Research Article

Molecular Structure, FT-IR, FT-Raman, HOMO-LUMO, Dipole Moment and First Hyperpolarizability Investigations of 3-Methyl-2,6-di (Naphthalen-1-yl) Phenylpiperidin-4-one

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Abstract

In the present study structural properties of 3-methyl-2,6-di(naphthalen-1-yl) phenylpiperidin-4-one (3-MDP) was made by using B3LYP level with 6-31G(d,p) basis set. The optimized geometrical parameters are in better agreement with analogues single XRD data. The optimized parameters showed that the piperidin-4-one ring adopts chair conformation. The FT- IR and FT-Raman spectra were recorded in the region 4000–400 cm^{-1} and 4000-10 cm^{-1}, respectively. A resemblance was achieved between the experimental and calculated frequencies by refinement of the scale factor. The results of the HOMO and LUMO energies gave clear evidence for the intramolecular charge transfer (ICT). In addition, Mulliken and Molecular electrostatic potential (MEP) analyses were performed to predict the reactive sites of the molecule.
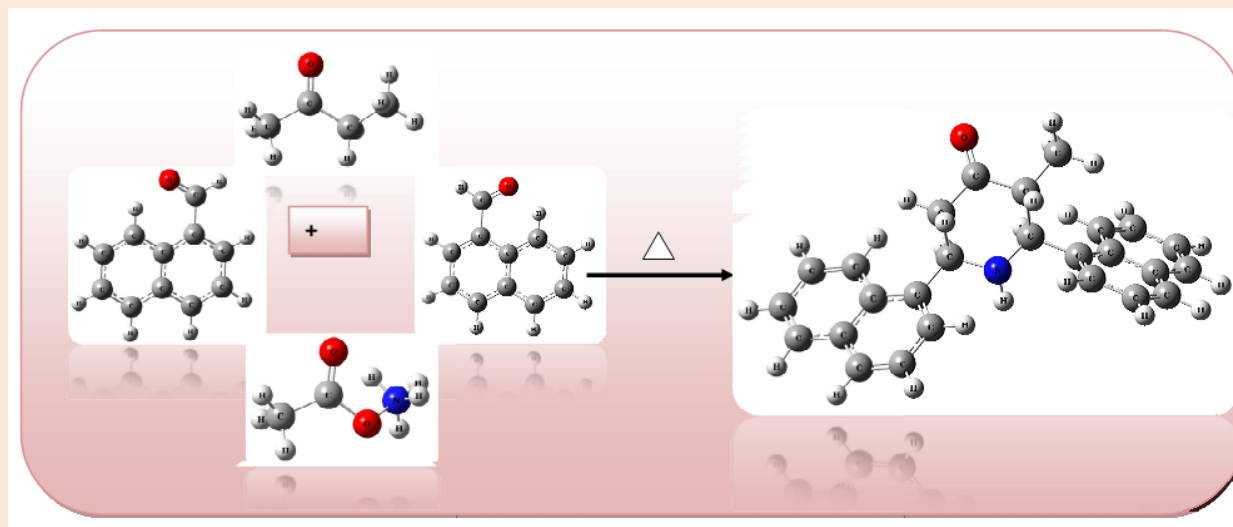
The electrical dipole moment (µ) and first hyperpolarizability (βo) values have been computed using DFT/B3LYP-6-31G(d,p) method. The calculated result (βo) shows that the 3-MDP might have nonlinear optical (NLO) behaviour.

Keywords: *3-MDP, FT-IR, FT-Raman, HOMO – LUMO, hyperpolarizability*

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Introduction

Piperidin-4-one constitute an excellent class of structural motifs which have been found widely present in biologically active molecules [1] The compounds of this family exhibit a broad spectrum of pharmacological properties such as antitumor, antibacterial, antiviral, antimalarial and antiprotozoal activities [2-4]. Furthermore, this type of compound with their huge potential in non- linear optical fields [4, 5] has drawn the concentration of photoscientists. Further, there has been growing interest in the modification and functionalization of this class of compounds by both organic and medicinal chemists, aiming to find new applications from these compounds. On the other hand, the biological importance of piperidin-4-one and its derivatives have strongly stimulated the investigation of computational properties available for these compounds [6-9]. DFT calculations offer accurate results on systems like large organic molecules [10]. In this regard, Our research group decided in developing new piperidine ring incorporation of napthyl group at 2,6-position of piperidine ring and to extend the study to 3-methyl-2,6-di (naphthalene-1-yl) phenylpiperidin-4-one. The aim of characterizing them from the FT- IR and FT-Raman spectra and to study their quantum chemical descriptor in gas phase adopting computational approach. In this article, DFT/B3LYP-6-31G (d,p) level theory was used to determine the optimized geometry, vibrational wavenumbers within in the ground state, non-linear optical properties, HOMO–LUMO energies and Mulliken charges of the molecules.

Experimental
Synthesis of 3-methyl-2,6-di(naphthalen-1-yl)phenylpiperidin-4-one

3-methyl-2,6-di(naphthalen-1-yl)phenylpiperidin-4-one was prepared according to the procedure given in literature with a little modification [11]. Dry ammonium acetate (0.05 mol) was dissolved in 50 mL ethanol and the solution was mixed with 1-napthaldehyde (0.1mol) and ethyl methyl ketone (0.05mol) to give a homogenous mixture. Then, the mixture was heated to boiling for about 30 minutes. After cooling, the viscous liquid was dissolved in ether (300 mL) and shaken with 10 mL concentrated hydrochloric acid and the hydrochloride of 3-methyl-2,6-di(naphthalen-1-yl)phenylpiperidin-4-one obtained was separated by filtration and washed with a mixture of ethanol and ether (1:1) to remove most of the coloured impurities. The product was liberated from an alcoholic solution by adding aqueous ammonia and then diluted with water. The crude sample was recrystalized from ethanol. Yield 82%; m.p.: 184-186 (ºC); MF: $C_{26}H_{23}NO$; Elemental analysis: Calcd (%): C, 85.45; H, 6.34; N, 3.83; Found (%):C, 84.40; H, 6.28; N, 2.77; IR (KBr) (cm-1): 3303 (N-H stretching), 3043 (ArC-H stretching), 2985 Ali.C-H stretching), 1704(C=O stretching), 1479 (C=C stretching), 961,801,774 (Aromatic C-C in-plane bending vibration), 669 (Aromatic C-H out-of-plane bending vibration).

Spectral measurements

The FT-IR spectrum of 3-MDP was taken in the range 4000-400 cm^{-1} on an AVATAR-330 FT-IR spectrometer (Thermo Nicolet) using KBr (pellet form). The FT-Raman spectral measurements were run from Sophisticated Analytical Instrument Facility (SAIF), Indian Institute of Technology (IIT), Chennai.

Theoretical background

All calculations were carried out by Density Functional Theory (DFT) on a personal computer using Gaussian 03W program package [12]. The calculations were done with the B3LYP level and the basis set 6-31G(d,p) was used in the present study to investigate the molecular and vibrational frequency of molecules in the ground state in order to support and explain the experimental observations. Mulliken, frontier molecular orbital and Non-linear optics (NLO) were calculated from optimized geometry of the molecule.

Results and Discussion
Geometry Optimization

The optimized bond lengths, bond and dihedral angles of 3-MDP were calculated by B3LYP method with 6-31G (d,p) level theory and the results are listed in **Table 1**, in accordance with optimized structure as shown in **Figure 1**.

Table 1 Selected bond lengths, bond and dihedral angles of 3-MDP

Bond length (Å)	DFT	XRD[a]	Bond angle (°)	DFT	XRD[a]
C1-N12	1.472	1.471	C2-C1-H10	106.54	109
C1-C2	1.563	1.549	C2-C1-N12	108.86	109.32
C1-H10	1.102	1.000	C2-C1-C18	112.39	112.3
C1-C18	1.524	1.513	N12-C1-C18	109.29	108.71
C2-H7	1.100	1.000	C1-C18-C20	118.15	120.94
C2-C3	1.530	1.526	C1-C18-C19	122.63	120.46
C2-C14	1.527	1.531	C4-C5-N12	107.77	107.47
C3-C4	1.520	1.506	C4-C5-C35	111.56	110.8
C3-O13	1.217	1.211	C4-C5-H9	107.28	109
C4-H11	1.092	1.000	N12-C5-C35	111.37	110.6
C4-H8	1.097	1.000	C5-C35-C37	119.82	119.91
C4-C5	1.550	1.5323	C5-C35-C36	120.89	121.16
C5-H9	1.104	1.000	Dihedral(°)		
C5-N12	1.466	1.466	N12-C1-C2-C14	-179.28	-178.04
C5-C35	1.522	1.5139	C18-C1-C2-C3	-175.07	-172.73
N12-H6	1.017	0.911	C14-C2-C3-C4	176.10	171.84
C18-C19	1.436	1.39	C14-C2-C3-O13	-2.74	-7.74
C18-C20	1.384	1.395	N12-C1-C2-C3	-53.86	-51.99
			N12-C5-C4-C3	53.94	54.81
			C2-C3-C2-C14	176.10	171.84

[a]Values are taken from Ref. [15]
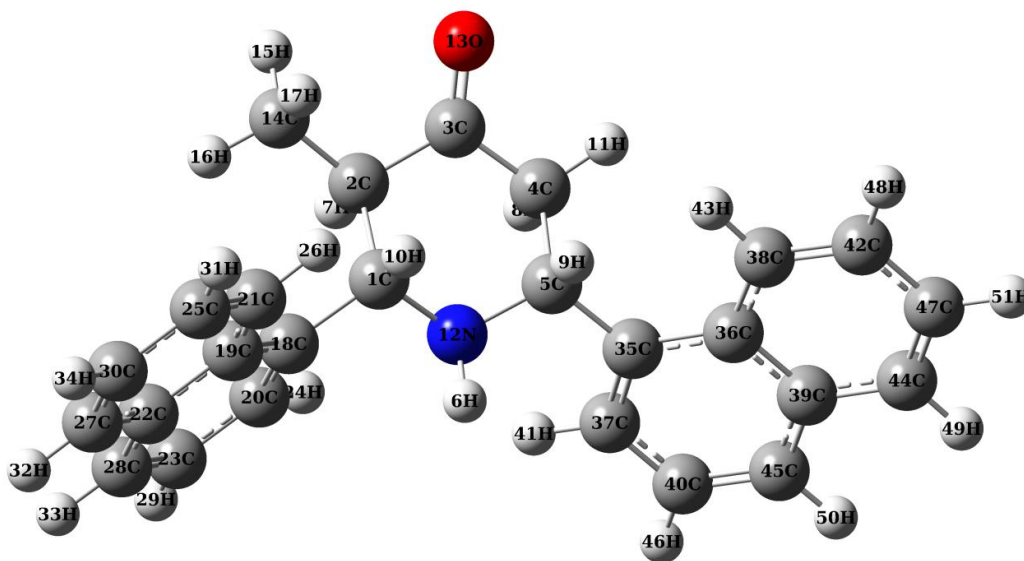
Figure 1 Optimized structures of 3-MDP

It is found that some of the calculated parameters slightly deviate from experimental values, due to the fact that theoretical calculations belong to the molecule in the gaseous phase, because of the way that the experimental results belong to molecules in the solid state. The optimized C3=O13 bond length is calculated as 1.217 Å by B3LYP. This value well matches with the experimental value of 1.211 Å. As seen in Table 1, the calculated bond length N12–H6 is 1.017 Å which differs from the experimental value by 0.106 Å. This difference is due to the reality that the experimental result corresponds to the intermolecular coulombic interaction with the neighbouring molecules in the solid state [13, 14].

The optimized geometrical parameters are compared with the crystal structure of *t*-3-pentyl-*r*-2,*c*-6-diphenylpiperidin-4-one [15]. It is known from previous studies [6-9] and results from **Table 1** that the piperidone ring essentially adopts chair conformation and also it is evident from the torsional angles N12-C1-C2-C3 (-53.86 and -51.99°at B3LYP and XRD, respectively) and N12-C5-C4-C3 [53.94 (B3LYP) and 54.81° (XRD)].The equatorial orientation of alkyl and aryl groups are identified by their important angles N12-C1-C2-C14 [-179.28 (B3LYP) and -178.04° (XRD)] and C2-C3-C2-C14 [176.10 (B3LYP) and 171.84° (XRD)].

Vibrational analysiss

In this study, the vibrational spectra of the title compound was interpreted on the basis of B3LYP/6-31G(d,p) level theory. The observed and calculated vibrational spectra of the 3-MDP are shown in **Figure 2(a-d)**. A vibrational mode including experimental and vibrational frequencies, their assignments are given in **Table 2**.
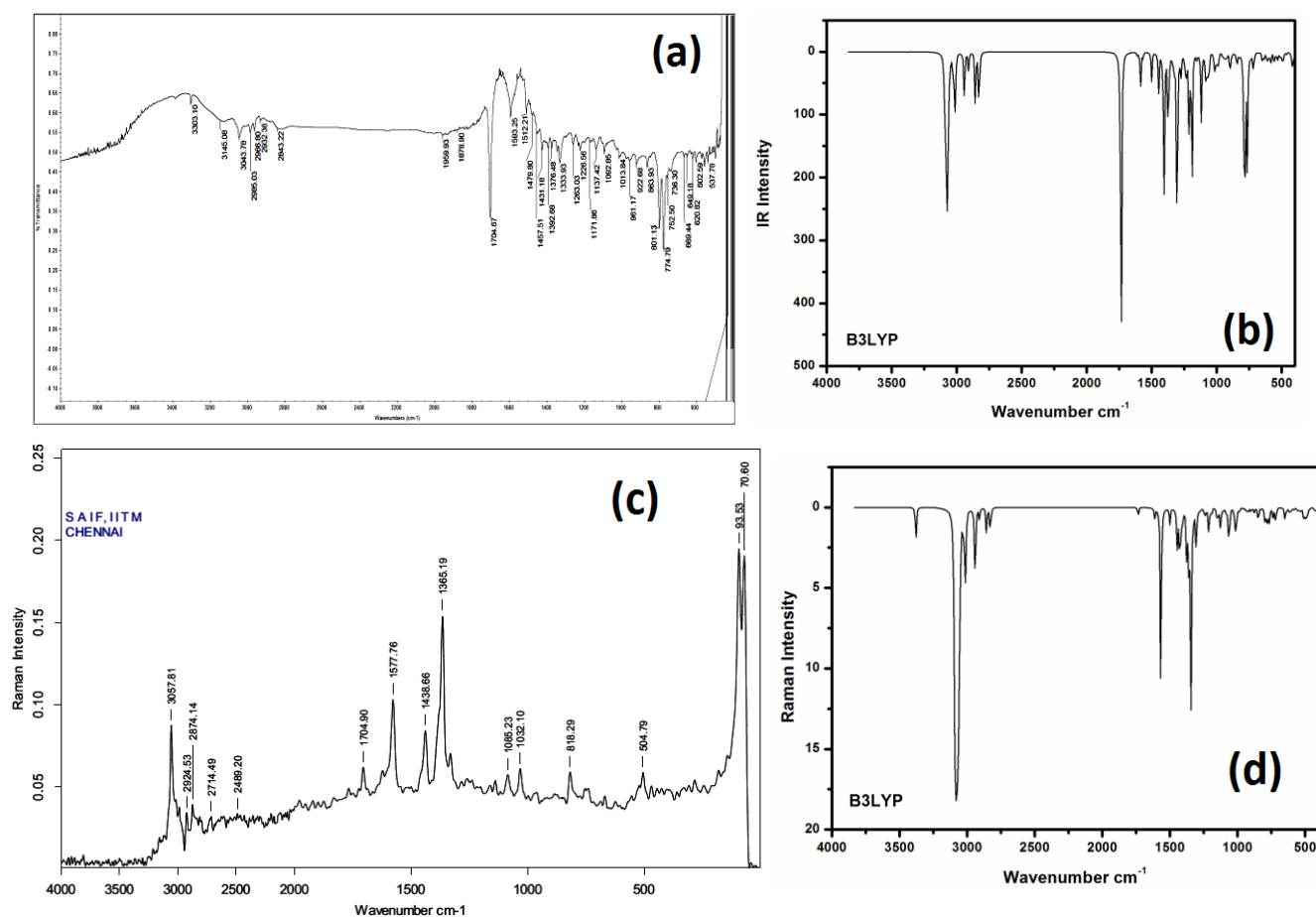

Figure 2 (a) Experimental FT-IR and (b) calculated IR spectra of 3-MDP, (c) Experimental FT-Raman and (d) calculated Raman spectra of 3-MDP

The calculated frequencies are scaled by 0.9608 for DFT [16]. It is stated that in amines, the N–H [17] stretching vibrations occur in the region 3500–3300 cm^{-1}. With the above reference, the vibrational frequency observed at 3303 cm^{-1} in the infrared spectrum is assigned to the N- H stretching mode, the corresponding computed value matches at 3378 cm^{-1} by B3LYP. In 3-MDP, the C-H stretching vibrations appeared in the range 3095 cm^{-1} (B3LYP). The observed frequencies showed at 3043 (FT-IR) and 3057 cm^{-1} (FT-Raman) for C-H stretching vibrations. These C-H Stretching vibrations are well agreement with the theoretical values. The C-H stretching in alkanes occurs at lower frequencies than those of aromatic ring (3150-3050 cm^{-1}). The CH$_3$ stretching is expected at 2980-2870 cm^{-1} [18] and usually the bands are weak. Methyl group symmetric stretching appeared at 2985 cm^{-1} in FT-IR and at 2924 cm^{-1} as in FT- Raman spectrum are in agreement with the theoretical value in the range 2985 cm^{-1} by B3LYP/6-31 G(d,p) basis set.

Table 2 Observed and calculated wavenumbers (cm^{-1}) and their vibrational assignments of 3-MDP

| Experimental | | Calculated | | IR intensity | Raman activity | Vibrational Assignments |
FT-IR	FT-Raman	Unscaled	scaled[a]			
	611	672	645	0.376	1.0255	Γ_{C-H}
669		678	651	3.698	10.5826	
774		805	774	0.856	3.5597	β_{C-H}
801	818	862	829	2.1092	1.4443	
961		960	923	1.2925	1.5147	
1013	1085	1052	1011	9.5142	25.8538	ν_{C-N}
1479		1509	1450	8.2023	16.0565	$\nu_{C=C}$
1704	1704	1807	1736	182.847	12.4906	$\nu_{C=O}$
2985	2924	3134	3011	15.5173	56.614	ν_{C-H}
3043	3057	3221	3095	13.3738	146.5197	ν_{ArC-H}
3303		3516	3378	0.2684	70.3207	ν_{N-H}
a- scale factor:0.9608- B3LYP/6-31G(d,p)						
b- ν: stretching; β-in-plane bending: Γ- out-of-plane bending						

The carbonyl group (>C=O) stretching is most important in the vibration spectrum because of its strong intensity absorption [19, 20]. Savithiri *et al*. [8] assigned C=O stretching in the region of 1716 cm^{-1} in 3-pentyl-2,6-diphenylpiperidin-4-one picrate . In this case, the carbonyl C=O stretching appeared at 1704 cm^{-1} (FT-IR) and 1704 cm^{-1} (FT-Raman). The gas phase value 1736 cm^{-1} is in line with experimental values. The C-N stretching vibration appeared in 1013 (FT-IR), 1085 cm^{-1} (FT-Raman) and its corresponding theoretical value appeared in 1011 cm^{-1}. The experimental vibration bands at 961, 801 cm^{-1} (FT-IR) and 818 cm^{-1} (FT-Raman) is assigned to –CH$_2$– in-plane bending mode mode. The theoretically observed value ranges from 923-774 cm^{-1}. The out-of- plane bending mode of –CH$_2$– is observed at 669 (FT- IR) and 611(FT-Raman) cm^{-1} and its corresponding theoretical value is 651 and 645 cm^{-1} byB3LYP.

Mulliken atomic charges analysis

The Mulliken atomic charges are calculated by determining the electron population of each atom [21]. The Mulliken atomic charges of 3-MDP molecule calculated by B3LYP level using 6-31G (d,p) basis set and are presented in **Table 3** and **Figure 3**. Mulliken population analysis calculation plays a vital role for the application of quantum chemical calculation of the molecular system. In 3-MDP, the maximum positive charge (0.4081) for C3 atom than other atoms is due to the presence of largely electronegative oxygen atoms (O13) in the closest position. The nitrogen and oxygen atoms have more negative charges. The aromatic carbons carbon such as C20, C21, C23, C25, C27, C28, C30, C37, C40, C42, C44, C45, and C47 possess negative charge. This is mainly owing to the substitution of negative charge of oxygen, and nitrogen atoms. From the above we conclude the migration of charges and this can be related to molecular interaction.
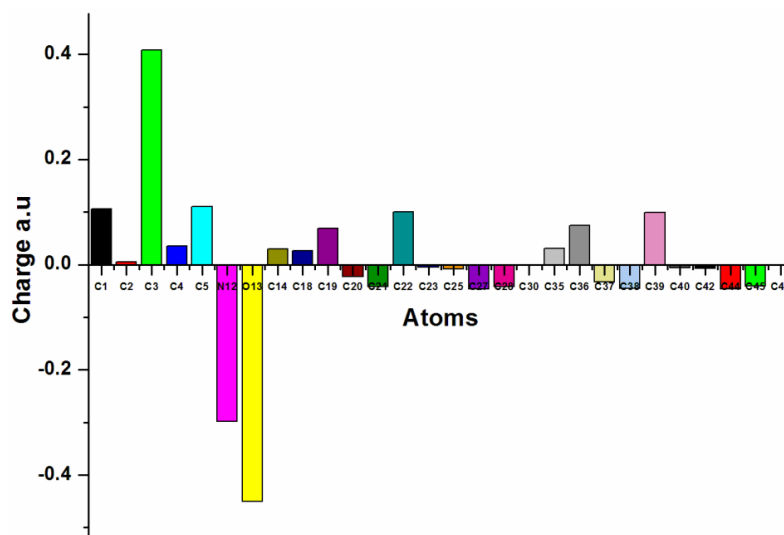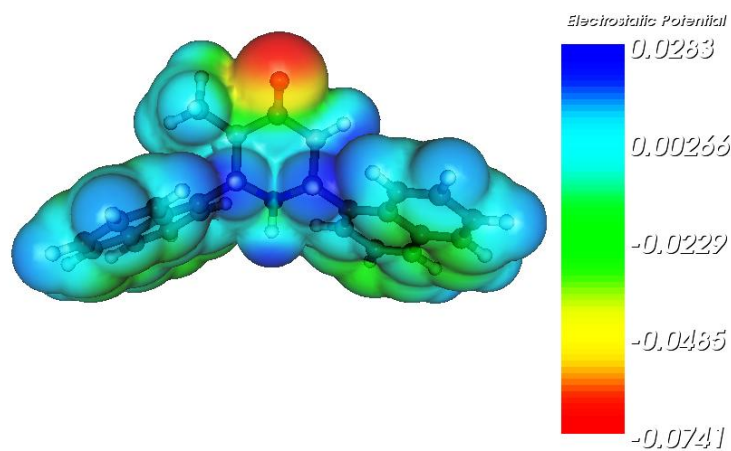
MEP analysis

MEP is a very valuable descriptor in accepting spots for nucleophilic reaction and electrophilic attack as well as hydrogen bonding interactions [22]. It also gives visual thoughtful of virtual polarity of the compounds. The shape, charge, size, reactive sites and density of the molecule are represented by an electron density iso-surface mapped with electro potential surface. Reactive sites for the studied molecule are calculated by obtaining electrostatic surface potential at the B3LYP/6-31G (d,p) optimized geometry. The title molecule has a number of potential sites for electrophilic and nucleophili attack as evidenced from **Figure 4**.

From Figure 4, it is observed that the maximum value negative region is mainly localized over the C=O group which are electrophilic. The maximum positive region is localized on the N-H and hydrogen atoms which are nucleophlic.

Table 3 Mulliken atomic charges of 3-MDP

| Atom	Charge	Atom	Charge
C1	0.1053	C25	-0.0078
C2	0.0047	C27	-0.0465
C3	0.4081	C28	-0.0417
C4	0.0355	C30	-0.0002
C5	0.1100	C35	0.0304
N12	-0.2979	C36	0.0745
O13	-0.4500	C37	-0.0331
C14	0.0296	C38	-0.0450
C18	0.0266	C39	0.0992
C19	0.0689	C40	-0.0063
C20	-0.0223	C42	-0.0075
C21	-0.0421	C44	-0.0465
C22	0.1001	C45	-0.0411
C23	-0.0045	C47	-0.0005

Figure 3 Mulliken atomic charges of 3-MDP

Figure 4 MEP surface of 3-MDP

Frontier molecular orbital analysis

The energies of four important molecular orbitals of 3-MDP the second highest and highest occupied MO's (HOMO and HOMO-1), the lowest and the second lowest unoccupied MO's (LUMO and LUMO + 1) were calculated and are presented in **Table 4** and the pictorial illustration of the frontier molecular orbitals and their respective positive and negative regions are shown in **Figure 5**. The frontier molecular orbital analysis 3-MDP was taken into account for the TD-DFT calculation in order to investigate the properties of electronic absorption. The calculations were also performed with ethanol and CHCl$_3$ solvent phase. It is clear from the figure that the HOMO is located mainly over the entire napthyl ring. The napthyl ring at methyl side chain covered in LUMO values.

Table 4 Calculated energy values (eV) of 3-MDP in gas phase

TD-DFT/B3LYP/6-31G(d,p)	Gas	ETOH	CHCl$_3$
Etotal (Hartree)	-1134.65	-1134.67	-1134.69
E$_{HOMO}$	-5.79	-5.72	-5.74
E$_{LUOMO}$	-1.20	-1.12	-1.13
E$_{LUMO-HOMO}$ (ΔE)	4.59	4.60	4.61
E$_{HOMO-1}$	-5.90	-5.82	-5.83
E$_{LUMO+1}$	-1.11	-1.03	-1.04
E$_{(HOMO-1)-(LUMO+1)}$	4.79	4.79	4.79
Electrinegativity(χ)	-3.50	-3.42	-3.44
Hardness(η)	2.30	2.30	2.30
Electrophilicity index(ψ)	2.67	2.54	2.56
Softness(s)	161.24	160.92	160.92
Dipole moment (Debye)	2.84	3.8	3.56
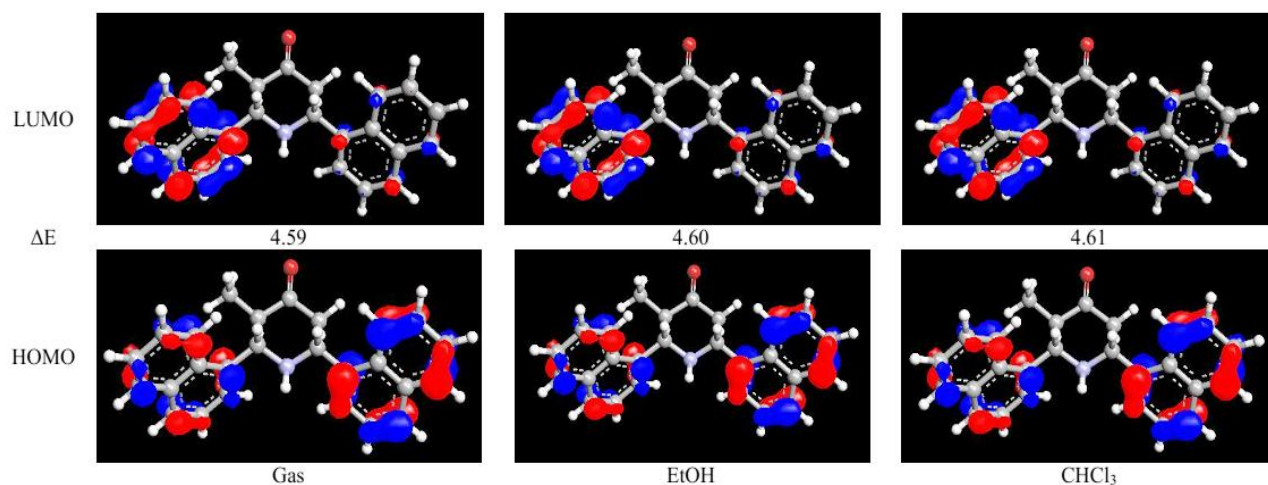
Figure 5 Molecular orbitals and energies for the HOMO and LUMO in gas phase

The calculated energy values of HOMO are -5.79, -5.72, and -5.74 eV in gas, ethanol and chloroform, respectively. LUMO is -1.20, -1.12, and -1.13 eV in gas, ethanol and chloroform, respectively. The value of the energy separation between HOMO and LUMO is 4.59, 4.60 and 4.61 eV in gas, ethanol and chloroform, respectively. The energy gap of HOMO-LUMO explains the eventual charge transfer interaction taking place within the molecule, which influences the biological activity of the molecule. Furthermore, in going from the solution to the gas phase, an increasing value of the energy gap shows that the molecule becomes more stable.

The absolute electronegativity (χ), hardness (η), electrophilicity index (ψ) and softness (ζ) are calculated using the following equations

$$\eta = (IP-EA)/2 \approx (E_{LUMO}-E_{HOMO})/2$$
$$\chi = (IP+EA)/2 \approx - (E_{LUMO}+E_{HOMO})/2$$

$$\psi = \mu^2/2\ \eta$$

$$\zeta = 1/2\ \eta$$

For 3-MDP, electronegativity (χ), hardness (η), electrophilicity index (ψ) and softness (ζ) are given in Table 4. The dipole moment is another important electronic property in a molecule. For example higher the dipole moment, the stronger will be the intermolecular interactions. The calculated dipole moment values are given in Table 4. Based on predicted dipole moment values, it is found that, in going to the solvent phase from (3.80 D in ethanol) from gas phase (2.84 D), the dipole moment value decreases that indicates the polarity of solvent influences the dipole moment of the studied molecule.

Non-linear optical activity

DFT has been used as an effective method to investigate the organic non-linear optical (NLO) materials. As seen in from recent research works illustrated that the organic non-linear optical materials are having high optical non-linearity than inorganic materials [23]. In the occurrence of an applied electric field, the energy of a system is a function of the electric field. Polarizability and first order hyperpolarizability values characterize the response of a system in an applied electric field [24-27]. For this theme, in this study the electronic dipole moment, molecular polarizability, mean anisotropy of polarizability and first order hyperpolarizability of title compound were investigated.

The quantum chemical descriptors calculated from the Gaussian output have been explained in detail earlier work [28]. From **Table 5**, the first order hyperpolarizability of 3-MDP material is comparatively larger than the NLO reference material Urea [29]. The increase of first order hyperpolarizability is due to the increasing of charge transfer interaction inside the molecule, which leads the greater NLO activity of 3-MDP than Urea.

Table 5 Dipole moment, Polarisabiltiy, first order hyperpolarizability of 3-MDP calculated using B3LYP method using 6-31G(d,p) basis set

Parameter	Dipolemoment	Parameter	First order hyperpolarizability (a.u)
μ_x	-0.2647	β_{xxx}	16.1145
μ_y	-2.6548	β_{yyy}	-58.5909
μ_z	0.9924	β_{zzz}	-13.2832
μ_{total} (Debye)	2.8465	β_{xyy}	3.2136
Parameter	Polarisability (a.u)	β_{xxy}	-34.3202
α_{xx}	145.69	β_{xxz}	54.0473
α_{yy}	167.93	β_{xzz}	-16.0547
α_{zz}	158.34	β_{yzz}	11.8567
α_{xy}	0.67	β_{yyz}	9.9689
α_{xz}	0.45	β_{xyz}	2.5539
α_{yz}	11.14	β_0 (esu)	0.827×10^{-30}
α_o (esu)	2.33×10^{-23}		
$\Delta\alpha$ (esu)	3.57×10^{-24}		

Conclusions

In this study, we investigate the properties of the molecular structure have been calculated by using B3LYP/6-31G(d) basis set. From the optimized results we conclude that the piperidone ring adopts chair conformation with equatorial orientation of substituents. Also, the other experimental results are in good agreement with the theoretical results. The theoretically (B3LYP/6-31G(d, p) constructed IR and Raman spectra are in line with experimentally observed counter parts. The reactive sites within the molecules are understood with the help of Mulliken and MEP surface analyses. The HOMO-LUMO energy gap confirmed the charge transfer taking place within the molecule. The calculated dipolemoment and first order hyperpolarizability results indicate that the molecule has a reasonably good nonlinear optical behaviour.

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