was also used for comparison. By combining the results of the Chemcraft program(10) with symmetry coordinates, vibrational frequency assignments were made with a high degree of accuracy. However, the defined coordinate form complete set and matches quite well with the motions observed using Chemcraft program.

## 4. Results and Discussion

#### 4.1 Molecular geometry

The optimized structure parameters of diazepam by AM1, RHF and DFT levels with 6-31G(d,p) basis set are **listed in Table 1** in accordance with the atom numbering scheme given in **Figure 1. Tables 1** compares the bond lengths, bond angles of diazepam with the experimentally available data(11,12,13). From the theoretical values it is found that most of the optimized bond angles are slightly larger than the experimental values due to theoretical calculations belong to isolated molecules in gaseous phase whereas experimental results belong to the molecules in solid phase.

#### 4.2 Vibrational analysis of diazepam

Vibrational band assignments of diazepam have been made in accordance with the magnitude and relative intensities of the recorded spectra. Also the assignments have been made in analogy with the structurally related molecules. FTIR spectrum of diazepam is presented in Figure 2. Figure 1 represents the overlay spectra of Clobazam using FTIR, Ab initio and DFT methods.

			DUE	B3LYP
Bond length	Fyn	A m1	KHF /6-31G(d n)	/6- 31G(d n)
	1.271	1.402	1 275	1 205
$N_1$ - $C_2$	1.371	1.402	1.375	1.395
$N_1$ - $C_7$	1.403	1.412	1.411	1.415
$N_1 - C_{19}$	1.464	1.445	1.459	1.466
C <sub>2</sub> -C <sub>3</sub>	1.521	1.529	1.518	1.527
C <sub>2</sub> -O <sub>12</sub>	1.222	1.241	1.195	1.218
C <sub>3</sub> -N <sub>4</sub>	1.465	1.432	1.446	1.454
C <sub>3</sub> -H <sub>24</sub>	1.1	1.129	1.078	1.09
C <sub>3</sub> -H <sub>25</sub>	1.1	1.129	1.089	1.101
N <sub>4</sub> -C <sub>5</sub>	1.291	1.295	1.258	1.286
C <sub>5</sub> -C <sub>6</sub>	1.487	1.482	1.496	1.492
C <sub>5</sub> -C <sub>13</sub>	1.494	1.483	1.497	1.494
C <sub>6</sub> -C <sub>7</sub>	1.413	1.416	1.397	1.417
C <sub>6</sub> -C <sub>8</sub>	1.4	1.401	1.394	1.406
C <sub>7</sub> -C <sub>11</sub>	1.399	1.418	1.395	1.406
C <sub>8</sub> -C <sub>9</sub>	1.377	1.392	1.375	1.388
C <sub>8</sub> -H <sub>21</sub>	1.1	1.103	1.073	1.083
C <sub>9</sub> -C <sub>10</sub>	1.387	1.399	1.384	1.395
$C_9$ - $Cl_{20}$	1.742	1.698	1.742	1.757
C <sub>10</sub> -C <sub>11</sub>	1.383	1.386	1.378	1.388
C <sub>10</sub> -H <sub>22</sub>	1.1	1.102	1.074	1.084
C <sub>11</sub> -H <sub>23</sub>	1.1	1.102	1.073	1.084
C <sub>13</sub> -C <sub>14</sub>	1.406	1.401	1.39	1.404

Table	1Bond	length	and	Bond	angles	for	diaze	pam
								_

C <sub>13</sub> -C <sub>18</sub>	1.4	1.4	1.393	1.405
C <sub>14</sub> -C <sub>15</sub>	1.38	1.393	1.386	1.395
C <sub>14</sub> -H <sub>29</sub>	1.1	1.101	1.075	1.085
C <sub>15</sub> -C <sub>16</sub>	1.372	1.395	1.383	1.395
C <sub>15</sub> -H <sub>30</sub>	1.1	1.1	1.075	1.086
C <sub>16</sub> -C <sub>17</sub>	1.381	1.394	1.387	1.398
C <sub>16</sub> -H <sub>31</sub>	1.1	1.1	1.076	1.086
C <sub>17</sub> -C <sub>18</sub>	1.392	1.395	1.382	1.391
C <sub>17</sub> -H <sub>32</sub>	1.1	1.1	1.076	1.086
C <sub>18</sub> -H <sub>33</sub>	1.1	1.101	1.073	1.084
C <sub>19</sub> -H <sub>26</sub>	1.1	1.121	1.081	1.091
C <sub>19</sub> -H <sub>27</sub>	1.1	1.123	1.085	1.096
C <sub>19</sub> -H <sub>28</sub>	1.1	1.124	1.078	1.089

Bond angle	Exp	Am1	RHF/6- 31G(d,p)	B3LYp/6- 31G(d,p)
$C_2 - N_1 - C_7$	123.1	122.4	122.7	123.4
$C_2 - N_1 - C_{19}$	116.6	117.7	116.6	116.1
$N_1-C_2-C_3$	115.3	118.9	116	115.3
$N_1$ - $C_2$ - $O_{12}$	121.8	120.1	121.6	121.6
$C_{7}-N_{1}-C_{19}$	119	117.5	119.4	119.3
$N_1$ - $C_7$ - $C_6$	122	122.4	122	122.2
$N_1$ - $C_7$ - $C_{11}$	118.5	119.3	119.1	118.9
N <sub>1</sub> -C <sub>19</sub> -H <sub>26</sub>	109	109.6	109	109.3
N <sub>1</sub> -C <sub>19</sub> -H <sub>27</sub>	111.3	111.3	112.1	112.2
N <sub>1</sub> -C <sub>19</sub> -H <sub>28</sub>	109	108.7	108.6	107.9
C <sub>3</sub> -C <sub>2</sub> -O <sub>12</sub>	122.9	120.9	122.4	123.1

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C <sub>2</sub> -C <sub>3</sub> -N <sub>4</sub>	110.5	114.5	110.3	110.3
C <sub>2</sub> -C <sub>3</sub> -H <sub>24</sub>	108.5	107	106.6	106.6
C <sub>2</sub> -C <sub>3</sub> -H <sub>25</sub>	109	108	109.6	109.2
N <sub>4</sub> -C <sub>3</sub> -H <sub>24</sub>	109	106.4	109.1	109.3
N <sub>4</sub> -C <sub>3</sub> -H <sub>25</sub>	111.3	112.4	112.2	112.3
C <sub>3</sub> -N <sub>4</sub> -C <sub>5</sub>	108	121	119.7	118.6
H <sub>24</sub> -C <sub>3</sub> -H <sub>25</sub>	109.4	108.4	108.8	108.9
N <sub>4</sub> -C <sub>5</sub> -C <sub>6</sub>	123.6	125.4	123.3	123.6
N <sub>4</sub> -C <sub>5</sub> -C <sub>13</sub>	120	119.4	117.9	117.3
C <sub>6</sub> -C <sub>5</sub> -C <sub>13</sub>	120	115.2	118.8	119.1
C <sub>5</sub> -C <sub>6</sub> -C <sub>7</sub>	122.2	122.3	121.6	122
C <sub>5</sub> -C <sub>6</sub> -C <sub>8</sub>	117.9	117.7	119.1	119
C <sub>5</sub> -C <sub>13</sub> -C <sub>14</sub>	119.5	119.6	121.6	122
C <sub>5</sub> -C <sub>13</sub> -C <sub>18</sub>	120.4	120.6	119.4	119.2
C <sub>7</sub> -C <sub>6</sub> -C <sub>8</sub>	118.2	119.9	119.3	118.9
C <sub>6</sub> -C <sub>7</sub> -C <sub>11</sub>	119.4	118.2	118.9	118.9
C <sub>6</sub> -C <sub>8</sub> -C <sub>9</sub>	121.1	120.7	120.7	120.9
C <sub>6</sub> -C <sub>8</sub> -H <sub>21</sub>	120	119	119.6	119.3
$C_7-C_{11}-C_{10}$	121.5	121.3	121.3	121.6

Bond angle	Exp	Aml	RHF/6- 31G(d,p)	B3LYp/6- 31G(d,p)
C <sub>7</sub> -C <sub>11</sub> -H <sub>23</sub>	119.6	120	119.6	119.5
C <sub>9</sub> -C <sub>8</sub> -H <sub>21</sub>	120	120.3	119.8	119.8
C <sub>8</sub> -C <sub>9</sub> -C <sub>10</sub>	121	120	120.4	120.6
C <sub>8</sub> -C <sub>9</sub> -Cl <sub>20</sub>	119.3	120	119.9	119.8

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$C_{10}$ - $C_{9}$ - $Cl_{20}$	119.7	119.9	119.8	119.7
C <sub>9</sub> -C <sub>10</sub> -C <sub>11</sub>	118.8	119.8	119.4	119.1
C <sub>9</sub> -C <sub>10</sub> -H <sub>22</sub>	120	120.3	120.3	120.3
C <sub>11</sub> -C <sub>10</sub> -H <sub>22</sub>	120	119.9	120.4	120.5
C <sub>10</sub> -C <sub>11</sub> -H <sub>23</sub>	119.6	118.7	119.1	119
C <sub>14</sub> -C <sub>13</sub> -C <sub>18</sub>	119.9	119.8	119	118.7
C <sub>13</sub> -C <sub>14</sub> -C <sub>15</sub>	120.2	120	120.5	120.6
C <sub>13</sub> -C <sub>14</sub> -H <sub>29</sub>	119.8	119.9	120.1	119.9
C <sub>13</sub> -C <sub>18</sub> -C <sub>17</sub>	120.2	119.9	120.4	120.6
C <sub>13</sub> -C <sub>18</sub> -H <sub>33</sub>	119.7	120.2	119	118.4
C <sub>15</sub> -C <sub>14</sub> -H <sub>29</sub>	119.9	120.2	119.3	119.5
$C_{14}$ - $C_{15}$ - $C_{16}$	120.3	120.2	120.1	120.2
C <sub>14</sub> -C <sub>15</sub> -H <sub>30</sub>	119.8	119.8	119.7	119.7
C <sub>16</sub> -C <sub>15</sub> -H <sub>30</sub>	119.8	120.1	120.2	120.2
$C_{15}$ - $C_{16}$ - $C_{17}$	119.7	119.9	119.8	119.7
C <sub>15</sub> -C <sub>16</sub> -H <sub>31</sub>	120.2	120	120.1	120.1
C <sub>17</sub> -C <sub>16</sub> -H <sub>31</sub>	120.2	120.1	120.1	120.2
$C_{16}$ - $C_{17}$ - $C_{18}$	120.8	120.2	120.2	120.2
C <sub>16</sub> -C <sub>17</sub> -H <sub>32</sub>	119.7	120.1	120.1	120
C <sub>18</sub> -C <sub>17</sub> -H <sub>32</sub>	119.7	119.7	119.8	119.7
C <sub>17</sub> -C <sub>18</sub> -H <sub>33</sub>	119.8	120	120.5	121
H <sub>26</sub> -C <sub>19</sub> -H <sub>27</sub>	109	109.4	109.5	109.5
H <sub>26</sub> -C <sub>19</sub> -H <sub>28</sub>	109	109.5	109.5	110.2
H <sub>27</sub> -C <sub>19</sub> -H <sub>28</sub>	109	108.4	108.1	107.8

#### 4.2.1 C-H vibrations

The bands around 3100-2800 cm<sup>-1</sup> are assigned to the C-H stretching vibrations in aromatic compounds. The C-H stretching frequency of such compounds falls very nearly in the region of 3100- 2900cm<sup>-1</sup> for asymmetric stretching and 2980 - 2900cm<sup>-1</sup> for symmetric stretching modes of vibration. They are not appreciably affected by the nature of the substituents. In the present work, the bands observed at 3524, 3377, 3346 cm<sup>-1</sup> in FTIR were assigned to the C-H stretching vibration of diazepam.

The aromatic CH stretching vibrations calculated theoretically in the region  $3229-3182 \text{ cm}^{-1}$  for B3LYP and  $3395-3342 \text{ cm}^{-1}$  for Restricted HF predicts the CH stretching bands which supports the literature values (14,15).Vibration at 710 cm<sup>-1</sup> is due to four adjacent free Hs and aromatic CH out of plane bending and at 837 cm<sup>-1</sup> is due to two adjacent free Hs and aromatic C-H out of plane bending. The C-H in plane and out of plane bending vibrations of the molecule were given in **Tables 2**.



Figure 1 Atom numbering adopted in this study for diazepam



Figure 2 FTIR spectrum of Diazepam



Figure 2 Overlay spectra of Clobazam using FTIR, Ab initio and DFT methods.

			B3LYP/6-						
	A	M1	RHF	/6-31G(d,p)	3	1G(d,p)	F	TIR	
Mode	Wave						Wave		
no	number	Intensity		Intensity		Intensity	number	Intensity	Assignments
1	3200	35.8941	3395	1.5337	3228	1.4368	3524(vs)	0.96493	v CH
2	3191	97.0384	3394	1.3786	3227	2.4955	3377(vs)	1.495277	v CH
3	3186	34.2014	3394	7.8484	3224	4.9715	3346(vs)	1.4877	v CH
4	3183	80.184	3378	2.9148	3214	2.4145			v CH
5	3182	13.8981	3376	16.2066	3211	12.5175			v CH
6	3181	12.9826	3366	40.3283	3202	29.7844			v CH
7	3171	19.4684	3354	10.7442	3192	9.6975			v CH
8	3164	70.1726	3342	0.2682	3182	0.4763			v CH
9	3101	4.2679	3335	7.5642	3180	1.5886			$v_{as}CH_3$
10	3036	37.4467	3315	22.6255	3143	18.1649	2976(m)	0.33563	$v_{as}CH_2$
11	3023	7.6527	3283	26.5944	3128	15.9748	2932(s)	0.566053	$v_{as}CH_3$
12	3001	4.7616	3202	46.7994	3044	39.9673	2918(s)	0.53966	$v_s CH_3$
13	2968	16.8795	3181	27.3249	2999	26.0417	2900(s)	0.64277	$v_s CH_2$
14	2003	596.3074	1972	604.3244	1792	472.5905	1685(m)	0.34271	v C=O
15	1935	31.8413	1901	148.0552	1679	53.39	1605(w)	0.16316	v C=N
16	1776	2.1331	1807	1.9559	1655	11.8089			v C=C
17	1774	22.4881	1800	1.2289	1643	0.5657			v C=C
18	1763	0.6897	1778	4.0531	1631	7.5203	1601(w)	0.15143	v C=C
19	1737	36.9824	1762	23.8008	1605	24.2497	1580(w)	0.12332	v C=C
20	1672	311.8482	1667	34.3248	1535	1.8591			v C=C
21	1635	20.6487	1660	120.563	1530	8.3279			CH <sub>3</sub> deformation

# Table 2 Observed and calculated IR wavenumber for diazepam using AM 1, RHF/6-31G(d,p) and B3LYP/6-31G(d,p)

	A	M1	RHF/	/6-31G(d,p)	<b>B3LYF</b>	2/6-31G(d,p)	F	TIR	
Mode	Wave						Wave		
no	number	Intensity		Intensity		Intensity	number	Intensity	Assignments
22	1600	92.6451	1650	18.8974	1521	123.8779	1490(m)	0.28536	v C=C
23	1567	13.3275	1635	5.1466	1504	6.4481			$\delta CH_2$
24	1538	83.0995	1623	17.8452	1499	27.5987			CH <sub>3</sub> deformation
25	1525	62.5498	1606	17.2165	1487	11.3619			CCC bending
26	1477	52.3747	1595	6.8524	1457	10.6025			CH <sub>3</sub> bending
27	1456	15.5924	1556	82.1067	1433	47.9948	1424(s)	0.60985	Ring deformation
28	1447	14.1694	1502	149.1517	1364	2.7608	1393(s)	0.551128	CCH bending
29	1394	51.1003	1482	18.558	1362	109.3158	1383(s)	0.55681	v C-N
30	1376	1.1942	1468	15.1899	1355	27.2762			βСН
31	1373	7.752	1453	76.9245	1343	3.1631			βСН
32	1368	4.5029	1432	78.7876	1338	34.4952	1366(s)	0.547078	$\omega CH_2$
33	1363	14.6293	1404	11.3526	1328	16.9959			βCN
34	1355	9.7711	1347	10.3435	1301	72.7447	1359(s)	0.565048	γ CN
35	1330	7.0484	1339	1.93	1288	19.031	1341(s)	0.585015	β CH, $ω$ CH <sub>2</sub>
36	1318	0.6291	1298	2.7863	1229	30.016	1260(s)	0.4321	t CH <sub>2</sub>
37	1309	6.9597	1293	11.223	1208	13.1262	1201(s)	0.505693	βСН
38	1251	3.0924	1266	41.9472	1191	4.7646			β СН
39	1235	1.6694	1259	14.2221	1188	0.9949			CN bending
40	1231	5.8766	1248	7.2915	1167	5.1706	1167(vs)	0.861635	CN bending
41	1218	10.228	1225	26.4776	1152	37.2071			CH₃ bending
42	1201	12.9799	1219	5.6556	1147	18.8263	1142(vs)	1.03447	$\rho CH_2$

	A	M1	RHF/	6-31G(d,p)	B3LYP	/6-31G(d,p)	F	ΓIR	
Mode	Wave						Wave		
no	number	Intensity		Intensity		Intensity	number	Intensity	Assignments
43	1197	0.0232	1212	20.3226	1127	19.7064			βСН
44	1179	2.8706	1189	26.6173	1112	6.0192			CCC bending
45	1170	4.3782	1183	3.3912	1094	19.5686			CCC bending
46	1151	1.9481	1145	25.7498	1058	6.5916	1115(vs)	1.11531	βСН
47	1113	4.2659	1131	0.4481	1044	13.0934	1093(vs)	1.267483	N-CH₂ be <b>nding</b>
48	1105	7.211	1128	0.2346	1017	1.4771	1083(vs)	1.23863	CCC trigonal bending
49	1044	6.927	1110	0.9602	1005	0.7751	1072(vs)	1.292585	γ CH
50	1018	10.0961	1096	0.4331	1000	8.1562	1058(vs)	1.231628	$ρ CH_2 + ρ CH_3$
51	1014	21.6755	1095	11.2821	983	1.8696	1036(vs)	1.358873	γ CH
52	1008	1.9336	1090	2.4581	963	7.3368	1019(vs)	1.220081	γ CH Ring deformation,
53	989	0.1692	1060	4.7431	958	12.4027	1004(vs)	0.95216	,trigonal bending CH
54	985	0.4948	1046	7.9593	945	0.8734	988(vs)	0.909343	γCH
55	959	0.5084	1032	17.5149	928	14.0931	(,		CCN bending
56	953	5.2944	1006	25.3191	913	13.5529	915(w)	0.1796	NCO bending
57	933	40.1736	960	1.0431	865	2.3017	899(w)	0.188408	γ CH
58	890	0.2483	944	31.1536	838	23.9075			CCN bending
59	885	48.3379	893	73.957	822	65.5008	876(w)	0.166759	Ring breathing
60	832	15.7985	882	5.1935	801	7.8308	837(vw)	0.041924	γ CH
61	820	6.2258	858	6.1294	776	1.3687	778(s)	0.5709	CCH bending
62	795	19.0534	826	28.4471	749	24.2838			γ CH
63	776	32.2793	782	45.7228	713	29.3271	710(m)	0.367678	γ CH
64	743	3.3756	765	1.4511	703	0.7707			$\rho CH_2$
65	711	35.6784	754	0.5851	697	0.8732			Ring pluckering
66	673	0.9391	722	8.0576	667	9.0317	672(m)	0.287005	CC=O bending

	A	M1	RHF	-/6-31G(d,p)	B3LY	′P/6-31G(d,p)	FTIR		
Mode	Wave						Wave		
no	number	Intensity		Intensity		Intensity	number	Intensity	Assignments
67	657	2.3721	691	9.8962	636	4.8515			CNC bending
68	653	6.488	678	0.2079	632	1.3341	632(s)	0.41784	CCC bending
69	597	11.0235	646	15.43	591	9.8028	580(m)	0.34345	CCI stretching
70	581	8.3656	608	9.5341	557	10.1639	552(m)	0.367405	CCC bending
71	539	3.6333	576	13.2236	530	9.7975			Ring floating
72	533	5.7489	555	3.9224	512	2.7677			CC=N bending
73	497	8.9749	514	4.773	475	3.1092	468(vw)	0.07337	CCCI bending
74	469	4.6293	505	3.4692	463	3.997			CCH bending
75	448	7.0291	467	4.6039	432	4.0831			HCH bending
76	389	2.6118	457	0.3622	418	0.0417			Ring wagging
77	386	6.7795	431	1.0924	395	0.9393			CCH bending
78	371	0.0534	415	12.7519	391	10.401			C=O bending, $\omega$ CH <sub>3</sub>
79	352	0.5579	369	4.5933	340	2.1034			N-CH₃ bending
80	338	2.7589	363	0.0881	337	0.6611			CCH bending
81	308	2.3949	320	4.4315	300	3.76			$\omega CH_2$
82	283	2.6699	313	1.4534	291	1.6876			$\omega$ CH <sub>2</sub>
83	263	6.1276	278	2.2967	262	2.6514			Ring floating
84	199	1.8568	241	1.4211	225	0.7929			$\rho CH_2$
85	183	0.5174	198	1.4103	185	0.3335			$\rho CH_2$
86	171	2.0576	195	0.2392	182	1.0433			CCI bending
87	163	0.8181	189	0.3482	165	0.2325			τ CH <sub>3</sub>

	AM1		RHF	-/6-31G(d,p)	B3LY	B3LYP/6-31G(d,p)		3LYP/6-31G(d,p)		ΓIR	
Mode	Wave						Wave				
no	number	Intensity		Intensity		Intensity	number	Intensity	Assignments		
88	118	2.2134	132	1.7106	124	1.2338			C=O bending		
89	92	1.4359	115	2.8789	106	2.5346			ρ CH₃		
90	71	0.2903	81	0.3656	76	0.3001			Ring floating		
91	58	1.5882	73	2.5412	68	1.9648			C=O bending, $\rho$ CH <sub>3</sub>		
92	41	0.7103	56	0.2544	54	0.2334			Phenyl ring butterfly		
93	24	0.0867	44	0.6018	41	0.6861			Phenyl ring butterfly		

 $v_s$  --- sym stretching ;  $v_{as}$  --- asym stretching ;  $\beta$  --- in plane bending ;  $\gamma$  --- out of plane bending;  $\omega$  --- wagging;  $\rho$  --- rocking;  $\tau$  --- torsion; t --- twisting;  $\delta$  ---scissoring

#### 4.2.2 Aromatic CC vibrations

The ring carbon-carbon stretching vibrations occur in the region 1625–1430 cm<sup>-1</sup>. For aromatic six-membered rings, e.g., benzenes and pyridines, there are two or three bands in this region due to skeletal vibrations, the strongest usually being at about 1500 cm<sup>-1</sup>. In the case where the ring is conjugated further, a band at about 1580  $\text{cm}^{-1}$  is also observed. In general, the bands are of variable intensity and are observed at 1625-1590, 1590-1575, 1525–1470 and 1465–1430 cm<sup>-1</sup>. For substituted benzenes with identical atoms or groups on all parapairs of ring carbon atoms, the vibrations causing the band at 1625–1590 cm<sup>-1</sup> are infrared-inactive due to symmetry considerations, the compound having a centre of symmetry at the ring centre. If the groups on a para-pair of carbon atoms are different then there is no centre of symmetry and the vibrations are infrared-active (16). Chithambarathau et al. (17) have observed the FTIR bands at 1574, 1498 and 1468 cm<sup>-1</sup> in 1,3,5- triphenyl-4.5-dihydro pyrazole. Neville and Shurvell (18) have identified the IR bands at 1470, 1484, 1561, 1575, 1590 cm<sup>-1</sup> in diazepam and closely related compounds of benzodiazepines due to aromatic CC stretching vibrations. Based on these factors, in the present study the FTIR band observed at 1490, 1580 and 1601 cm<sup>-1</sup> are assigned to aromatic CC stretching vibrations.

#### 4.2.3 C-Cl vibrations

The CCl stretching vibrations give generally strong bands in the region 710 - 505 cm<sup>-1</sup>. Compounds with more than one chlorine atom ex-hibit very strong bands due to the asymmetric and symmetric stretching modes. Vibrational coupling with other groups may result in a shift in the absorption to as high as 840 cm<sup>-1</sup>. For simple organic chlorine compounds, C-Cl absorptions are in the region 750-700 cm<sup>-1</sup> whereas for the trans- and gauche-forms they are near 650 cm<sup>-1</sup> (19,20). Neville and shurvel (21) have observed the FTIR band at 583 cm<sup>-1</sup> in diazepam. Considering these factors, the bands observed at 580 cm<sup>-1</sup> in FTIR has been assigned to C-Cl stretching vibration in the present investigation. The above result is in close agreement with the literature values (22,23).

#### 4.2.4 C=O Vibrations

The C=O stretching frequencies usually lie in the region between 1800 -1600 cm<sup>-1</sup>. Various other vibrations, such as C=C, C=N stretching and N-H bending vibrations, also occur in this region. However, C=O stretching is normally more intense than any other vibrations in this region. The position of C=O stretching depends upon conjugation, hydrogen bonding and the size of the ring to which it is attached. Because of its high intensity (24) and the relatively interference –free region in which it occurs this band is reasonably easy to recognize. In the present work the band observed at 1685 cm<sup>-1</sup> in FTIR spectrum was due to C=O stretching mode of vibration. The theoretically predicted wave number at 1792 and 1972 cm<sup>-1</sup> by B3LYP/6-31G(d,p) and RHF/6-31G(d,p) method for diazepam exactly coincides with experimental observation.

#### 4.2.5 Methyl group vibrations

The molecule Diazepam consists of CH<sub>3</sub> group attached in the diazepine (7 membered ring) ring. For the assignment of CH<sub>3</sub> group frequencies one can expect that there are nine fundamentals, viz., the symmetrical stretching in CH<sub>3</sub> (CH<sub>3</sub> sym. stretch) and asymmetrical stretching (in plane hydrogen stretching mode), the symmetrical (CH<sub>3</sub> sym. deform) and asymmetrical (CH<sub>3</sub> asym. deform) deformation modes, the in-plane bending (CH<sub>3</sub> ipb), out of plane bending (CH<sub>3</sub> opb), twisting (t CH<sub>3</sub>) and bending modes. For methyl compounds the symmetric stretching mode appears in the range 2825-2870 cm<sup>-1</sup>, the asymmetric stretching mode lie in the region 2925-2985 cm<sup>-1</sup>. The FTIR bands observed at 2932, 2918 cm<sup>-1</sup> represent asymmetric and symmetric CH<sub>3</sub> stretching vibrations in diazepam. The theoretically computed values of CH<sub>3</sub> asymmetric stretching gives calculated at 3128 cm<sup>-1</sup> and CH<sub>3</sub> symmetric stretching calculated at 3044 cm<sup>-1</sup> for B3LYP shows an excellent agreement with experimental results. Rocking vibration 1058 cm<sup>-1</sup> are well comparable with of CH<sub>3</sub> at theoretically calculated values. The CH<sub>3</sub> torsional mode was assigned at 165 and 190 cm<sup>-1</sup> for B3LYP and RHF levels respectively

#### 4.4.6 C=N, C-N vibrations

The identification of the C-N stretching frequency in the side chains is a task since there are problems in identifying these frequencies from other vibrations. Silverstein et al. (25) assigned C-N stretching absorption in the region  $1382 - 1266 \text{ cm}^{-1}$  for aromatic amines. In benzamide the band observed at 1368 cm<sup>-1</sup> is assigned to be due to C-N stretching (26). Sundaraganesan et al (27) had assigned the C-N stretching of 2,4-dinitro phenyl hydrazine at 1335 cm<sup>-1</sup> in FTRaman spectrum. Kahovec and Kohlreusch (28) identified the stretching vibration of C=N band in salicyclic aldoxime at 1617 cm<sup>-1</sup>. In analogy with the literature the band at 1605 and 1383 cm<sup>-1</sup> in FTIR spectrum have been assigned to C-N and C=N stretching vibration respectively. The theoretically computed value of C-N stretching vibration

at 1362 cm<sup>-1</sup> and C=N stretching vibration at 1679 cm<sup>-1</sup> exactly matches with experimental value.

#### 4.4.7 Methylene vibration

For the assignments of CH<sub>2</sub> group frequencies, basically six fundamentals can be associated to each CH<sub>2</sub> group, namely CH<sub>2</sub> symmetric stretching, CH<sub>2</sub> asymmetric stretching, CH<sub>2</sub> scissoring and CH<sub>2</sub> rocking which belong to in-plane vibrations. In addition to this two outof-plane vibrations viz., CH<sub>2</sub> wagging and CH<sub>2</sub> twisting modes, which are expected to be depolarized. The asymmetric stretching vibrations are generally observed in the region 3000 - 2900 cm<sup>-1</sup>, while the symmetric stretch will appear between  $2900 - 2850 \text{ cm}^{-1}$  (27). Arun Balaji et al(12) assigned the asymmetric and symmetric vibration of CH<sub>2</sub> group at 3135 and 2947 cm<sup>-1</sup> using the B3LYP(d) basis set. FTIR band observed at 2976 and 2900 cm<sup>-1</sup> represent asymmetric and symmetric CH<sub>2</sub> stretching vibrations in diazepam. The asymmetric and symmetric stretching vibrations of CH<sub>2</sub> group have been assigned at 3143 and 2999 cm<sup>-1</sup> for diazepam using B3LYP(d,p) basis set matches exactly with literature. The bands corresponding to scissoring and bending vibrations of  $CH_2$  group are presented in **table 2**.

### 5. Conclusion

Ab initio and density functional theory calculations have been carried out on the structure and vibrational spectrum of diazepamm. Comparison between the calculated and experimental parameters indicates that the results of B3LYP/6-31G(d,p) are in good agreement with experimental ones. Therefore the assignments made at higher level of theory with higher basis set with only reasonable deviations from the experimental values seem to be correct. This study demonstrates that DFT/B3LYP calculations are a powerful approach for understanding the vibrational spectra of medium sized organic compounds.

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