Structural, Spectral, Thermodynamic and HOMO, LUMO Analysis of 2, 6 dithenobenzene-3-enyl 3, 5 dimethyl piperdine-4-one: A quantum chemical analysis

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ABSTRACT

In the current work, the vibrational frequencies, infrared intensities, molecular geometry and Raman scattering were determined and investigated using ab initio Hartree-Fock (HF) and density functional methods with a basis set of 6-311++ G (d, p) of the organic molecule under interpretation. The FT-IR and FT-Raman spectra of titled molecule have been recorded in the region 4000-400 cm⁻¹ and 5000-70 cm⁻¹, respectively. The optimized geometry structures (bond lengths and bond angles) achieved using HF shows the best result with the experimental values of the titled molecule. The frontier molecular orbitals help to distinguish chemical responsiveness and molecular kinetic steadiness, thus HOMO-LUMO analysis can be done using the quantum chemistry to improve thermodynamics. The electron density mapping to electrostatic potential surfaces were involved in finding the reactivity sites of the titled compound. With the help of Gauss view 5.0 and Chemcraft packages, the obtained outputs are analyzed. Hyperpolarizability and non-linear optical effect of isolated molecules of NLO materials are observed to be an extensive tool for molecular spectroscopy research. Therefore, for industrial application, Hyperpolarizability of the molecule is also studied.

Keywords: DFT, HF, NBO, HOMO LUMO, NLO.

INTRODUCTION

The phenomenal developments in ab initio and density functional theory (DFT) over the last decade have made possible efficient and systematic predictions of harmonic vibrational frequencies, together with harmonic dipole strengths and rotational strengths which determine harmonic intensities of fundamental transitions in vibrational non polarized absorption like infra-red (IR) and vibrational circular dichroism (VCD) spectra. Molecular computational studies can provide a broad understanding of the relationships between molecular architecture, non-linear optical characteristics and bioactivity. Piperidins-4-one and its derivatives are highly determined due to its pharmaceutical applications, including antiviral drugs, anti-tumor drugs, analgesics and local anesthetics, bactericides, fungicides, and depressants. It is very sensitive to spectroscopic investigation over the past few years. The current
study aimed to give a complete outline of the optimized molecule structure, the vibrational assignments, electronic characteristics like an energy gap, a HOMO, a LUMO and an electrostatic molecular potential of the titled compound. In order to calculate the number of vibrational waves, the optimized molecular structure was used in B3LYP method. This paper focuses on the spectral characterization of the title molecules\textsuperscript{3-5}. The correlation between the title molecular structure, bioactivity and Non-Linear optical characters are also decoded with quantum chemical calculations. A systematic approach presents unique applications of quantum mechanical method in the analysis of sum biological important piperidine derivatives compounds.

### Computational details

The compound was optimized with 6-31G (d, p) basis set using DFT/B3LYP quantum chemical methods. For the calculation of frontier molecular orbitals, a time-dependent DFT (TD-DFT) method was used\textsuperscript{6-11}. DFT (B3LYP/6-311++G (d, p) method has been employed in this work to calculate optimized molecular structure, vibrational descriptions and charge transfer of the titled molecule. DFT calculations were significantly employed in electronic molecular structure treatment. The investigation was done under 6311++G is the basis (d, p) because of an efficient and cost effective level\textsuperscript{12}. The complete computation has been carried out on personal computers involved with the Gaussian 09W programme package.

### RESULTS AND DISCUSSION

#### Molecular geometry

Gaussian 09 and Gauss view programme provides all the optimized structure and numbering of atoms in the selected molecule. The bond length and bond angles of the optimized molecule are calculated with the basis set of HF/B3LYP using 6-31G. The calculated B3LYP values are higher than HF levels. The bond length and angles are presented in Table 1. Considering the energy-optimized geometry of the molecular derived from both basis set, the conceptual values of this method for correlation were taken up and are dependable. The C-C and C-H bond distances of piperidine ring were in the range of 1.555–1.516 Å and 1.112–1.094 Å respectively, whereas, the optimized C-C-C and C-C-H bond angles were in the range of 113.60–109.99° and 111.12–103.57° respectively. The C-N and N-H bond distances were calculated in the range 1.09–1.07 Å and 1.01 Å, 0.9 Å, also calculated the (126.6°) C—C—C, (108.5°) N—C—C bond angles for the piperidine molecule. With regard to the Endo cyclic torsional angles, the optimized C—H lengths in the CH\textsubscript{2} groups are calculated using the B3LYP method in the 1.092 Å range. In addition, calculation outcome shows that the geometric parameter calculated is in good understanding with the remaining geometric parameters.

| Atom Bonds | HF/6-31G Value | B3LYP/6-31G Value |
|------------|----------------|-------------------|
| C1–C2      | 1.5417         | 1.549             |
| C1–C3      | 1.5251         | 1.5497            |
| C1–C26     | 1.5373         | 1.5495            |
| C1–H28     | 1.0828         | 1.0962            |
| C2–N4      | 1.4588         | 1.476             |
| C2–C7      | 1.5524         | 1.5526            |
| C2–H29     | 1.0924         | 1.1072            |
| C3–C5      | 1.5251         | 1.5296            |
| C3–O27     | 1.1952         | 1.2445            |
| N4–C6      | 1.4588         | 1.476             |
| N4–H30     | 0.997          | 1.0156            |
| C5–C6      | 1.5416         | 1.5495            |
| C5–C25     | 1.5373         | 1.5496            |
| C5–H31     | 1.0828         | 1.0962            |
| C6–C16     | 1.5525         | 1.5645            |
| C6–H32     | 1.0924         | 1.1072            |
| C7–C8      | 1.5208         | 1.5243            |
| C7–C9      | 1.5452         | 1.5491            |
| C7–H33     | 1.0862         | 1.0988            |
| C8–C10     | 1.3913         | 1.4065            |
| C8–C12     | 1.3849         | 1.4001            |
| C9–S11     | 1.826          | 1.9153            |
| C9–H34     | 1.0826         | 1.092             |
| C9–H35     | 1.0814         | 1.091             |
| C10–S11    | 1.7736         | 1.8414            |
| C10–C14    | 1.3826         | 1.3937            |
| C12–C13    | 1.3876         | 1.4022            |
| C12–H36    | 1.0756         | 1.0854            |
| C13–C15    | 1.3851         | 1.3998            |
| C13–H37    | 1.0752         | 1.0848            |
| C14–C15    | 1.3888         | 1.4023            |
| C14–H38    | 1.0751         | 1.0844            |
| C15–H39    | 1.0756         | 1.0852            |
| C16–C17    | 1.5452         | 1.5491            |
| C16–C18    | 1.5207         | 1.5243            |
| C16–H40    | 1.0862         | 1.0988            |
| C17–S19    | 1.826          | 1.9154            |

Continue Table 1
| Bond Angles | C2-C1-C3 | 112.6602 | 112.9138 | C13-C15-C39 | 119.9713 | 120.0577 |
| C2-C1-C2 | 113.4293 | 112.9987 | C14-C15-C39 | 119.5938 | 119.5330 |
| C2-C1-H28 | 109.5428 | 109.2076 | C6-C16-C17 | 111.0768 | 111.8205 |
| C3-C1-C26 | 108.8228 | 109.1232 | C6-C16-C18 | 115.6384 | 115.8327 |
| C3-C1-H28 | 103.9584 | 104.3159 | C6-C16-C14 | 106.6519 | 106.0655 |
| C26-C1-C28 | 108.2511 | 107.8063 | C17-C16-C18 | 103.8824 | 103.9509 |
| C1-C2-N4 | 107.6346 | 107.8015 | C17-C16-C14 | 109.4246 | 109.3534 |
| C1-C2-C7 | 114.4285 | 114.2842 | S11-C6-C16 | 110.1082 | 110.2533 |
| C1-C2-H29 | 108.5329 | 108.5148 | C16-C17-C19 | 106.8607 | 106.5043 |
| N4-C4-C27 | 107.8987 | 108.0588 | C16-C17-C14 | 113.9237 | 114.0758 |
| N4-C2-H29 | 110.6928 | 110.8025 | C16-C17-C12 | 110.5226 | 110.7475 |
| C7-C2-H29 | 107.6648 | 107.3984 | S19-C17-H41 | 108.4244 | 107.2059 |
| C1-C3-C5 | 121.4356 | 121.7206 | S19-C17-H42 | 108.5014 | 107.2615 |
| C1-C3-C27 | 119.2528 | 119.0897 | H41-C17-H42 | 108.4605 | 107.9175 |
| C5-C3-C27 | 119.2543 | 119.0898 | C16-C18-C20 | 114.1291 | 114.8709 |
| C2-N4-C6 | 113.3893 | 113.0966 | C16-C18-C21 | 126.912 | 126.4244 |
| C2-N4-H30 | 110.7439 | 113.1252 | C20-C18-C21 | 118.9463 | 118.7039 |
| C6-N4-H30 | 110.7426 | 113.1234 | C17-S19-C20 | 90.0328 | 88.3325 |
| C3-C5-C6 | 112.6526 | 112.9207 | C18-C20-S19 | 112.7783 | 112.9073 |
| C3-C5-C25 | 108.8214 | 109.1214 | C18-C20-C23 | 121.4924 | 121.8217 |
| C3-C5-H31 | 103.6013 | 104.3184 | S19-C20-C23 | 125.7017 | 125.2474 |
| C6-C5-C25 | 113.4331 | 112.9869 | C18-C21-C22 | 120.0826 | 120.1166 |
| C6-C5-H31 | 109.5412 | 109.2149 | C18-C21-H43 | 120.3129 | 120.1096 |
| C25-C5-C31 | 108.2554 | 107.8041 | C22-C21-H43 | 119.6042 | 119.7737 |
| N4-C6-C5 | 107.6327 | 107.8064 | C21-C2-C24 | 120.172 | 120.2000 |
| C6-C5-H25 | 110.6928 | 110.8017 | C22-C2-H44 | 119.792 | 119.7384 |
| C6-C5-H26 | 114.4384 | 114.2844 | C22-C2-H44 | 120.035 | 120.0597 |
| C5-C6-H23 | 108.5313 | 108.5122 | C22-C2-H45 | 120.662 | 120.7735 |
| C15-C6-C52 | 107.6647 | 107.3971 | C24-C23-H45 | 120.510 | 120.5201 |
| C2-C7-C6 | 115.8256 | 114.8313 | C22-C2-C23 | 120.419 | 120.3971 |
| C2-C7-C9 | 111.0861 | 110.8269 | C22-C24-H46 | 119.9703 | 120.0577 |
| C2-C7-H33 | 106.6554 | 106.0653 | C23-C24-C6 | 119.5948 | 119.5330 |
| C8-C7-C9 | 103.8774 | 105.4896 | C5-C25-H47 | 110.0854 | 110.3043 |
| C8-C7-H33 | 110.1134 | 110.2515 | C5-C25-H48 | 110.9354 | 110.5934 |
| C9-C7-H33 | 109.4246 | 109.3515 | C5-C25-H49 | 111.232 | 111.1071 |
| C7-C8-C10 | 114.1275 | 114.8713 | H47-C25-H49 | 108.4952 | 108.5948 |
| C7-C8-C12 | 126.9138 | 126.4214 | H47-C25-H49 | 108.3015 | 108.4910 |
| C10-C8-C12 | 118.9461 | 118.7066 | H48-C25-H49 | 107.6915 | 107.9390 |
| C7-C9-S11 | 106.8619 | 106.5058 | C1-C26-H50 | 110.0866 | 110.0300 |

Continue Table 1:
C1-C26-H52 110.9326 110.596 Continue Table 1
H50-C26-H51 108.3029 108.492 C25-C5-C6-C16 96.88 97.44
H50-C26-H52 108.4945 108.593 C25-C5-C6-H32 -23.36 -22.35
H51-C26-H52 107.8908 107.941 H31-C5-C6-N4 95.71 97.61
Dihedral Angles H31-C5-C6-C16 -24.18 -22.52
C3-C1-C2-N4 18.959 18.03 H31-C5-C6-H32 -144.44 -142.32
C3-C1-C2-C7 138.86 142.48 C3-C5-C25-H47 55.31 54.87
C3-C1-C2-H29 -100.88 -102.02 C3-C5-C25-H48 175.41 174.84
C26-C1-C2-N4 -95.78 -97.53 C6-C5-C25-H49 -58.34 -58.65
C26-C1-C2-C7 24.12 22.60 H31-C5-C25-H47 56.65 -57.84
C8-C1-C2-H29 144.37 142.40 H31-C5-C25-H48 63.44 62.12
C2-C1-C3-C5 25.33 26.01 H31-C5-C25-H49 -176.70 -178.02
C2-C1-C3-O27 -157.43 -158.32 N4-C6-C16-C17 75.44 73.03
C26-C1-C2-N4 -101.35 -100.53 N4-C6-C16-C18 -166.50 -167.56
C26-C1-C2-C7 75.86 75.12 N4-C6-C16-H40 -43.71 -45.55
H28-C1-C2-N4 -95.78 -97.53 H31-C5-C25-H47 56.65 -57.84
H28-C1-C2-C7 24.12 22.60 H31-C5-C25-H48 63.44 62.12
C2-C1-C26-H50 178.45 178.69 H31-C5-C25-H49 -176.70 -178.02
C2-C1-C2-H51 -61.49 -61.14 H32-C6-C16-C17 -44.06 -46.54
C2-C1-C26-H52 58.35 58.71 H32-C6-C16-C18 73.98 72.85
C3-C1-C26-H50 -55.29 -54.81 H32-C6-C16-H40 -163.22 -165.1
C3-C1-C26-H51 64.75 65.35 C2-C7-C8-C10 96.21 95.56
C3-C1-C6-H52 -175.39 -174.78 C2-C7-C8-C12 -85.09 -84.76
H28-C1-C26-H50 56.66 57.90 C9-C7-C8-C10 -25.75 -26.76
H28-C1-C26-H51 176.72 178.07 C9-C7-C8-C12 152.92 152.9
H28-C1-C26-H52 -63.43 -62.06 H33-C7-C8-C10 -142.84 -144.7
C1-C2-N4-C6 -69.72 -68.05 H33-C7-C8-C12 155.38 153.4
C1-C2-N4-H30 165.07 160.73 H33-C7-C9-S11 35.84 34.95
C7-C2-N4-C6 166.30 167.95 C2-C7-C9-S11 -89.28 -89.45
C7-C2-N4-H30 41.10 36.74 C2-C7-C9-H34 152.84 153.7
H29-C2-N4-C6 48.73 50.54 C2-C7-C9-H35 28.60
H29-C2-N4-H30 -76.46 -80.66 C8-C7-C9-S11 35.65 35.40
C1-C2-C7-C8 46.79 47.58 C8-C7-C9-H34 -82.21 -81.42
C1-C2-C7-C9 164.83 166.98 C8-C7-C9-H35 155.38 153.4
C1-C2-C7-H33 -75.99 -74.42 C8-C7-C9-S11 35.84 34.95
C1-C2-C7-H34 166.55 167.58 C8-C7-C9-S11 153.21 153.9
C1-C2-C7-H35 43.76 45.56 H33-C7-C9-S11 35.34 37.13
C1-C2-C7-H36 -73.93 -72.83 H33-C7-C9-S11 -87.05 -87.97
C2-C7-C8-C10 44.10 46.55 C7-C8-C9-S11 3.713 4.68
C2-C7-C8-C9 163.26 165.14 C7-C8-C9-C10 -178.09 -177.3
C2-C7-C8-C10 -25.30 -26.04 C8-C10-C11-C17 0.50 0.42
C2-C7-C8-C12 178.57 177.7 C8-C10-C11-C10 178.57 177.7
C2-C7-C9-C11 152.92 152.9 C8-C10-C11-C10 -153.47 -151.3
C2-C7-C9-C10 152.84 153.7 C8-C10-C11-C10 155.38 153.4
C2-C7-C9-H40 -85.09 -84.76 C8-C10-C11-C10 -153.47 -151.3
C8-C7-C9-C10 -175.08 -175.0 C8-C10-C11-C10 155.38 153.4
C8-C7-C9-C12 3.10 2.99 C8-C10-C11-C10 -153.47 -151.3
C8-C7-C9-C13 152.84 153.7 C8-C10-C11-C10 155.38 153.4
C8-C7-C9-C14 3.10 2.99 C8-C10-C11-C10 -153.47 -151.3
C8-C7-C9-C15 -1.21 -1.25 C8-C10-C11-C10 155.38 153.4
C8-C7-C9-C16 -1.51 -2.50 C8-C10-C11-C10 -153.47 -151.3
C8-C7-C9-C17 -2.71 -2.53 C8-C10-C11-C10 155.38 153.4
C8-C7-C9-C18 28.60 C8-C10-C11-C10 -153.47 -151.3
C8-C7-C9-C19 46.55 C8-C10-C11-C10 155.38 153.4
C8-C7-C9-C20 -178.09 -177.3 C8-C10-C11-C10 -153.47 -151.3
C8-C7-C9-C21 0.50 0.42 C8-C10-C11-C10 155.38 153.4
A total of 52 atoms and 150 vibrational frequencies are observed in the spectroscopic study. The spectroscopic vibrational modes are calculated by HF and DFT/6-311+G (d, p) basis set. The frequencies, intensities of IR, Raman and characteristic group frequencies have also been calculated. In organic chemistry, vibrational spectroscopy is used to detect functional group\textsuperscript{13}. It is also used to study molecular tests, kinematics, etc. The molecules, however are made up of different vibration modes, there is therefore a various vibrational spectrum in the study of the title molecule. Fig. 2 and 3 show the calculated frequencies. Table 2 shows the calculated and observed vibrational assignments with the HF and the B3LYP/6-311++G method.

\begin{table}[h]
\centering
\begin{tabular}{lll}
C8-C12-C13-H37 & -179.83 & -179 \\
H36-C12-C13-C15 & -179.32 & -179 \\
H36-C12-C13-H37 & 0.33 & 0.32 \\
C12-C13-C15-C14 & 1.41 & 1.35 \\
C12-C13-C15-H39 & 179.9 & 179 \\
H37-C13-C15-C14 & -178.23 & -178 \\
H37-C13-C15-H39 & 0.30 & 0.3 \\
C10-C14-C15-C13 & -1.05 & -0.93 \\
C10-C14-C15-H39 & -179.60 & -179.5 \\
H38-C14-C15-C13 & 177.64 & 177.70 \\
H38-C14-C15-H39 & -0.90 & -0.93 \\
C6-C16-C17-S19 & 89.31 & 89.4 \\
C6-C16-C17-H41 & -30.40 & -28.58 \\
C6-C16-C17-H42 & -152.81 & -153.7 \\
C18-C16-C17-S19 & -35.64 & -35.40 \\
C18-C16-C17-H41 & -155.36 & -153.45 \\
C18-C16-C17-H42 & 82.23 & 81.43 \\
H40-C16-C17-S19 & -153.20 & -153.95 \\
H40-C16-C17-H41 & 87.08 & 87.98 \\
H40-C16-C17-H42 & -35.32 & -37.12 \\
C6-C16-C18-C20 & -96.22 & -95.55 \\
C6-C16-C18-C21 & 85.08 & 84.76 \\
C17-C16-C18-C20 & 25.74 & 26.76 \\
C17-C16-C18-C21 & -152.93 & -152.91 \\
H40-C16-C18-C20 & 142.83 & 144.72 \\
C18-C16-C18-C21 & -35.85 & -34.95 \\
C16-C17-S19-C20 & 30.25 & 28.88 \\
H41-C17-S19-C20 & 153.45 & 151.37 \\
H42-C17-S19-C20 & -88.93 & -90.90 \\
C16-C18-C20-C19 & -3.70 & -4.69 \\
C16-C18-C20-C23 & 178.09 & 177.29 \\
C21-C18-C20-C19 & 175.09 & 175.01 \\
C21-C18-C20-C23 & -3.10 & -2.99 \\
C16-C18-C21-C22 & -178.65 & -177.79 \\
C16-C18-C21-H43 & 1.51 & 2.51 \\
C20-C18-C21-C22 & 2.71 & 2.54 \\
C20-C18-C21-H43 & -177.11 & -177.15 \\
C17-C19-C20-C18 & -15.98 & -14.53 \\
C17-C19-C20-C23 & 162.11 & 163.39 \\
C18-C20-C23-C24 & 1.21 & 1.25 \\
C18-C20-C23-H45 & 179.92 & 179.89 \\
S19-C20-C23-C24 & -176.72 & -176.49 \\
S19-C20-C23-H45 & 1.97 & 2.13 \\
C18-C21-C22-C24 & -0.50 & -0.42 \\
C18-C21-C22-H44 & 179.84 & 179.97 \\
H43-C21-C22-C24 & 179.32 & 179.27 \\
H43-C21-C22-H44 & -0.32 & -0.33 \\
C22-C22-C24-C23 & -1.41 & -1.35 \\
C22-C22-C24-H46 & -179.95 & -179.98 \\
H44-C22-C24-C23 & 178.23 & 178.24 \\
H44-C22-C24-H46 & -0.30 & -0.37 \\
C20-C23-C24-C22 & 1.05 & 0.94 \\
C20-C23-C24-H46 & 179.60 & 179.57 \\
H45-C23-C24-C22 & -177.64 & -177.69 \\
H45-C23-C24-H46 & 0.90 & 0.93 \\
\end{tabular}
\end{table}

**Vibrational Assignments**

Fig. 1. Optimized structure of the organic molecule obtained at B3LYP/6-31G level of theory

Fig. 2. Theoretical vibrational spectrum using HF/6-311++G for title molecule
Table 2: Calculated vibrational frequencies (cm\(^{-1}\)) and assignments title compound based on HF/6-311++G (d, p) and B3LYP/6-311++G (d, p) methods

| Vibrational Assignments       | HF 6-311G | HF 6-31++G | B3LYP 6-311G | B3LYP 6-31++G |
|-------------------------------|-----------|------------|--------------|--------------|
| Ring deformation              | -229.9653 | -229.9015  | -234.9466    | -219.1928    |
| C-C wagging and ring deformation | -197.7089 | -197.4371  | -208.4349    | -190.6649    |
| Ring stretching               | -64.792   | -66.0186   | -124.1784    | -51.1752     |
| Ring bending                  | -41.0665  | -41.8883   | -106.4637    | 17.6728      |
| C=O wagging and ring twisting  | 58.4204   | 60.062     | -99.7258     | 54.9081      |
| C=O wagging and ring Twisting  | 75.373    | 75.0479    | 42.3406      | 63.7788      |
| C=O wagging and ring Twisting  | 99.333    | 101.0364   | 66.7223      | 94.9203      |
| Ring breathing and twisting    | 154.7052  | 153.7594   | 116.3911     | 134.5907     |
| Ring bending                  | 178.8022  | 177.8274   | 141.2279     | 158.0064     |
| Ring stretching and C-H rocking | 183.9821  | 183.2629   | 146.8225     | 159.746      |
| Ring stretching               | 189.8117  | 188.5251   | 158.6888     | 165.8716     |
| Ring stretching               | 208.9179  | 209.0036   | 187.1049     | 190.4608     |
| Ring deformation and C-H rocking | 237.4691  | 237.5488   | 199.3726     | 205.6494     |
| Ring breathing                | 266.7524  | 266.3947   | 228.7993     | 233.6933     |
| Ring breathing                | 272.5417  | 272.3757   | 238.9764     | 245.5082     |
| Ring stretching and C-S out plan bending | 288.6973  | 288.0281   | 248.7996     | 257.3432     |
| Ring deformation and C-H rocking | 306.8084  | 306.0891   | 269.2158     | 267.4396     |
| Ring deformation              | 350.3618  | 350.9602   | 323.1495     | 319.4722     |
| C-H rocking                   | 376.0731  | 377.3177   | 339.3296     | 335.6433     |
| Ring stretching               | 389.7852  | 389.8144   | 343.792      | 341.0143     |
| Ring deformation and C-H rocking and ring deformation | 395.046   | 395.5424   | 360.9819     | 356.8177     |
| C-H rocking                   | 422.4164  | 423.1322   | 363.2598     | 360.3997     |
| Ring deformation and C-H rocking and ring deformation | 429.9013  | 428.2786   | 390.2312     | 387.322      |
| C-H rocking                   | 484.0331  | 482.8366   | 418.927      | 406.004      |
| Ring deformation              | 493.7563  | 494.1814   | 459.9176     | 451.7972     |
| Ring deformation and C-H rocking | 514.0624  | 513.339    | 463.8629     | 458.6466     |
| C-H rocking                   | 519.1581  | 518.1794   | 466.8887     | 464.5253     |
| Ring deformation              | 538.5809  | 537.9589   | 490.1502     | 483.1624     |
| Ring deformation              | 550.413   | 549.7329   | 502.5644     | 494.4182     |
| C-H wagging                   | 567.5258  | 567.3939   | 510.3295     | 501.7365     |

Continue Table 2
|        |        |        |        |                        |
|--------|--------|--------|--------|-----------------------|
| 582.7368 | 583.9799 | 531.9834 | 530.0417 | Ring stretching        |
| 600.9812 | 600.1037 | 539.9481 | 535.8637 | Ring breathing          |
| 616.14  | 616.7398 | 561.7379 | 553.4781 | Ring deformation        |
| 627.203 | 627.1937 | 575.4665 | 568.9549 | Ring deformation        |
| 646.0239 | 645.8668 | 589.3565 | 581.1875 | Ring deformation        |
| 655.1498 | 654.5796 | 603.8106 | 594.485  | Ring deformation and N-H rocking |
| 698.1099 | 697.7662 | 642.6309 | 632.4736 | Ring deformation and C-H rocking |
| 702.0815 | 701.5741 | 647.9494 | 635.5417 | Ring deformation and C-H rocking |
| 714.0517 | 713.8855 | 649.8632 | 637.1369 | Ring deformation and C-H rocking |
| 740.462  | 740.6503 | 687.0236 | 672.6354 | Ring deformation and C-H rocking |
| 744.1232 | 744.0099 | 689.0506 | 677.9077 | Ring deformation and C=O,N-H wagging |
| 785.8559 | 786.7782 | 727.7485 | 706.1245 | Ring deformation and C-H rocking |
| 791.3242 | 791.3688 | 731.4054 | 713.5378 | Ring deformation and C-S stretching |
| 839.1609 | 840.0747 | 753.0798 | 765.2063 | C=O, N-H wagging and ring deformation |
| 870.9846 | 869.9239 | 791.343  | 774.9497 | Ring deformation and C-H wagging |
| 881.1406 | 881.3927 | 792.3548 | 776.3088 | Ring deformation and C-H rocking |
| 892.4164 | 892.1166 | 829.1346 | 816.7441 | Ring breathing and C-H rocking |
| 914.724  | 914.705  | 841.0573 | 825.0769 | Ring breathing and C-H rocking |
| 968.5293 | 966.2263 | 862.8071 | 839.9625 | C-H wagging             |
| 996.142  | 994.4025 | 875.8364 | 847.6034 | C-H wagging             |
| 1000.018 | 999.8391 | 891.3911 | 893.2602 | Ring breathing and C-H bending |
| 1005.7455 | 1005.3395 | 908.6649 | 902.956  | Ring deformation and C-H wagging |
| 1021.3447 | 1021.7178 | 949.602  | 925.617  | C-H twisting and C-S stretching |
| 1032.097 | 1033.9909 | 964.1402 | 935.1974 | C-S stretching          |
| 1034.5141 | 1036.325  | 977.5419 | 950.2878 | C-H wagging             |
| 1044.7215 | 1045.3036 | 987.4671 | 958.3716 | C-H wagging             |
| 1057.2137 | 1057.681  | 989.5713 | 968.7278 | C-H twisting            |
| 1078.7418 | 1079.0423 | 998.8103 | 982.6365 | Ring deformation and C-H rocking |
| 1086.7718 | 1087.4327 | 1003.6359 | 986.2575 | Ring breathing and C-H twisting |
| 1095.0551 | 1095.8576 | 1013.132 | 1000.3396 | Ring breathing          |
| 1104.1023 | 1103.1149 | 1033.6935 | 1011.2327 | Ring deformation and C-H twisting |
| 1116.1952 | 1115.5555 | 1040.6599 | 1015.7436 | Ring deformation and C-H rocking |
| 1123.0419 | 1123.4044 | 1046.1253 | 1017.5342 | Ring deformation and C-H rocking |
| 1128.275  | 1129.2571 | 1052.0511 | 1022.2435 | Ring deformation and C-H rocking |
| 1132.8151 | 1133.3653 | 1053.9672 | 1027.8967 | Ring deformation and C-H rocking |
| 1136.4018 | 1137.4183 | 1061.0005 | 1031.9701 | Ring deformation and C-H rocking |

Continue Table 2
| Frequency (cm⁻¹) | Ring deformation and C-H rocking | C-H rocking | C-H twisting and rocking | C-H wagging and rocking | C-H wagging | C-H twisting | C-H rocking | C-H wagging | C-H rocking | C-H wagging | C-H twisting | C-H rocking | C-H wagging | C-H wagging | C-H rocking | C-H wagging | C-H rocking |
|-----------------|----------------------------------|-------------|-------------------------|-------------------------|---------------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|-------------|--------------|-------------|-------------|------------|
| 1138.8026       | 1138.944                         | 1061.7903   | 1038.7215               | Ring deformation and C-H rocking |
| 1149.4985       | 1149.7295                        | 1076.3219   | 1052.9522               | Ring deformation and C-H rocking |
| 1174.7591       | 1174.0216                        | 1079.659    | 1058.2829               | Ring deformation and C-H twisting |
| 1177.4643       | 1177.3652                        | 1087.926    | 1065.6865               | Ring deformation and C-H rocking |
| 1186.2782       | 1186.3641                        | 1100.8396   | 1083.9865               | Ring deformation and C-H twisting |
| 1192.9383       | 1193.1815                        | 1103.1899   | 1085.0626               | Ring deformation C-H rocking |
| 1193.7124       | 1194.7236                        | 1130.4886   | 1109.2998               | Ring deformation and C-H wagging and rocking |
| 1212.3907       | 1210.1853                        | 1143.4984   | 1122.4819               | Ring deformation and C-H rocking |
| 1213.8668       | 1211.2829                        | 1150.3136   | 1128.6193               | Ring deformation and C-H rocking |
| 1226.1481       | 1224.5593                        | 1165.8715   | 1139.0741               | Ring deformation and C-H rocking |
| 1235.7552       | 1234.6732                        | 1172.9482   | 1142.1047               | Ring deformation and C-H bending |
| 1260.5388       | 1258.0619                        | 1178.5707   | 1149.614                | Ring deformation and C-H rocking |
| 1279.8835       | 1277.546                         | 1185.4593   | 1167.0785               | Ring deformation and C-H wagging |
| 1305.1793       | 1304.1336                        | 1195.6647   | 1181.6884               | Ring deformation and C-H twisting |
| 1310.901        | 1309.6981                        | 1223.7745   | 1198.9568               | Ring deformation and C-H rocking |
| 1323.6257       | 1320.8807                        | 1230.3274   | 1205.3265               | Ring deformation and C-H rocking |
| 1334.0922       | 1331.7754                        | 1238.3741   | 1205.8497               | Ring deformation and C-H rocking |
| 1338.3194       | 1335.5194                        | 1251.4193   | 1227.2436               | Ring deformation and C-H rocking |
| 1342.9036       | 1340.1095                        | 1255.4694   | 1228.631                | C-H twisting and wagging |
| 1348.5897       | 1346.8178                        | 1266.4931   | 1238.9583               | C-H twisting and rocking |
| 1381.9072       | 1378.3352                        | 1272.0954   | 1242.1408               | C-H twisting and rocking |
| 1400.2423       | 1395.7662                        | 1281.4487   | 1245.7012               | C-H twisting and rocking |
| 1415.1201       | 1412.235                         | 1285.594    | 1262.0967               | C-H twisting |
| 1420.8765       | 1417.899                         | 1300.6325   | 1268.0356               | C-H wagging |
| 1425.1358       | 1421.0844                        | 1307.8837   | 1277.7265               | C-H wagging |
| 1431.8808       | 1429.0995                        | 1310.5914   | 1290.8372               | C-H twisting |
| 1436.6867       | 1434.0305                        | 1325.1579   | 1296.0829               | C-H twisting |
| 1447.8105       | 1445.6143                        | 1336.6448   | 1308.1699               | C-H rocking |
| 1494.91         | 1492.5972                        | 1368.7083   | 1337.9642               | C-H wagging |
| 1512.7839       | 1509.2183                        | 1378.8874   | 1351.1258               | C-H wagging |
| 1517.5159       | 1514.8413                        | 1389.4823   | 1357.1497               | C-H wagging |
| 1523.0336       | 1519.6343                        | 1394.0807   | 1366.8168               | C-H wagging |
| 1531.587        | 1528.0701                        | 1403.0751   | 1369.4993               | C-H Wagging |
| 1549.5016       | 1541.9211                        | 1411.9181   | 1379.2735               | C-H Wagging |
| 1567.0541       | 1560.6581                        | 1430.6842   | 1390.1801               | C-H Wagging |
| 1567.5519       | 1562.0163                        | 1433.5468   | 1393.8097               | C-H Wagging |
| 1570.3472       | 1567.9337                        | 1435.7215   | 1409.3893               | C-H rocking |
| 1581.7624       | 1577.566                         | 1446.5708   | 1417.6663               | C-H Wagging |
| 1586.0539       | 1582.3054                        | 1456.4304   | 1427.632                | C-H Wagging |
| 1587.7337       | 1584.0311                        | 1459.948    | 1438.6632               | C-H rocking |
| 1595.4597       | 1592.1041                        | 1473.682    | 1444.8595               | C-H rocking |
| 1603.1257       | 1599.8848                        | 1475.1923   | 1446.3295               | C-H Wagging |
| 1610.5187       | 1607.148                         | 1482.1595   | 1449.7688               | C-H rocking |
C–H vibrations

A C–H stretching vibration in the region 3,100–3000 cm\(^{-1}\) has been shown by the heteroaromatic structure. This is the only area where the C–H stretching vibration can be identified. The nature of the substitutions in this region does not greatly affect the bands. Due to the influence from N–H stretching vibration, which was found very dominant in this molecule. The vibrational frequency in the region of 2816-1142 cm\(^{-1}\) was evident of title molecule in this study. In the expected range of vibration, the functional group vibrations were observed.

N–H vibration

The N–H stretching frequencies of vibration are always higher than the other stretching vibrations, and the length of the bond is smaller than the length of other molecules. Usually N–H stretching vibrations\(^{15}\) are continued at 3500-3300 cm\(^{-1}\) for any heterocyclic compound. Six vibrational modes are required by nitrogen hydrogen bonds and this is part of the entire vibrational pattern. The N–H vibration takes place in the area 3464 cm\(^{-1}\) in this research. This is due to strong hydrogen bonding during the gas phase, whereas in the solid phase it is absent.

C=O vibrations

The C=O stretching vibration band visualized from the carboxylic group in which the C=O stretching position is dependent on physical
state, mass and electronic effects, intermolecular and intra molecular hydrogen bonding\(^{16}\), usually in this region between 1750 and 1700 cm\(^{-1}\). This band position determines the bond strength of the hydrogen. In this research the carboxyl group, assigned below 1000 cm\(^{-1}\) in the region, are directly linked to its electronic structure as well as its geometric positioning. The effect of the inductive, mesomeric and conjugating efficiency in both inter and intermolecular factors on carbonyl absorption of frequent organic compounds.

**C-C Vibrations**

The visible spectrum of the benzene and its derivatives, the ring vibration is very remarkable and characteristic of the aromatic ring itself. This is not so much because of the nature of the substituent but because of the way the chain is substituted. In this study, the title molecule found that the region is generally observed below 700 cm\(^{-1}\) at external vibration bending. The chains vibrations were observed at 190 cm\(^{-1}\).

**Ring vibrations**

The benzene ring has six stretching vibration. The bending vibration of the benzene ring in the plane and out of the plane is usually seen in the literature below 1000 cm\(^{-1}\), and those modes are non-pure but are significantly affected by other vibrations. The title molecule affects to a great extent the in-plan and out-of-plane bending modes of the rings, producing bands less than 600 cm\(^{-1}\).

**C–S vibrations**

The C–S stretching bands are normally noticed in the range of 670–930 cm\(^{-1}\). For our study, the title compound shows the frequency range from 713 to 935 cm\(^{-1}\). The out-of-plane C–S bending vibrations bands are predicted in the regions 420–320 cm\(^{-1}\), respectively. In the current research work, the C–S out of plane bending vibrations are assigned to below 300 cm\(^{-1}\). All the C–S vibrational bands of the molecule are well determined with the previous research work. Also, the observed values by B3LYP/6-311++G (d, p) are almost related to the computed values.

**Mulliken atomic charge**

The effect of atomic charges determines the molecular polarization, dipole moment, electronic structure and few molecular system properties. The classification of charges across the atoms proposes that donor and recipient pair molecules are established. The investigation of Mulliken atomic charges plays a vital role in the implementation of quantum chemicals in the molecular system. Fig. 4 shows the Mulliken charge arrangement structure of the title compound. The negative charge carrier is more in oxygen and Sulphur atoms, while positive charge occupies all hydrogen atoms. In addition, the S19 atom has a greater electron-negative (-0.38886e) charge than the S11 atom in Mulliken atomic chargers. This is because the electron-negative Sulphur atom is present. Thus Mulliken population analysis interprets the reaction behavioral analysis of various chemicals.

![Fig. 4. Schematic representation of Mullikan atomic charges](image)

**Frontier molecular orbitals**

The frontier molecular orbitals play an important role in understanding the electrical and optical properties of the titled molecule. The HOMO energy defines the ability to supply electrons while the LUMO shows that electrons can be accepted. The molecular chemical ability is defined by the HOMO-LUMO gap. A molecule with a small energy gap in the orbit is more polarized and usually combined with the high chemical responsiveness. The energy gap between HOMO and LUMO is more influential for structural stability. Fig. 5 shows the difference in energy level between HOMO and LUMO. The estimated energy difference is 9.3387eV. This wide energy gap therefore means high excitement, good stability and high chemical durability.

\[
\begin{align*}
\text{HOMO energy} & = -8.4165\text{eV} \\
\text{LUMO energy} & = 0.9222\text{eV} \\
\text{HOMO–LUMO energy gap} & = 9.3387\text{eV}
\end{align*}
\]
The smaller energy band gap increases the chemical activity of the titled molecule. The HOMO-LUMO energy and its gap are determined using HF/6-11++G (d, p) level.

**Molecular orbital studies**

Furthermore, the difference of energy band values is known to help us identify the chemical reactivity and stability of titled molecule. The energy band gap of the molecule is small and this gap is usually combined with a high reactivity of chemicals and a low kinetic stability. In terms of the degree of orbital reactivity of the atom\(^1\), the quantum chemical calculations are performed. Mulliken was introduced a new formulation, which allowed to extend the concept to molecules, in terms of two further periodic properties, namely ionizing potentials and affinity. The affinity of electron refers exactly to the ability to accept an electron. The greater HOMO-LUMO gap means a hard molecule, and a smaller HOMO-LUMO gap means a soft molecule, due to its chemical hardness. The reactivity of the selected compound is also associated with the molecule's hardness. The values of ionization and electron affinity are calculated with both HOMO and LUMO. For Mulliken electron negativity, the mean of HOMO and LUMO energy value can be used. The index of electrophilicity is the amount of energy reduction due to the greater electron movement between donor and recipient. The values of electronegativity, chemical potential, chemical hardness, softness, and electrophilicity index are 3.74715 eV, -3.74715 eV, 4.66935 eV, 0.107081 eV, 1.503543 eV, respectively, for the title Compound.

**Thermodynamic Parameters**

Several thermodynamic parameters such as heat capacity, entropy and enthalpy changes for the titled compound were determined using, the DFT/B3LYP with 6-31G (d, p) basic sets. Such estimated frequencies of the title compound provide the information of all structural thermodynamic characteristics including rotational constants, null point vibration power, heat capacity, and entropy\(^1\). These values are calculated using the basis set of 6-311++G (d, p) levels using B3LYP and HF method and presented in the Table 3. For further understanding the selected molecules, the collected thermodynamic parameters are used to analysis the thermodynamic functional relationships and the direction of chemical reactions in accordance with the thermodynamics law.

| Basis set          | HF 6-311G   | HF 6-311++G | B3LYP 6-311G | B3LYP 6-311++G |
|--------------------|-------------|-------------|--------------|---------------|
| Zero-Point Vibrational | 290.6913    | 290.4561    | 273.5251     | 271.3272      |
| Energy (Kcal mol⁻¹)   | 0.34304     | 0.34304     | 0.34304      | 0.34304       |
| Rotational Constants  | 0.09194     | 0.09194     | 0.09194      | 0.09194       |
| Frequency (GHz)       | 0.07810     | 0.07810     | 0.07810      | 0.07810       |
| Specific heat (Cal mol⁻¹K⁻¹) | 72.466   | 72.518      | 78.239       | 83.756        |
| Entropy (S) (Cal mol⁻¹K⁻¹) | 128.996  | 128.979     | 133.915      | 143.786       |
| Dipole Moment (µ) (Debye) | 4.7568    | 4.6720      | 4.0293       | 3.6527        |

**Molecular electrostatic potential (MEP) mapping**

The electrostatic potential diagram illustrates the probability that the electron densities are integrated throughout the system. In other words, it provides functional information to the reactive section. Electrophillic and nucleophilic molecular system centers are suitable for the development of biochemical system. The electrostatic potential of the title compound shown in Fig. 6. The molecular surface contours are also illustrated in Fig. 7. The region with the most negative potential is shown in a red colour in the MEP diagram, while the blue colour shows the most positive potential surface. Red, blue, light blue, yellow and green are shown on the surface of the MEP.
Red surface is electron-rich and moderately negative; blue, electron-deficient and partially positive; light-blue, light electron-deficient; yellow colour; a type of region rich in electrons; and green, neutral.

**Fig. 6. Molecular electrostatic potential surface**

**Hyperpolarizability studies**

As an extensive tool for research on spectroscopy analysis, hyper polarizability and the non-linear optical properties of the titled molecule of potential NLO materials are considered. Non-linear response, Hyperpolarizability (βijk) and linear polarization (αij) of first order may be furnished as Taylor expansion in the form

\[ \mu_{tot} = \mu_0 + \alpha_{ij}E^i + \beta_{ijk}E^iE^j + \ldots \]

The dipole moment (μ), mean polarizability (α) and the first order Hyperpolarizability (β) for the titled molecule is illustrated using following equations:

\[ \mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \]

\[ \alpha = \frac{\alpha_{xx} + \alpha_{xy} + \alpha_{xz}}{3} \]

\[ \beta = (\beta_{xx} + \beta_{yy} + \beta_{zz}) + (\beta_{xy} + \beta_{yz} + \beta_{zx})^2 + (\beta_{zz} + \beta_{xx} + \beta_{yy})^2 \]

The estimated dipole moment, mean polarizability and first order hyperpolarization of first-order values are 7,478 Debye, 0.402 Å esu and 1,402 x 10^{-31} cm^5 esu^-1. A β-electron donor-acceptor movement which makes the molecule highly polarizable as a vital behavior for NLO activities.

**CONCLUSION**

The results presented and discussed in the report of procedure seemed appropriate to be summarized. The theoretical analysis of DFT provides information on the orbital interactions and vibrational frequency systems, nature of the electronic structure, functional groups. In the organic synthesis of perfume, drugs, dyes and pharmaceuticals, heterocyclic compounds play significant role. The use of such a base set of 6-311 and 6-311++is availed to optimize the geometry of piperidine products by HF and DFT/B3LYP methods. The computed data is based on proof of the gaseous phase. The different calculated bonding angles are satisfactorily compatible with the normal values. The B3LYP/6-311++G (d, p), then used to generate dependable geometry and associated piperidine derivatives properties. The method further tends to produce a vibration analysis. The orbital bond analysis provides the natural structure of Lewis with maximum accuracy. The highest rate of electron density will be achieved. In addition, the HOMO–LUMO band gap assists the molecule’s biologically active properties. It provides information on the distribution of the charge density and differentiates the chemical molecule reactivity. The mapping electron density with electrostatic potential surface has been achieved to explain the size, the shape, the charging density distribution and the location of the chemical reactivity of the molecules. Finally, the Hyperpolarizability of the tile compound is analyzed for optical industrial applications.

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**Conflict of Interest**

The authors claim no conflict of interest in the current research work.
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