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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 (4000-450cm^{-1}), FT-RAMAN(4000-50cm^{-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 hetrocycles which are found to possess a variety of biological activities including cytotoxic and anticancer properties[1]. 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[2,3]. CNS stimulant and recent reports suggest that compounds containing piperdin-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 mathylene groups, resulting in the formation of 2,6diarylpipeidin was first reported by Noller and Baliah[4].The phenyl or para substituted phenyl substituent at C2and C6 positions have wide range of antimicrobial activity[5]. 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. The1-Methyl 2,6-diphenyl pipeidin4-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 cm^{-1} using BRUKERRFS27 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 4000-100cm^{-1}. The frequencies of all sharp bands are accurate to ±1cm^{-1}.

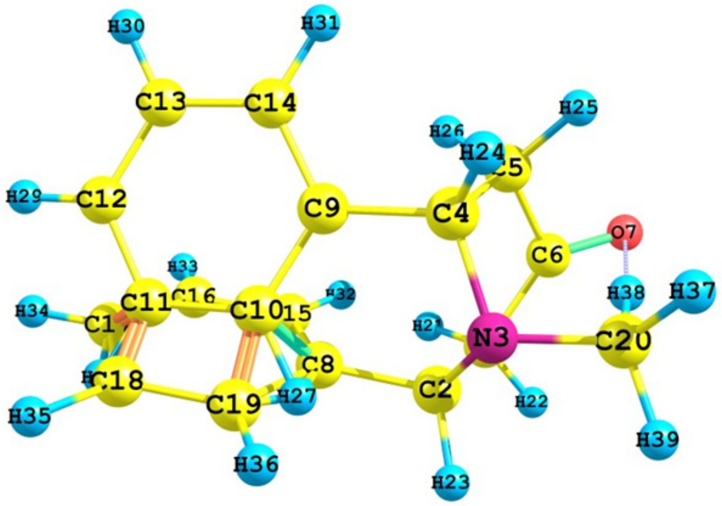

Fig. 1: Molecular structure of 1methyl 2,6 diphenyl piperdine 4one

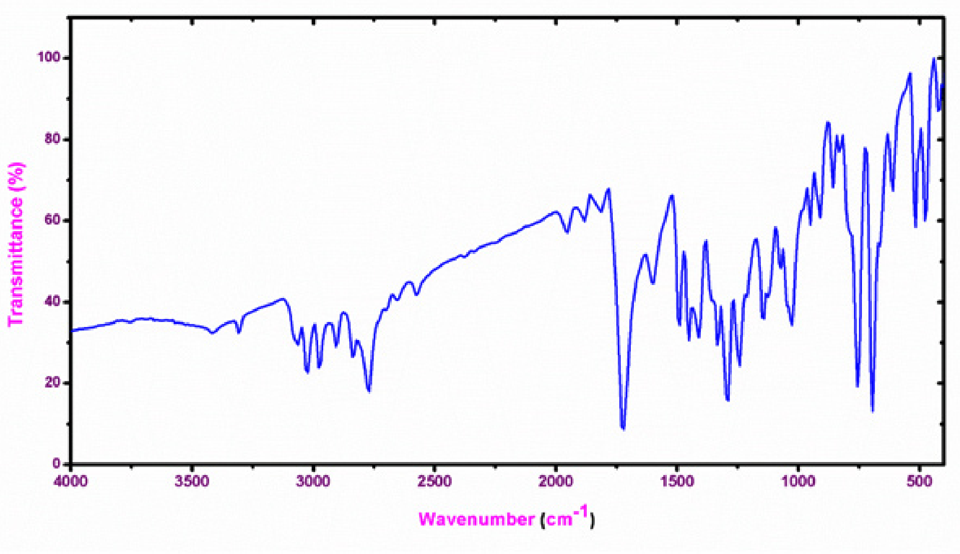

Fig. 2: Experimental FT-IR spectrum of 1methyl2,6 diphenyl piperdine 4one

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 1700cm^{-1}are scaled as 0.958 and below 1700cm^{-1} scaled as 0.983for B3LYP[6]. The DFT was also used to calculate the dipole moment, mean and the first static hyperpolarizability (â) of the title compounds. Calculation of total molecular dipole moment $ì_t$ and its components, total molecular first order hyperpolarizability â and its components of PIP41 were made at HF and B3LYP/6-311++G level. All the calculations were performed using Gaussian 09 programme[7].

RESULTS AND DISCUSSION

Vibrational analysis

Complete vibrational assignments where 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 cm^{-18} The CH stretching vibrations due to pyridine ring are observed at 3140,3081,2971cm^{-1}in IR and 3098,3010,3212cm^{-1} in Raman[9,10] In present investigation the experimental values shows the CH stretching vibrations at 3054,2977.2907 cm^{-1} in Raman and in IR 3024.2978,2908 cm^{-1} are observed

Various normal vibrations of phenyl rings are assigned according to Wilson's numbering convention[11]. 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 cm^{-1}. Normal mode appear to be very weak in IR at 3054 cm^{-1}, which is due to steric interaction that induces effective conjugation and charge carrier localization resulting in phenyl ring twisting[12]

The carbon-carbon stretching modes of the pyridine are expected in the range 1650-1100 cm^{-1} which is significantly influenced by the nature of the substituent[13] the six ring carbon atoms undergo coupled vibrations. The ring C=C and C-C vibrations usually occur in the region1625-1430cm^{-1}The experimental frequency observed at 1600 cm ^{1}in

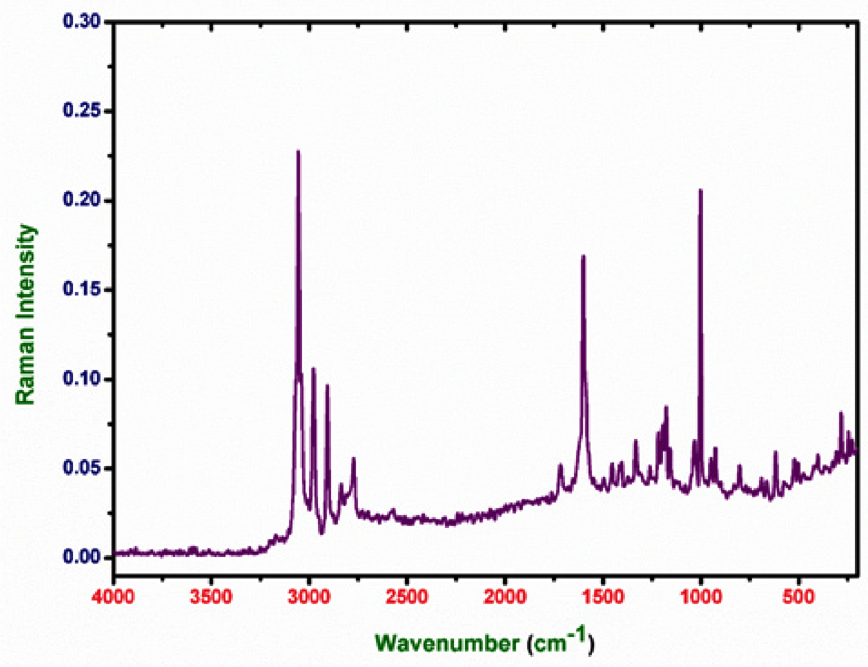

Fig. 3: Experimental FT-Raman spectrum of 1 methyl 2,6 diphenyl piperdine 4 one

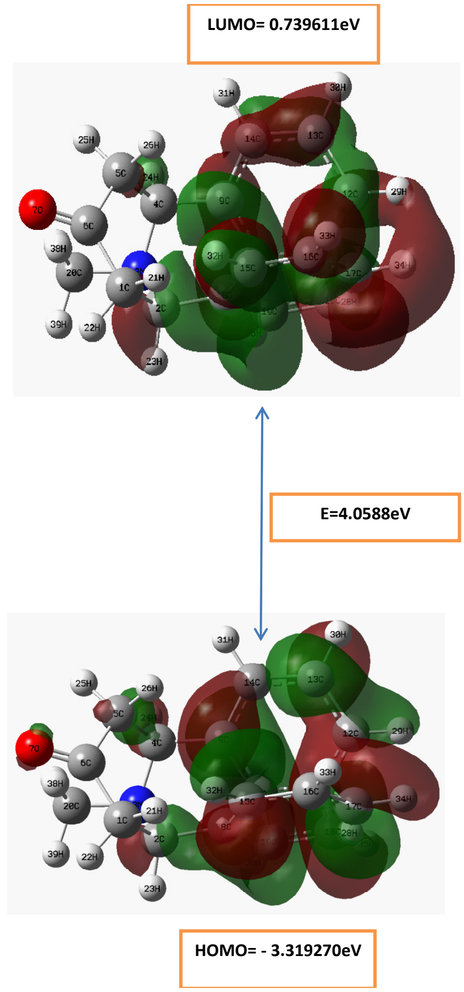

Fig. 4: Frontier molecular orbital surfaces and energy level HOMO, LUMO of the compound

Raman. The calculated frequencies in1602 cm^{-1} HF and in1358cm^{-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 cm^{-1} in Raman and as a medium and at 1600 cm-1 in IR respectively. IR has contribution to mode at 1528 cm^{-1}whereas IR appears in separately as a weak band at 1408 $cm^{-1}$with its counterpart appearing uniquely in Raman as a weak band at 1395 cm^{-1}. Very strong band exists in Raman at1324 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 cm^{-1} and weak band in IR at818 $cm^{-1}$are assigned to normal stretching modes.

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

C=O stretching vibrations in saturated aliphatic aldehydes, ketones and acids have frequencies in range 1740-1700 cm^{-1}. In amides the frequency is lowered to 1690 cm^{-115} which is due to existence of resonance structures. C=O stretching band occurs at 1686 cm^{-1}in urea[16] and is observed

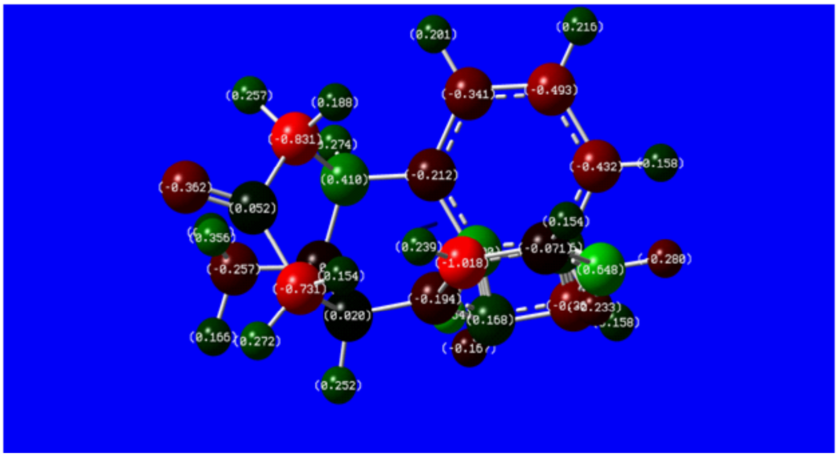

Fig. 5: Mulliken charges of 1 methyl 2,6 diphenyl piperdine 4 one

Table 1: Comparison of the experimental (FT-IR and FT-Raman) and theoretical harmonic wave numbers (cm^{-1}) of 1-Methyl 2,6-diphenyl pipeidin4-one

Experimental frequency Assignment		Calculated frequency								Vibrational
		HF/6-311++ G (d p)				B3LYP/6-311++ G (d p)				
RAMAN	IR	Scaled	I^{IR}	S^{RA}	I^{RA}	scaled	I^{IR}	S^{RA}	I^{RA}	
		3142	3658.9	703139.3	34298.1	3415	270.7	17541.4	658.4	ν C-C
3054	3024	2988	3489.5	497027.9	28087.1	2839	298.1	3547.4	231.2	ν C-H
2977	2978	2986	36.8	456.9	25.9	2755	17.9	3818.7	270.1	sym ν C-H
2907	2908	2966	212.0	17162.8	990.8	2739	14.8	18215.7	1308.3	asy ν C-H
2947			30.8	1266.3	74.5	2731	11.7	88696.1	6420.0	sym ν C-H
2936			27.7	276.9	16.5	2718	30.9	9976.5	731.3	ν C-H
2897			483.2	45314.2	2793.7	2708	136.6	25516.6	1888.1	ν C-H
2883			188.5	33109.9	2070.5	2670	57.8	17395.8	1335.2	ν $C-H_3$
2870			413.6	33389.8	2112.5	2663	5.0	105.8	8.2	ν $C-H_2$
2865			29.2	204.7	13.0	2655	23.5	165.7	12.9	ν $C-H_2$
2859			24.7	178.0	11.4	2648	24.7	81.7	6.4	ν $C-H_2$
2836		2838	35.4	7465.7	487.1	2641	11.2	202.2	16.0	ν $C-H_2$
2772	2769	2828	15.4	2842.5	187.4	2613	50.1	310.1	25.2	ν $C-H_2$
2700		2816	21.4	984.7	65.6	2596	66.2	340.0	28.1	ν C-H
2812			27.4	195.1	13.1	2595	0.8	178.9	14.8	ν $C-H_3$
2810			15.8	1020.8	68.4	2582	33.7	125.9	10.5	ν C-H
2659	2692	2689	26.5	783.9	59.1	2562	88.6	680.8	58.0	asy ν C-H
2654		2643	60.0	89292.8	7037.0	2509	207.6	7292.0	654.5	ν C-H
2573	2576	2580	282.5	57437.0	4812.1	2501	169.1	4609.6	417.3	asy ν C-H
2376		2025	781.5	130792.6	19085.1	2439	637.6	27729.4	2668.0	ν C=C
1951		1964	4264.4	113228.7	17617.5	1991	73.0	5444.1	823.0	ν C=C
1813		1828	2502.4	136424.5	24506.9	1615	407.4	107.6	24.5	asy ν $C-H_3$
1716	1720	1751	62.2	43.7	8.5	1559	83.0	77.3	18.7	ν C=O
1600	1495	1672	488.9	57.6	12.3	1506	15.3	11328.7	2918.8	ν C=C
1668			62.1	1789.5	383.2	1446	65.6	5450.7	1507.4	out plane β C-H
1494	1489	1573	33.2	5854.6	1396.4	1435	39.0	197.1	55.2	in plane β C-H
1614			24.6	85.1	19.4	1367	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	ν 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	β C-H
1557			16.5	1375.3	334.1	1307	114.7	8328.3	2732.7	outplane β C-H_2
1549			64.9	10746.0	2633.9	1295	105.3	1146.4	381.8	inplane β C-H_2
1288		1544	47.2	1830.8	451.2	1289	30.4	959.8	322.1	β C-H
1532			109.1	2072.4	517.8	1277	14.5	1556.6	530.1	β C-H
1504			6.3	5276.3	1362.3	1264	35.1	422.6	146.4	β C-H
1501			7.6	4389.8	1137.9	1259	0.8	250.0	87.2	β C-H
	1242	1484	84.0	6972.9	1842.8	1244	3.6	4792.8	1704.3	β C-H
1477			9.6	743.2	198.2	1231	16.0	565.2	204.4	β C-H
1471			43.1	3586.1	963.4	1226	23.1	417.3	151.9	outplane β C-H
	1203	1455	15.2	1462.4	400.3	1205	101.3	1223.4	457.3	outplane β C-H
1438			49.0	9386.3	2622.6	1184	64.9	14117.1	5429.7	outplane β C-H
		1400	287.8	1256.7	367.3	1175	21.3	121.3	47.3	outplane β C-H
1390			235.1	3563.4	1054.4	1150	20.8	3365.3	1355.3	phenyl ring vib
1370			8.9	4686.5	1421.3	1139	21.2	26061.8	10654.1	β C-H
1126		1351	37.3	735.9	228.6	1127	87.6	727.9	302.3	β C-H
1332		1329	196.7	18607.5	5940.2	1119	48.5	855.6	359.5	ring β
1311			20.2	1428.3	466.4	1108	322.1	7274.4	3099.5	ν COH
1295			30.4	3413.1	1135.8	1090	20.6	284.3	124.3	outplane β C-H
1278			17.0	741.0	252.1	1088	59.3	185.6	81.4	ν C-H
1261		1275	68.5	11906.1	4067.7	1070	52.3	313.1	140.7	β C-H
1248			22.5	1974.3	698.4	1051	8.1	521.9	241.0	outplane β C-H
		1238	55.9	7587.0	2718.2	1035	27.9	657.5	310.9	outplane β C-H
1216		1216	107.2	8323.8	3067.7	1015	27.3	726.7	353.8	β C-H
1204			25.2	7977.1	2986.8	1005	8.3	4306.7	2126.6	β C-H_3
1194		1191	26.3	8369.2	3188.8	989	7.4	4722.6	2388.2	outplane β C-H
1157		1160	80.0	29793.4	11831.6	987	69.7	4261.0	2160.8	outplane β C-H
1148			20.9	3227.3	1302.7	969	8.0	1574.3	820.4	outplane β C-H
1122	14.4		1393.5		582.4	968	75.7	2071.6	1080.5	ν C-C
948		1111	73.8	24697.8	10482.2	945	14.6	569.2	307.7	ν C-C
1078	910	1077	79.2	2002.2	892.0	916	14.4	5841.4	3299.8	β C-H
		1063	79.0	11437.1	5196.2	909	4.0	4382.7	2504.8	ν C-H

1054	0.8		485.1	223.0		886	34.7	1092.0	647.3	β C-H
1031		1024	32.9	7701.6	3701.2	855	26.4	891.2	555.0	β C-H_2
1020			21.8	10882.1	5255.2	837	5.4	92.3	59.2	ν C-C
1001		1011	1.4	2761.4	1352.5	826	14.5	403.0	263.4	ν C-N
984			17.3	3645.4	1856.1	812	53.8	1141.8	764.5	ν C-C-C
981		141.6	13483.6	6904.8	794	16.7	86.7		59.9	β C-N
947		934	22.7	18975.2	10431.2	774	61.7	1945.4	1390.0	β C-H
925		917	26.7	2022.6	1142.2	726	157.1	2762.3	2153.3	outplane β C-H
907			146.8	99858.2	57263.9	721	34.8	7781.0	6122.7	ν 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	ν C-C
843			39.1	13222.0	8403.9	663	40.8	4676.2	4110.1	β C-C
825			106.6	19124.7	12523.4	629	40.5	12721.6	11971.9	β C-C
801	856	801	241.8	68778.9	46944.4	601	33.3	1626.8	1621.2	ν C-C
756		739	113.4	21093.3	16055.4	591	6.6	1538.6	1566.7	ν C-H
716			302.8	31184.9	24732.7	555	21.2	10917.0	12025.3	ν C-H
694		663	67.9	1024.4	899.6	542	38.0	1667.5	1891.2	ν C-H
646			16.0	7655.0	6953.7	516	10.0	493.6	596.2	ring β
617	609	632	29.1	2007.2	1877.4	497	7.4	115.7	146.1	ν C-C
		599	202.3	1623.0	1623.9	475	7.5	1429.5	1908.3	β C-H_2
595			162.6	12817.5	12931.5	468	52.3	8079.9	10976.0	ν C-H
566	8.5		7502.8	8065.5		439	13.9	61.9	90.8	ν C-C
521	516	551	37.3	17857.3	19875.9	422	25.0	1133.6	1745.8	β C-C
		513	240.4	5583.2	6784.5	412	14.3	1658.8	2628.9	ν C-H
502	478	494	3.7	200.0	254.3	383	0.5	24.6	42.4	ν C=C
		483	39.6	2476.8	3237.4	356	5.2	300.3	563.8	ν C=C
461			0.4	17867.0	24711.6	333	23.7	779.8	1581.7	ν C=C
424		440	114.9	110820.6	162397.4	309	28.4	398.9	879.7	β C-C
402		402	66.4	22577.2	36806.4	285	71.0	1474.1	3574.9	ν C=C
377			13.3	8042.3	14137.8	261	35.2	1241.2	3318.3	ν C=C
327			4.3	675.5	1399.7	236	77.8	7344.0	21899.2	β C-C
283		292	5.1	12537.1	29527.9	223	5.1	136.0	431.8	τ ring C=C
227		255	49.2	20994.2	57485.4	165	7.3	511.7	2249.2	ν C=C

í Stretching â, bending; in plane bending, out plane bending, ô torsion, á rocking

Table 2: Mulliken atomic charges of 1-Methyl 2,6-diphenyl pipeidin4-one

Atoms	HF/6-311++ G(d, p)	B3LYP/6-311++ G (d, p)
C_1	-0.7308	-0.5293
C_2	0.0201	-0.1554
N_3	-0.0595	-0.0709
C_4	0.4104	0.1570
C_5	-0.8307	-0.6656
C_6	0.0521	-0.1031
O_7	-0.3620	-0.2555
C_8	-0.1938	0.3433
C_9	-0.2119	0.0789
C_{10}	0.5003	-0.1680
C_{11}	0.2763	-0.0367
C_{12}	-0.4318	0.4200
C_{13}	-0.4935	-0.8275
C_{14}	-0.3405	-0.6018
C_{15}	-1.0183	-1.0348
C_{16}	-0.0710	0.0500
C_{17}	0.6484	0.6238
C_{18}	-0.3666	-0.3548
C_{19}	0.1684	-0.0718
C_{20}	-0.2572	-0.1621
H_{21}	0.1542	0.1610
H_{22}	0.2724	0.2370
H_{23}	0.2520	0.2662
H_{24}	0.2741	0.2513
H_{25}	0.2568	0.2088
H_{26}	0.1884	0.1917
H_{27}	0.7537	0.7048
H_{28}	-0.2335	-0.1190
H_{29}	0.1580	0.1536
H_{30}	0.2163	0.1398
H_{31}	0.2010	0.1256
H_{32}	0.2393	0.1584
H_{33}	0.1538	0.1524
H_{34}	-0.2795	0.1537
H_{35}	0.1578	-0.0639
H_{36}	-0.1666	0.0130
H_{37}	0.1722	0.1715
H_{38}	0.3557	0.3144
H_{39}	0.1656	0.1440

at 1716 cm^{-1}as a week band in Raman.1720 cm^{-1} in IR experimental. The computed HF value1751 cm^{-1} 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^{-1} in Raman. These vibrations are assigned at 1011 cm^{-1} and1352 cm^{-1} 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[15].

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 -3.31927eV, the LUMO energy value is 0.73961eV respectively. It is seen that the HOMO-LUMO gap is 4.0588eV. 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[17, 18]

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 pipeidin4-one are obtained by Mulliken population analysis shown in Table 2. The results show that substitution of methyl group in 2,6-diphenyl pipeidin4-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_1	-0.45658	1.99918	4.44024	0.01717	6.45658
C_2	0.04620	1.99928	3.92817	0.02636	5.95380
N_3	-0.59171	1.99950	5.57410	0.01810	7.59171
C_4	-0.00271	1.99924	3.97474	0.02873	6.00271
C_5	-0.45181	1.99922	4.43772	0.01487	6.45181
C_6	0.58081	1.99924	3.37758	0.04237	5.41919
O_7	-0.67007	1.99976	6.65846	0.01185	8.67007
C_8	-0.00635	1.99796	3.98081	0.02758	6.00635
C_9	-0.27141	1.99913	4.24233	0.02994	6.27141
C_{10}	0.00859	1.99750	3.95846	0.03546	5.99141
C_{11}	-0.24449	1.99566	4.19005	0.05878	6.24449
C_{12}	-0.20089	1.99925	4.16979	0.03185	6.20089
C_{13}	-0.42925	1.99919	4.39610	0.03396	6.42925
C_{14}	-0.11010	1.99918	4.08619	0.02473	6.11010
C_{15}	-0.35440	1.99906	4.32225	0.03308	6.35440
C_{16}	-0.08692	1.99923	4.06106	0.02664	6.08692
C_{17}	-0.03145	1.99725	3.98414	0.05005	6.03145
C_{18}	- 0.02079	1.99419	3.94104	0.04398	5.97921
C_{19}	-0.25050	1.99556	4.23102	0.02392	6.25050
C_{20}	-0.27947	1.99934	4.26572	0.01442	6.27947
H_{21}	0.24268	0.00000	0.75578	0.00154	0.75732
H_{22}	0.22837	0.00000	0.77031	0.00132	0.77163
H_{23}	0.21437	0.00000	0.78470	0.00093	0.78563
H_{24}	0.18915	0.00000	0.80849	0.00236	0.81085
H_{25}	0.21554	0.00000	0.78287	0.00158	0.78446
H^{26}	0.24017	0.00000	0.75853	0.00130	0.75983
H_{27}	0.28792	0.00000	0.70019	0.01189	0.71208
H_{28}	-0.05451	0.00000	1.02283	0.03168	1.05451
H_{29}	0.18948	0.00000	0.80400	0.00651	0.81052
H_{30}	0.20500	0.00000	0.79399	0.00101	0.79500
H_{31}	0.19420	0.00000	0.80498	0.00083	0.80580
H_{32}	0.22692	0.00000	0.77149	0.00159	0.77308
H_{33}	0.20462	0.00000	0.78666	0.00872	0.79538
H_{34}	0.22511	0.00000	0.74520	0.02969	0.77489
H_{35}	0.12623	0.00000	0.84143	0.03234	0.87377
H_{36}	0.27985	0.00000	0.71433	0.00582	0.72015
H_{37}	0.20423	0.00000	0.79486	0.00091	0.79577
H_{38}	0.17725	0.00000	0.81989	0.00286	0.82275
H_{39}	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_3	1.91714	-0.48261
LP (1) O_7	1.97056	-0.92002
LP (1) O_7	1.91613	-0.45138
BD*(1) C_1-C_2	0.0263	0.56918
BD*(1) C_2-C_8	0.04956	0.56005
BD*(1) N_3-C_4	0.02060	0.60953
BD*(1) N_3-C_{20}	0.01100	0.58890
BD*(1) C_{13}-H_{30}	0.01112	0.69617
BD*(1) C_{15}-C_{32}	0.09844	0.66598
BD*(1) C_6-O_7	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_3, O_7 and C_1 have charges -0.5971,-0.67007and -0.45658 respectively. The most electro positive atom is C_6 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_3	BD*(1) C_1 - C_2	9.99	1.05	0.093
LP (1) N_3	BD*(1) C_2 - C_8	0.87	1.07	0.027
LP (1) N_3	BD*(1) C_2 - H_{23}	4.13	1.04	0.059
LP (1) N_3	BD*(1) C_4 - C_5	9.18	1.10	0.091
LP (1) N_3	BD*(1) C_4 - H_{24}	3.78	1.10	0.058
LP (1) N_3	BD*(1) C_{20} - H_{37}	1.86	1.06	0.040
LP (1) N_3	BD*(1) C_{20} - H_{38}	8.82	1.11	0.089
LP (1) N_3	BD*(1) C_{20} - H_{39}	1.61	1.05	0.038
LP (1) O_7	BD*(1) C_1 - C_6	3.81	1.52	0.068
LP (1) O_7	BD*(1) C_5 - C_6	1.97	1.53	0.049
LP (2) O_7	BD*(1) C_1 - C_6	28.74	1.05	0.156
LP (2) O_7	BD*(1) C_4 - C_5	0.92	1.07	0.028
LP (2) O_7	BD*(1) C_5 - C_6	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 pipeidin4- 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\cdot}$38 (O$_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\cdot}$65 (C$_{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 α_0, the anisotropy of the polarizability $\Delta\alpha$ and the mean first polarizability β are as follows:

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

$$\Delta\alpha = \frac{1}{\sqrt{2}}\begin{bmatrix}\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 \\ + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2\end{bmatrix}^{\frac{1}{2}} \quad ...(2)$$

$$\langle\beta\rangle = \begin{bmatrix}\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \\ \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\end{bmatrix}^{\frac{1}{2}} \quad ...(3)$$

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 pipeidin4- one

Basis Set	HF/ 6-311++G (d, p)	B3LYP/ 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: Hyperpolaraizability of 1-Methyl 2,6-diphenyl pipeidin4-one

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

approach. Calculated parameters are listed in Table8. The polarizabilities and hyperpolarizability are reported in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) (for α; 1 a.u = 0.1482 x10^{-24}esu, for α; 1 a.u = 8.6393 x10^{-33}esu). The calculated polarizability of PIP41 is 151.2x10^{-33}esu in HF method and139.9x10^{-33}esu.The magnitude of the molecular hyperpolarizability â, 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[6]. 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[26-29].

CONCLUSION

The extensive vibrational analysis of 1-Methyl 2,6-diphenyl pipeidin4-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 for bidden 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_7 and O_3 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 4.0588eV. 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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