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## **A Comprehensive Account of Spectral, NLO, NBO Analysis, Hartree Fock and Density Functional Theory Studies of 1-Methyl 2, 6-diphenyl piperidin-4-one**

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### **ABSTRACT**

Piperidin derivatives is found to play an important role in medicinal chemistry with a wide range of pharmacological activities the piperidin ring of the title compound  $C_{18}H_{19}N_1O_1$  adopts twin chair conformation The spectroscopic property of the target compound were examined by FT-IR (4000-450 $cm^{-1}$ ), FT-RAMAN(4000-50 $cm^{-1}$ ) techniques. Theoretical calculations have been performed to obtain IR and Raman spectra of the complexes using HF and DFT methods. The vibration frequency, atomic charges, dipole moments, and several thermo dynamical parameters are reported. The charge transfer property of the molecule was verified. The first order hyperpolarizability of the investigated molecule has been studied theoretically.

**Keywords:** Piperidin derivatives, HF and DFT methods, investigation.

### **INTRODUCTION**

Piperidones belongs to an important class of heterocycles which are found to possess a variety of biological activities including cytotoxic and anticancer properties<sup>1</sup>. Derivatives of piperidones have attracted chemists and also biologists due to their predicted mode of interaction with little or no affinity for hydroxyl and amino groups<sup>2,3</sup>.

CNS stimulant and recent reports suggest that compounds containing piperidin-4one moiety elicit excellent activity when aromatic substitutions are present at 2 and 6 positions. Mannich type condensation involving aromatic aldehydes and ketones have two methylene groups, resulting in the formation of 2,6diarylpipeidin was first reported by Noller and Baliah<sup>4</sup>. The phenyl or para substituted phenyl substituent at C2 and C6 positions have wide

range of antimicrobial activity<sup>5</sup>. The conformational features of piperidin-4-ones are quite interesting and thought provoking. Literature report reveals that the derivatives of 2,6-diphenylpiperidin-4-ones and their stereochemistry have been reported but however much work on N- methyl substituted in 2,6-diphenyl piperidin-4-ones have not been reported so far. This envisaged that in the present work. The 1-Methyl 2,6-diphenyl piperidin-4-one (PIP41) was synthesized and theoretical investigation was performed.

#### FT-Raman and FT-IR measurement

FT-Raman spectrum of PIP41 was recorded using ND-YAG laser as excitation wavelength in the region 50-4000  $\text{cm}^{-1}$  using BRUKER RFS27 stand alone spectrometer. The ND-YAG laser source operates at 1064nm line with 200mW powers. The FT-IR spectrum of the MDPO was recorded using PERKIN ELMER spectrometer in the region 4000-100 $\text{cm}^{-1}$ . The frequencies of all sharp bands are accurate to  $\pm 1\text{cm}^{-1}$ .

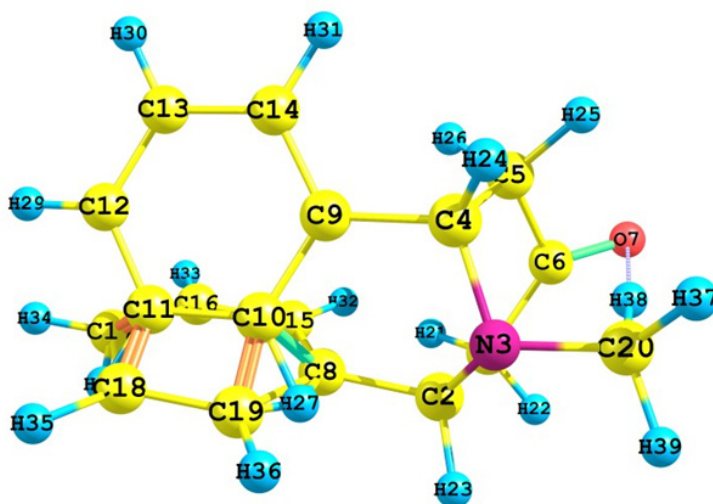


Fig. 1: Molecular structure of 1methyl 2,6 diphenyl piperidine 4one

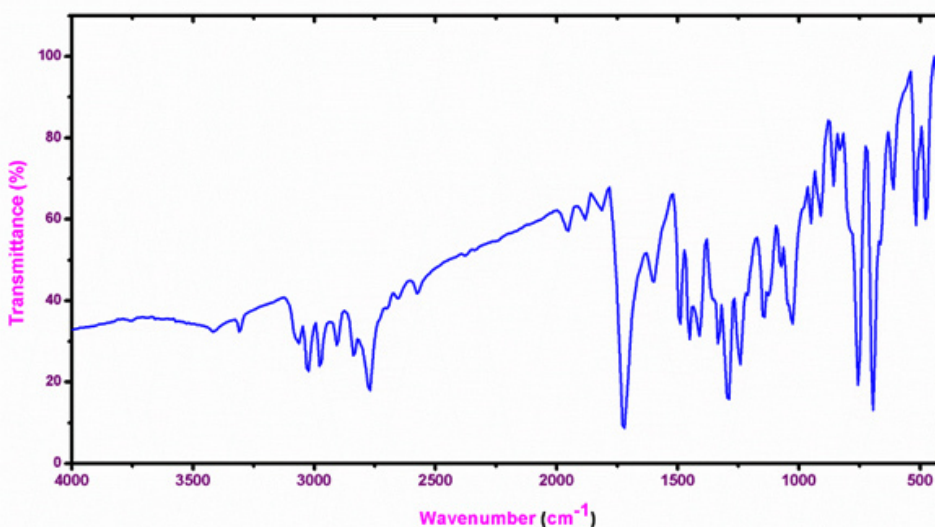


Fig. 2: Experimental FT-IR spectrum of 1methyl2,6 diphenyl piperidine 4one

### Computational details

The molecules under investigation have been analysed with density functional theory (DFT) employing Beckle's three parameter hybrid exchange functional B3LYP and Hartee Fock theory (HF). In order to fit the theoretical wave numbers to the experimental, the scaling factors have been introduced by using least square optimization of the computed to the experimental data. Vibrational frequencies are scaled as 0.9067 for HF and the range of wave numbers above 1700 $\text{cm}^{-1}$  are scaled as 0.958 and below 1700 $\text{cm}^{-1}$  scaled as 0.983 for B3LYP<sup>6</sup>. The DFT was also used to calculate the dipole moment, mean and the first static hyperpolarizability ( $\hat{\alpha}$ ) of the title compounds. Calculation of total molecular dipole moment  $\hat{\mu}$  and its components, total molecular first order hyperpolarizability  $\hat{\alpha}$  and its components of PIP41 were made at HF and B3LYP/6-311++G level. All the calculations were performed using Gaussian 09 programme<sup>7</sup>.

## RESULTS AND DISCUSSION

### Vibrational analysis

Complete vibrational assignments were made. Vibrational assignments of different functional groups are analyzed in detail are discussed below.

The nitrogenised heterocyclic aromatic compounds commonly shows CH stretching vibrations in the region 3010-3100  $\text{cm}^{-1}$ <sup>18</sup> The CH stretching vibrations due to pyridine ring are observed at 3140,3081,2971 $\text{cm}^{-1}$  in IR and 3098,3010,3212 $\text{cm}^{-1}$  in Raman<sup>9,10</sup> In present investigation the experimental values shows the CH stretching vibrations at 3054,2977.2907  $\text{cm}^{-1}$  in Raman and in IR 3024.2978,2908  $\text{cm}^{-1}$  are observed

Various normal vibrations of phenyl rings are assigned according to Wilson's numbering convention<sup>11</sup>. Selection rules allow the C-H stretching modes and in Raman spectrum, only the ring mode is active, exhibiting a medium polarized band at 2977  $\text{cm}^{-1}$ . Normal mode appear to be very weak in IR at 3054  $\text{cm}^{-1}$ , which is due to steric interaction that induces effective conjugation and charge carrier localization resulting in phenyl ring twisting<sup>12</sup>

The carbon-carbon stretching modes of the pyridine are expected in the range 1650-1100  $\text{cm}^{-1}$  which is significantly influenced by the nature of the substituent<sup>13</sup> the six ring carbon atoms undergo coupled vibrations. The ring C=C and C-C vibrations usually occur in the region 1625-1430 $\text{cm}^{-1}$  The experimental frequency observed at 1600  $\text{cm}^{-1}$  in

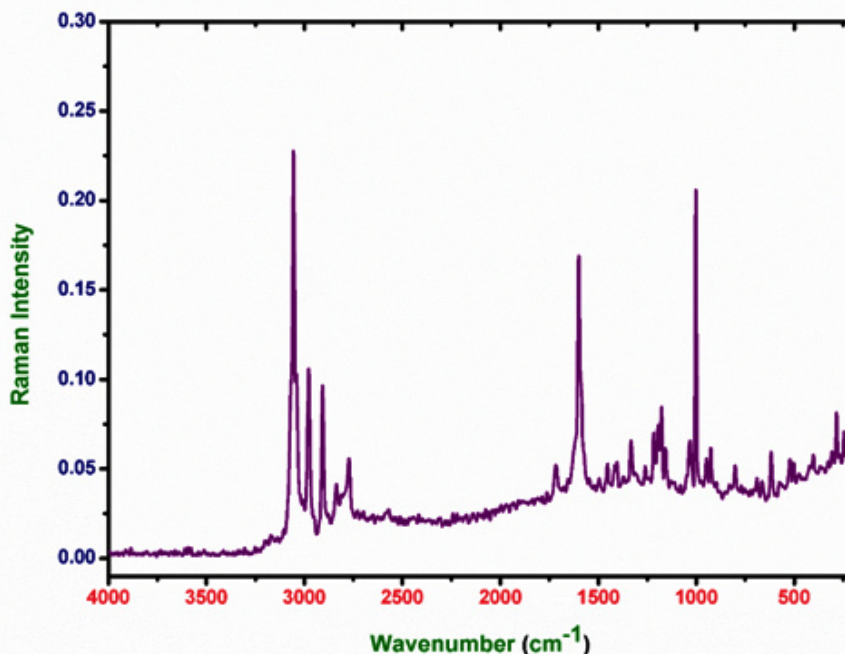
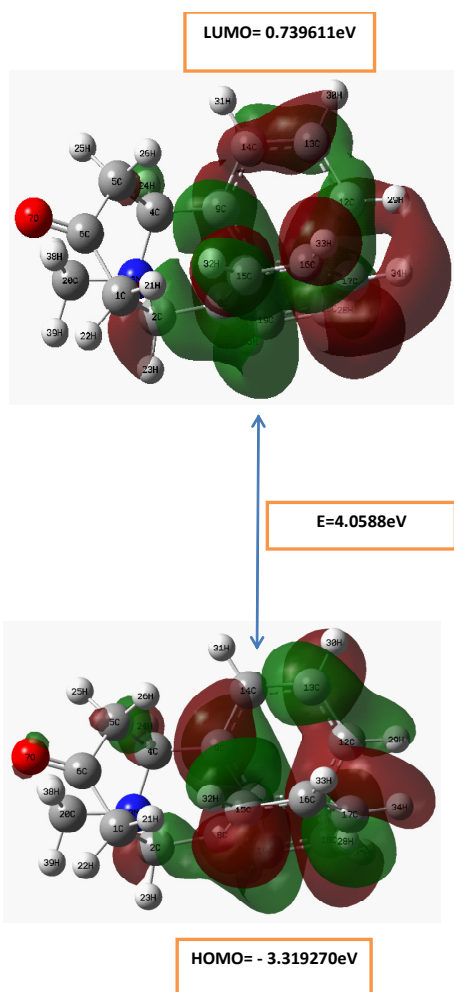


Fig. 3: Experimental FT-Raman spectrum of 1-methyl-2,6-diphenylpiperidine-4-one



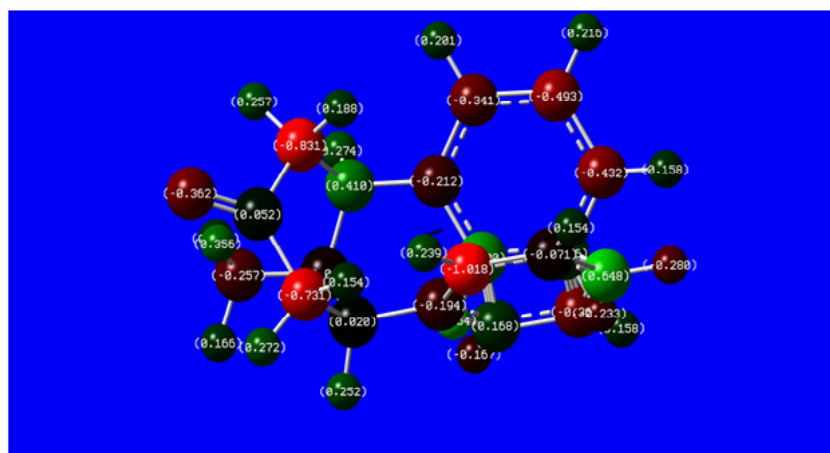
**Fig. 4: Frontier molecular orbital surfaces and energy level HOMO, LUMO of the compound**

Raman. The calculated frequencies in  $1602\text{ cm}^{-1}$  HF and in  $1358\text{ cm}^{-1}$  B3LYP are assigned to this value.

Selection rule for p-di substituted phenyl ring allows five C-C stretching modes, and degenerate vibrational pair expected to be larger than which is observed as a weak band at  $1495\text{ cm}^{-1}$  in Raman and as a medium and at  $1600\text{ cm}^{-1}$  in IR respectively. IR has contribution to mode at  $1528\text{ cm}^{-1}$  whereas IR appears in separately as a weak band at  $1408\text{ cm}^{-1}$  with its counterpart appearing uniquely in Raman as a weak band at  $1395\text{ cm}^{-1}$ . Very strong band exists in Raman at  $1324\text{ cm}^{-1}$  due to the ring mode. Normal vibrations are categorized as CH in-plane bending vibrations of p-di substituted phenyl rings which are given in Table 1. Allowed CH out-of-plane bending modes are very strong band in Raman at  $842\text{ cm}^{-1}$  and weak band in IR at  $818\text{ cm}^{-1}$  are assigned to normal stretching modes.

Normally, in plane deformation vibration occur at higher frequencies than that of out plane vibrations<sup>14</sup> the lower frequency region  $360\text{-}105\text{ cm}^{-1}$  in Raman is due to ring deforming vibrations. The band observed at  $521, 502, 402\text{ cm}^{-1}$  in IR and  $478, 424\text{ cm}^{-1}$  in Raman are assigned to C-C-C deformation mode in pyridine ring<sup>15</sup>

C=O stretching vibrations in saturated aliphatic aldehydes, ketones and acids have frequencies in range  $1740\text{-}1700\text{ cm}^{-1}$ . In amides the frequency is lowered to  $1690\text{ cm}^{-1}$  which is due to existence of resonance structures. C=O stretching band occurs at  $1686\text{ cm}^{-1}$  in urea<sup>16</sup> and is observed



**Fig. 5: Mulliken charges of 1 methyl 2,6 diphenyl piperidine 4 one**

**Table 1: Comparison of the experimental (FT-IR and FT-Raman) and theoretical harmonic wave numbers (cm<sup>-1</sup>) of 1-Methyl 2,6-diphenyl piperidin-4-one**

Experimental frequency Assignment RAMAN IR	Calculated frequency						Vibrational	
	HF/6-311++ G (d p)			B3LYP/6-311++ G (d p)				
Scaled	IR	S <sub>RA</sub>	IR <sub>A</sub>	scaled	IR	S <sub>RA</sub>	IR <sub>A</sub>	
3054	3142	3658.9	703139.3	34298.1	270.7	17541.4	658.4	v C-C
3024	2988	3489.5	497027.9	28087.1	298.1	3547.4	231.2	v C-H
2977	2986	36.8	456.9	25.9	17.9	3818.7	270.1	sym v C-H
2908	2966	212.0	17162.8	990.8	14.8	18215.7	1308.3	asy v C-H
2947		30.8	1266.3	74.5	11.7	88696.1	6420.0	sym v C-H
2936		27.7	276.9	16.5	30.9	9976.5	731.3	v C-H
2897		483.2	45314.2	2793.7	136.6	25516.6	1888.1	v C-H
2883		188.5	33109.9	2070.5	57.8	17395.8	1335.2	v C-H <sub>3</sub>
2870		413.6	33389.8	2112.5	5.0	105.8	8.2	v C-H <sub>2</sub>
2865		29.2	204.7	13.0	23.5	165.7	12.9	v C-H <sub>2</sub>
2859		24.7	178.0	11.4	24.7	81.7	6.4	v C-H <sub>2</sub>
2836	2838	35.4	7465.7	487.1	11.2	202.2	16.0	v C-H <sub>2</sub>
2772	2828	15.4	2842.5	187.4	50.1	310.1	25.2	v C-H <sub>2</sub>
2700	2816	21.4	984.7	65.6	66.2	340.0	28.1	v C-H
2812		27.4	195.1	13.1	0.8	178.9	14.8	v C-H <sub>3</sub>
2810		15.8	1020.8	68.4	33.7	125.9	10.5	v C-H
2659	2689	26.5	783.9	59.1	88.6	680.8	58.0	asy v C-H
2654	2643	60.0	89292.8	7037.0	207.6	7292.0	654.5	v C-H
2573	2580	282.5	57437.0	4812.1	169.1	4609.6	417.3	asy v C-H
2376	2025	781.5	130792.6	19085.1	637.6	27729.4	2668.0	v C=C
1951	1964	4264.4	113228.7	17617.5	73.0	5444.1	823.0	v C=C
1813	1828	2502.4	136424.5	24506.9	407.4	107.6	24.5	asy v C-H <sub>3</sub>
1716	1751	62.2	43.7	8.5	83.0	77.3	18.7	v C=O
1600	1672	488.9	57.6	12.3	15.3	11328.7	2918.8	v C=C
1668		62.1	1789.5	383.2	65.6	5450.7	1507.4	out plane β C-H
1494	1573	33.2	5854.6	1396.4	39.0	197.1	55.2	in plane β C-H
1614		24.6	85.1	19.4	15.4	75.3	22.9	out plane β C-H

1600		1602	18.7	811.1	187.1	1358	12.4	35.5	10.9	v C-C
1494	1334	1590	530.2	95714.7	22387.7	1341	10.2	4466.1	1404.2	twist C-H
1451		1581	96.8	33377.4	7886.5	1314	33.3	378.8	123.2	$\beta$ C-H
1557			16.5	1375.3	334.1	1307	114.7	8328.3	2732.7	outplane $\beta$ C-H <sub>2</sub>
1549			64.9	10746.0	2633.9	1295	105.3	1146.4	381.8	inplane $\beta$ C-H <sub>2</sub>
1288		1544	47.2	1830.8	451.2	1289	30.4	959.8	322.1	$\beta$ C-H
1532			109.1	2072.4	517.8	1277	14.5	1556.6	530.1	$\beta$ C-H
1504			6.3	5276.3	1362.3	1264	35.1	422.6	146.4	$\beta$ C-H
1501			7.6	4389.8	1137.9	1259	0.8	250.0	87.2	$\beta$ C-H
1477		1484	84.0	6972.9	1842.8	1244	3.6	4792.8	1704.3	$\beta$ C-H
1471			9.6	743.2	198.2	1231	16.0	565.2	204.4	$\beta$ C-H
1438			43.1	3586.1	963.4	1226	23.1	417.3	151.9	outplane $\beta$ C-H
1390		1455	15.2	1462.4	400.3	1205	101.3	1223.4	457.3	outplane $\beta$ C-H
1370			49.0	9386.3	2622.6	1184	64.9	14117.1	5429.7	outplane $\beta$ C-H
1332		1400	287.8	1256.7	367.3	1175	21.3	121.3	47.3	outplane $\beta$ C-H
1311			235.1	3563.4	1054.4	1150	20.8	3365.3	1355.3	phenyl ring vib
1295			8.9	4686.5	1421.3	1139	21.2	26061.8	10654.1	$\beta$ C-H
1278		1351	37.3	735.9	228.6	1127	87.6	727.9	302.3	$\beta$ C-H
1261		1329	196.7	18607.5	5940.2	1119	48.5	855.6	359.5	ring $\beta$
1248			20.2	1428.3	466.4	1108	322.1	7274.4	3099.5	v COH
1216		1275	30.4	3413.1	1135.8	1090	20.6	284.3	124.3	outplane $\beta$ C-H
1204			17.0	741.0	252.1	1088	59.3	185.6	81.4	v C-H
1194			68.5	11906.1	4067.7	1070	52.3	313.1	140.7	$\beta$ C-H
1157		1238	22.5	1974.3	698.4	1051	8.1	521.9	241.0	outplane $\beta$ C-H
1148		1216	55.9	7587.0	2718.2	1035	27.9	657.5	310.9	outplane $\beta$ C-H
1122			107.2	8323.8	3067.7	1015	27.3	726.7	353.8	$\beta$ C-H
948			25.2	7977.1	2986.8	1005	8.3	4306.7	2126.6	$\beta$ C-H <sub>3</sub>
1078		1111	26.3	8369.2	3188.8	989	7.4	4722.6	2388.2	outplane $\beta$ C-H
		1077	80.0	29793.4	11831.6	987	69.7	4261.0	2160.8	outplane $\beta$ C-H
		1063	20.9	3227.3	1302.7	969	8.0	1574.3	820.4	outplane $\beta$ C-H
			1393.5		582.4	968	75.7	2071.6	1080.5	v C-C
			73.8	24697.8	10482.2	945	14.6	569.2	307.7	v C-C
	910		79.2	2002.2	892.0	916	14.4	5841.4	3299.8	$\beta$ C-H
			79.0	11437.1	5196.2	909	4.0	4382.7	2504.8	v C-H

1054	0.8		485.1	223.0		886	34.7	1092.0	647.3	$\beta$ C-H
1031		1024	32.9	7701.6	3701.2	855	26.4	891.2	555.0	$\beta$ C-H <sub>2</sub>
1020			21.8	10882.1	5255.2	837	5.4	92.3	59.2	$\nu$ C-C
1001		1011	1.4	2761.4	1352.5	826	14.5	403.0	263.4	$\nu$ C-N
984			17.3	3645.4	1856.1	812	53.8	1141.8	764.5	$\nu$ C-C-C
981		141.6	13483.6	6904.8	794	16.7	86.7	59.9	59.9	$\beta$ C-N
947		934	22.7	18975.2	10431.2	774	61.7	1945.4	1390.0	$\beta$ C-H
925		917	26.7	2022.6	1142.2	726	157.1	2762.3	2153.3	outplane $\beta$ C-H
907			146.8	99858.2	57263.9	721	34.8	7781.0	6122.7	$\nu$ C-C
898			49.7	9449.7	5491.4	703	27.9	1068.9	868.7	phenyl ring vib
891			65.9	6088.2	3578.3	673	16.4	3057.7	2631.8	$\nu$ C-C
843			39.1	13222.0	8403.9	663	40.8	4676.2	4110.1	$\beta$ C-C
825			106.6	19124.7	12523.4	629	40.5	12721.6	11971.9	$\beta$ C-C
801	856	801	241.8	68778.9	46944.4	601	33.3	1626.8	1621.2	$\nu$ C-C
756		739	113.4	21093.3	16055.4	591	6.6	1538.6	1566.7	$\nu$ C-H
716			302.8	31184.9	24732.7	555	21.2	10917.0	12025.3	$\nu$ C-H
694		663	67.9	1024.4	899.6	542	38.0	1667.5	1891.2	$\nu$ C-H
646			16.0	7655.0	6953.7	516	10.0	493.6	596.2	ring $\beta$
617	609	632	29.1	2007.2	1877.4	497	7.4	115.7	146.1	$\nu$ C-C
595		599	202.3	1623.0	1623.9	475	7.5	1429.5	1908.3	$\beta$ C-H <sub>2</sub>
566	8.5		162.6	12817.5	12931.5	468	52.3	8079.9	10976.0	$\nu$ C-H
521	516	551	37.3	17857.3	19875.9	439	13.9	61.9	90.8	$\nu$ C-C
502	478	513	240.4	5583.2	6784.5	422	25.0	1133.6	1745.8	$\beta$ C-C
461		494	3.7	200.0	254.3	412	14.3	1658.8	2628.9	$\nu$ C-H
424		483	39.6	2476.8	3237.4	383	0.5	24.6	42.4	$\nu$ C=C
402		440	0.4	17867.0	24711.6	356	5.2	300.3	563.8	$\nu$ C=C
377		402	114.9	110820.6	162397.4	333	23.7	779.8	1581.7	$\nu$ C=C
327			66.4	22577.2	36806.4	309	28.4	398.9	879.7	$\beta$ C-C
283		292	13.3	8042.3	14137.8	285	71.0	1474.1	3574.9	$\nu$ C=C
227		255	4.3	675.5	1399.7	261	35.2	1241.2	3318.3	$\nu$ C=C
			5.1	12537.1	29527.9	236	77.8	7344.0	21899.2	$\beta$ C-C
			49.2	20994.2	57485.4	223	5.1	136.0	431.8	$\tau$ ring C=C
						165	7.3	511.7	2249.2	$\nu$ C=C

í Stretching  $\hat{a}$ , bending; in plane bending, out plane bending,  $\hat{o}$  torsion,  $\hat{a}$  rocking



**Table 2: Mulliken atomic charges of 1-Methyl 2,6-diphenyl piperidin-4-one**

Atoms	HF/6-311++ G(d, p)	B3LYP/6-311++ G (d, p)
C <sub>1</sub>	-0.7308	-0.5293
C <sub>2</sub>	0.0201	-0.1554
N <sub>3</sub>	-0.0595	-0.0709
C <sub>4</sub>	0.4104	0.1570
C <sub>5</sub>	-0.8307	-0.6656
C <sub>6</sub>	0.0521	-0.1031
O <sub>7</sub>	-0.3620	-0.2555
C <sub>8</sub>	-0.1938	0.3433
C <sub>9</sub>	-0.2119	0.0789
C <sub>10</sub>	0.5003	-0.1680
C <sub>11</sub>	0.2763	-0.0367
C <sub>12</sub>	-0.4318	0.4200
C <sub>13</sub>	-0.4935	-0.8275
C <sub>14</sub>	-0.3405	-0.6018
C <sub>15</sub>	-1.0183	-1.0348
C <sub>16</sub>	-0.0710	0.0500
C <sub>17</sub>	0.6484	0.6238
C <sub>18</sub>	-0.3666	-0.3548
C <sub>19</sub>	0.1684	-0.0718
C <sub>20</sub>	-0.2572	-0.1621
H <sub>21</sub>	0.1542	0.1610
H <sub>22</sub>	0.2724	0.2370
H <sub>23</sub>	0.2520	0.2662
H <sub>24</sub>	0.2741	0.2513
H <sub>25</sub>	0.2568	0.2088
H <sub>26</sub>	0.1884	0.1917
H <sub>27</sub>	0.7537	0.7048
H <sub>28</sub>	-0.2335	-0.1190
H <sub>29</sub>	0.1580	0.1536
H <sub>30</sub>	0.2163	0.1398
H <sub>31</sub>	0.2010	0.1256
H <sub>32</sub>	0.2393	0.1584
H <sub>33</sub>	0.1538	0.1524
H <sub>34</sub>	-0.2795	0.1537
H <sub>35</sub>	0.1578	-0.0639
H <sub>36</sub>	-0.1666	0.0130
H <sub>37</sub>	0.1722	0.1715
H <sub>38</sub>	0.3557	0.3144
H <sub>39</sub>	0.1656	0.1440

at 1716 cm<sup>-1</sup> as a weak band in Raman. 1720 cm<sup>-1</sup> in IR experimental. The computed HF value 1751 cm<sup>-1</sup> is assigned to this vibration.

The identification of C-N stretching vibration is difficult task, since the mixing of vibrations is possible in these regions. The C-N in plane bending vibrations is observed at 1001 cm<sup>-1</sup> in Raman. These vibrations are assigned at 1011 cm<sup>-1</sup> and 1352 cm<sup>-1</sup> in computed spectrum. Increase in the value of C-N stretching is explained by shortening of C-N bond, when the data is compared with urea<sup>15</sup>.

#### Frontier molecular Orbital's (FMOs)

The highest occupied molecular orbital's (HOMO) and the lowest unoccupied molecular orbital's (LUMO) are generally named as Frontier molecular orbital's (FMO). The FMO play important role in the optical and electric properties in quantum chemistry and UV visible spectra of compounds. The HOMO-LUMO energy gap of PIP41 have been computed by using ab-initio HF/6-31G levels and the results are shown in Fig 4. It shows that the energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor and represents the ability to accept an electron; HOMO represents ability of the orbital to donate an electron. HOMO is localized on almost the whole molecule. LUMO is especially localized on the ring. The calculated energy values of HOMO are -3.31927 eV, the LUMO energy value is 0.73961 eV respectively. It is seen that the HOMO-LUMO gap is 4.0588 eV. The energy gap between the HOMO and LUMO indicates the chemical stability of the molecules. It reveals that the molecules are soft and more reactive with chemical compounds<sup>17, 18</sup>

#### Mulliken atomic charges

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of atomic charge affects dipole moment electronic structure, molecular systems. The total atomic charges of 1-Methyl 2,6-diphenyl piperidin-4-one are obtained by Mulliken population analysis shown in Table 2. The results show that substitution of methyl group in 2,6-diphenyl piperidin-4-one leads to the redistribution of electron density. The charge distribution shows all

**Table 3: NBO analysis Accumulation of Natural charge population of electrons in Core, Valence and Rydberg orbitals**

Atom	Charge	Natural population			Total
		Core	Valence	Rydberg	
C <sub>1</sub>	-0.45658	1.99918	4.44024	0.01717	6.45658
C <sub>2</sub>	0.04620	1.99928	3.92817	0.02636	5.95380
N <sub>3</sub>	-0.59171	1.99950	5.57410	0.01810	7.59171
C <sub>4</sub>	-0.00271	1.99924	3.97474	0.02873	6.00271
C <sub>5</sub>	-0.45181	1.99922	4.43772	0.01487	6.45181
C <sub>6</sub>	0.58081	1.99924	3.37758	0.04237	5.41919
O <sub>7</sub>	-0.67007	1.99976	6.65846	0.01185	8.67007
C <sub>8</sub>	-0.00635	1.99796	3.98081	0.02758	6.00635
C <sub>9</sub>	-0.27141	1.99913	4.24233	0.02994	6.27141
C <sub>10</sub>	0.00859	1.99750	3.95846	0.03546	5.99141
C <sub>11</sub>	-0.24449	1.99566	4.19005	0.05878	6.24449
C <sub>12</sub>	-0.20089	1.99925	4.16979	0.03185	6.20089
C <sub>13</sub>	-0.42925	1.99919	4.39610	0.03396	6.42925
C <sub>14</sub>	-0.11010	1.99918	4.08619	0.02473	6.11010
C <sub>15</sub>	-0.35440	1.99906	4.32225	0.03308	6.35440
C <sub>16</sub>	-0.08692	1.99923	4.06106	0.02664	6.08692
C <sub>17</sub>	-0.03145	1.99725	3.98414	0.05005	6.03145
C <sub>18</sub>	-0.02079	1.99419	3.94104	0.04398	5.97921
C <sub>19</sub>	-0.25050	1.99556	4.23102	0.02392	6.25050
C <sub>20</sub>	-0.27947	1.99934	4.26572	0.01442	6.27947
H <sub>21</sub>	0.24268	0.00000	0.75578	0.00154	0.75732
H <sub>22</sub>	0.22837	0.00000	0.77031	0.00132	0.77163
H <sub>23</sub>	0.21437	0.00000	0.78470	0.00093	0.78563
H <sub>24</sub>	0.18915	0.00000	0.80849	0.00236	0.81085
H <sub>25</sub>	0.21554	0.00000	0.78287	0.00158	0.78446
H <sub>26</sub>	0.24017	0.00000	0.75853	0.00130	0.75983
H <sub>27</sub>	0.28792	0.00000	0.70019	0.01189	0.71208
H <sub>28</sub>	-0.05451	0.00000	1.02283	0.03168	1.05451
H <sub>29</sub>	0.18948	0.00000	0.80400	0.00651	0.81052
H <sub>30</sub>	0.20500	0.00000	0.79399	0.00101	0.79500
H <sub>31</sub>	0.19420	0.00000	0.80498	0.00083	0.80580
H <sub>32</sub>	0.22692	0.00000	0.77149	0.00159	0.77308
H <sub>33</sub>	0.20462	0.00000	0.78666	0.00872	0.79538
H <sub>34</sub>	0.22511	0.00000	0.74520	0.02969	0.77489
H <sub>35</sub>	0.12623	0.00000	0.84143	0.03234	0.87377
H <sub>36</sub>	0.27985	0.00000	0.71433	0.00582	0.72015
H <sub>37</sub>	0.20423	0.00000	0.79486	0.00091	0.79577
H <sub>38</sub>	0.17725	0.00000	0.81989	0.00286	0.82275
H <sub>39</sub>	0.18511	0.00000	0.81415	0.00074	0.81489

Core39.96791 (99.9198% of 40)

Valence101.29463 (99.3085% of 102)

Rydberg0.73746 (0.5193% of 142)

the hydrogen atoms and carbon atoms in few sets are positively charged where as the magnitude of the carbon atomic charges are found to be both positive and negative values The charge of N positive and negative at the basis set, however the highest value 0.1928 in B3LYP method with 6-311++G (d, p) is observed. The charge of the nitrogen atom -0.0672 is lowest in HF/6-311++G (d, p). The nitrogen and oxygen atoms have negative values only in all basis sets due to electron withdrawing nature. The Mulliken charge distribution is shown in Figure5.

**Table 4: Occupancy and energies of lone pair orbital's (LP) and anti bonding molecular orbital's (BD\*) of PIP41**

Atomic orbitals	Occupancy	Energy
LP (1) N <sub>3</sub>	1.91714	-0.48261
LP (1) O <sub>7</sub>	1.97056	-0.92002
LP (1) O <sub>7</sub>	1.91613	-0.45138
BD*(1) C <sub>1</sub> -C <sub>2</sub>	0.0263	0.56918
BD*(1) C <sub>2</sub> -C <sub>8</sub>	0.04956	0.56005
BD*(1) N <sub>3</sub> -C <sub>4</sub>	0.02060	0.60953
BD*(1) N <sub>3</sub> -C <sub>20</sub>	0.01100	0.58890
BD*(1) C <sub>13</sub> -H <sub>30</sub>	0.01112	0.69617
BD*(1) C <sub>15</sub> -C <sub>32</sub>	0.09844	0.66598
BD*(1) C <sub>6</sub> -O <sub>7</sub>	0.01332	0.85018

### NBO analysis

#### Accumulation of Natural charge population of electrons in Core, Valence and Rydberg orbitals

The natural population analysis performed on the electronic structure of the title molecule clearly explains the distribution of electron in various sub-shells of their atomic orbital. The accumulation of electron in the core, valence and Rydberg sub shells of the molecule are presented in Table3. The most electronegative atoms N<sub>3</sub>, O<sub>7</sub> and C<sub>1</sub> have charges -0.5971, -0.67007 and -0.45658 respectively. The most electro positive atom is C<sub>6</sub> with charge 0.58081 From the electrostatic point of view, electronegative atoms have a tendency to donate an electron whereas the electropositive atoms have a tendency to accept an electron The natural population analysis show that the distribution of 142 electrons in the title compound are distributed in sub-shells as follows:  
Core 39.96791 (99.9198% of 40)  
Valence 101.29463 (99.3085% of 102)  
Rydberg 0.73746 (0.5193% of 142)

The occupancies and energies of lone pair molecular orbital's (LP) and anti bonding (BD\*) molecular orbital's of the PIP41 are predicted at HF/6311++G level of theory and is presented in Table4. The variations in occupancies and energies of the title molecule directly give the evidence for the

**Table 5: Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis**

Donor NBO (i)	Acceptor NBO (j)	kcal/mol E(2)	a.u. E(j)-E(i)	a.u. F(i,j)
LP (1) N <sub>3</sub>	BD*(1) C <sub>1</sub> - C <sub>2</sub>	9.99	1.05	0.093
LP (1) N <sub>3</sub>	BD*(1) C <sub>2</sub> - C <sub>8</sub>	0.87	1.07	0.027
LP (1) N <sub>3</sub>	BD*(1) C <sub>2</sub> - H <sub>23</sub>	4.13	1.04	0.059
LP (1) N <sub>3</sub>	BD*(1) C <sub>4</sub> - C <sub>5</sub>	9.18	1.10	0.091
LP (1) N <sub>3</sub>	BD*(1) C <sub>4</sub> - H <sub>24</sub>	3.78	1.10	0.058
LP (1) N <sub>3</sub>	BD*(1) C <sub>20</sub> - H <sub>37</sub>	1.86	1.06	0.040
LP (1) N <sub>3</sub>	BD*(1) C <sub>20</sub> - H <sub>38</sub>	8.82	1.11	0.089
LP (1) N <sub>3</sub>	BD*(1) C <sub>20</sub> - H <sub>39</sub>	1.61	1.05	0.038
LP (1) O <sub>7</sub>	BD*(1) C <sub>1</sub> - C <sub>6</sub>	3.81	1.52	0.068
LP (1) O <sub>7</sub>	BD*(1) C <sub>5</sub> - C <sub>6</sub>	1.97	1.53	0.049
LP (2) O <sub>7</sub>	BD*(1) C <sub>1</sub> - C <sub>6</sub>	28.74	1.05	0.156
LP (2) O <sub>7</sub>	BD*(1) C <sub>4</sub> - C <sub>5</sub>	0.92	1.07	0.028
LP (2) O <sub>7</sub>	BD*(1) C <sub>5</sub> - C <sub>6</sub>	22.90	1.06	0.141

delocalization of charge upon substitution and this leads to the variation of bond lengths.

The interactions result in a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty Non Lewis orbital. NBO analysis of some pharmaceutical compounds has been performed by many spectroscopists [19-21] the lone pair anti bonding interactions can be quantitatively described by the second order perturbation interaction [22-25] is shown in table 5.

#### Electron contribution in s-type and p-type sub-shells

NBO analysis of title compound is performed to estimate the delocalisation patterns of electron density (ED) from the principle occupied Lewis –type (bond or lone pair) orbitals to unoccupied non- Lewis (anti bonding or Rydberg) orbitals. The

list of occupancies and energies of most interacting NBO's along with their percentage of hybrid atomic orbitals is listed in table 6. The percentage of hybrid atomic orbitals of oxygen lone pair atom  $O_7$  and nitrogen lone pair atom  $N_3$  shows that  $O_7$  is partially contributed to both s-type and p-type sub-shells, while  $N_3$  is predominantly contributed to p-type sub-shell..In contrast ,all the anti-bonding orbital's of the title compound are mainly contributed to p-type sub-shell, except in the  $BD^*(1) C_4-O_7$  orbital which shows that  $O_7$  is partially contributed to both s-type and p-type sub-shells as stated in table 6.

#### Thermo dynamical properties

The values of certain thermodynamic parameters (zero point vibrational, thermal energies, specific heat capacity, rotational constants, entropy) of PIP41 at 298.15K in ground state are listed in Table 7.All thermodynamic parameters are calculated in

**Table 6: Natural atomic orbital occupancies of most interacting (lone pair and anti bonding) NBOs of 1-Methyl 2,6-diphenyl piperidin-4- one**

Parameters	Occupancies	Hybrid	AO(%)
LP (1) $N_3$	(1.91714)	$sp^{5.91}$	(14.48%) (85.52%)
LP (1) $O_7$	(1.97056)	$sp^{0.77}$	(56.58%) (43.42%)
LP*(1) $C_{17}$	(0.68220)	$sp^{9.80}$	(9.26%) (90.74%)
$BD^*(1)$	(0.02643)	$sp^{2.65} (C_1)$	s(27.36%)p(72.64%)
$C_1 - C_2$		$sp^{2.57} (C_2)$	s (28.04%)p(71.96%)
$BD^*(1)$	(0.05481)	$sp^{2.71} (C_1)$	s(26.98%)p(73.02%)
$C_1 - C_6$		$sp^{1.77} (C_6)$	s(36.16%)p(63.84%)
$BD^*(1)$	(0.02643)	$sp^{2.65} (C_1)$	s (27.36%)p(72.64%)
$C_1 - C_2$		$sp^{2.57} (C_2)$	s (28.04%)p(71.96%)
$BD^*(1)$	(0.05481)	$sp^{2.71} (C_1)$	s (26.98%)p(73.02%)
$C_1 - C_6$		$sp^{1.77} (C_6)$	s (36.16%)p(63.84%)
$BD^*(1)$	(0.02458)	$sp^{3.26} (C_2)$	s (23.46%) p (76.54%)
$C_2 - N_3$		$sp^{2.72} (N_3)$	s (26.85%) p (73.15%)
$BD^*(1)$	(0.04956)	$sp^{2.87} (C_2)$	s( 25.82%) p ( 74.18%)
$C_2 - C_8$		$sp^{1.87} (C_8)$	s (34.87%)p (65.13%)
$BD^*(1)$	(0.01100)	$sp^{2.49} (N_3)$	s (28.62%)p (71.38%)
$N_3 - C_{20}$		$sp^{3.17} (C_{20})$	s (23.98%)p (76.02%)
$BD^*(1)$	(0.01332)	$sp^{2.29} (C_6)$	s (30.41%)p ( 69.59%)
$C_6 - O_7$		$sp^{1.38} (O_7)$	s (42.07%)p ( 57.93%)
$BD^*(1)$	(0.11762)	$sp^{3.95} (C_{10})$	s (20.20%) p (79.80%)
$C_{10} - C_{11}$		$sp^{3.14} (C_{11})$	s (24.13%) p (75.87%)
$BD^*(1)$	(0.06058)	$sp^{2.38} (C_{10})$	s (29.60%)p ( 70.40%)
$C_{10} - C_{19}$		$sp^{1.65} (C_{19})$	s (37.69%)p ( 62.31%)

gas phase.. The variation in zero point vibration energy (ZPVE) seems to be significant. HF method yielded higher ZPVE values than B3LYP method for the three compounds. There is only small difference in the total energy of the compound. Specific heat capacity values are computed for the molecule and these values are presented in Table 7. It is found that DFT method gave slightly higher  $C_v$  values than HF method. These observations are indicative of different type of hydrogen bonding in these three molecules. Dipole moment reflects the molecular charge distribution and is given as vector in three dimensions therefore it can be used as descriptor to depict the charge distribution in the molecules. Direction of the dipole moment vector in a molecule depends on the centre of positive negative charges. Dipole moments are strictly determined for neutral molecules. The computed dipole moment values are given in Table 7. It is found that HF method yielded higher dipole moment than B3LYP method. This may be due to higher atomic charges obtained by HF method.

### Hyperpolarizability

The complete equations for calculating, the mean polarizability  $\alpha_0$ , the anisotropy of the polarizability  $\Delta\alpha$  and the mean first polarizability  $\beta$  are as follows:

$$\alpha_{tot} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad \dots(1)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2 \right]^{\frac{1}{2}} \quad \dots(2)$$

$$\langle\beta\rangle = \left[ (\beta_{xxx} + \beta_{yyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{zzz} + \beta_{xxx})^2 + (\beta_{zzz} + \beta_{xxx} + \beta_{yyy})^2 \right]^{\frac{1}{2}} \quad \dots(3)$$

The Hyperpolarizability is calculated using HF, B3LYP method on the basis of finite field

**Table 7: The calculated thermodynamical parameters of 1-Methyl 2,6-diphenyl piperidin-4-one**

Basis Set	HF/	B3LYP/
	6-311++G (d, p)	6-311++G (d, p)
Zero point energy (Kcal/Mol)	234.031	219.244
Rotational constant	0.9295	0.9295
Rotational temperature (K)	0.04461	0.04461
Energy (E)		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	237.383	223.826
Total	239.561	25.604
Specific heat (Cv)		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	35.578	41.761
Total	41.539	47.723
Entropy(S)		
Translational	42.625	42.625
Rotational	33.442	33.442
Vibrational	18.463	22.647
Total	93.530	97.714

**Table 8: Hyperpolarizability of 1-Methyl 2,6-diphenyl piperidin-4-one**

$\beta$ component	HF/6-311++G	B3LYP/6-311++G
$\beta_{xxx}$	1.4453	5.0935
$\beta_{xxy}$	1.0005	3.0704
$\beta_{xyy}$	-2.3806	1.9994
$\beta_{yyy}$	-2.1045	-5.1696
$\beta_{xxz}$	5.8913	7.1620
$\beta_{xyz}$	3.1365	3.4060
$\beta_{yyz}$	-4.6828	-3.7473
$\beta_{xzz}$	3.8851	7.9850
$\beta_{yzz}$	-2.7437	-3.3824
$\beta_{zzz}$	-2.6479	-1.6916
$\beta_{TOTAL}$ (a.u.)	17.51	16.20
(esu $\times 10^{-33}$ )	151.2	139.9

approach. Calculated parameters are listed in Table 8. The polarizabilities and hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) (for  $\alpha$ ; 1 a.u =  $0.1482 \times 10^{-24}$  esu, for  $\beta$ ; 1 a.u =  $8.6393 \times 10^{-33}$  esu). The calculated polarizability of PIP41 is  $151.2 \times 10^{-33}$  esu in HF method and  $139.9 \times 10^{-33}$  esu. The magnitude of the molecular hyperpolarizability  $\hat{\alpha}$ , is one of the important factors in an NLO system.

The first order hyperpolarizability is a measure of non-linear optical (NLO) effects. NLO effects arise due to interaction of incident electromagnetic fields with media (NLO materials).

The effect is manifested as generation of new fields that differ in phase, frequency, amplitude or other propagation characteristics that differ from those of the incident fields<sup>6</sup>. NLO effects are important in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, optical memory for the emerging technologies in the area of telecommunications, signal processing and optical inter-connections<sup>26-29</sup>.

## CONCLUSION

The extensive vibrational analysis of 1-Methyl 2,6-diphenyl piperidin-4-one performed by HF and DFT methods with 6-311++G (d, p) basis sets. A good correlation was found between the theoretical and experimental wave numbers. The influences of acetone group, amino group to the vibrational frequencies of the title compounds were discussed. UV-visible spectra of the compound are discussed and wave lengths of maximum absorption are calculated. The UV analysis gives the electronic spectrum of PIP41 that has revealed the allowed and forbidden transitions with solvent effects. The N, O and H atoms contain negative charges and indicate that these molecules can behave as electron donors and form chelate complexes with metal ions. Especially N<sub>7</sub> and O<sub>3</sub> atoms favour the chelate formation as six member ring structure is possible when these two atoms are involved in the complex formation. The dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. Mulliken charges of PIP41 at different levels were calculated and the results discussed. HOMO-LUMO energies and HOMO-LUMO energy gap are calculated as 4.0588 eV. The delocalization pattern of charge and electron densities of PIP41 molecule have been explained by performing molecular orbital simulations at HF method with 6-311++G basis set. The stabilization of the structure has been identified by second order perturbation energy calculations. The calculation of the hyperpolarizability gives PIP41 suitability as catalyst to increase NLO properties.



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