Spectroscopic Investigation (FT-IR, FT-Raman, NMR and UV-Vis), Conformational Stability, NBO and Thermodynamic Analysis of 1-(2-Methoxyphenyl) Piperazine and 1-(2-Chlorophenyl) Piperazine by DFT Approach

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Abstract

The vibrational and electronic properties of phenyl substituted compounds 1-(2-methoxyphenyl)piperazine and 1-(2-chlorophenyl)piperazine have been investigated by FT-IR, FT-Raman, NMR and UV-Vis spectral measurements. Density functional theory (DFT) method, using B3LYP functional, with 6-311++G (d,p) basis set, has been performed for assigning vibrational frequencies of the title compounds, which also helps to derive useful information about the structure of the chosen compounds. A detailed interpretation of the Infrared and Raman spectra of the two molecules were calculated using the gauge independent atomic orbital (GIAO) method. These studies satisfactorily agree the experimental data. Charge density distribution and site of chemical reactivity of the molecule have been studied by mapping electron density isosurface with molecular electrostatic potential (MEP). Stability of the molecules arising from hyperconjugative interactions, charge delocalization have been analyzed using natural bond orbital (NBO) analysis. The compounds have similar HOMO (Highest Occupied Molecular Orbitals) - LUMO (Lowest Unoccupied Molecular Orbitals) gap due to similarity in their structures. The compounds show (n→π*) transitions in the UV-Visible range.

Keywords: DFT; NMR; Natural bond orbitals; HOMO- LUMO; 1-(2-methoxyphenyl)piperazine; 1-(2-chlorophenyl)piperazine

Introduction

Piperazines are a broad class of chemical compounds, with many important pharmacological properties. Various biologically active, heterocyclic compounds have two nitrogens in their structure. Piperazine is an organic compound that consists of a six-membered ring containing two nitrogen atoms at opposite positions in the ring. Piperazines are currently the most important building blocks in drug discovery. Piperazines are hygroscopic compounds that have antibiotic effects. It has been reported that some piperazine derivatives are capable of inducing apoptosis in cancer cells [1]. Sampson et al. investigated the effect of 1,4-bis-(4-(1H-benzo[d]imidazol-2-yl)-phenyl)piperazine on U937 leukemia cell viability [2]. Sharma and Ravani [3] reported the synthesis and screening of 2-(2-(2-(4-substituted piperazine-1-yl)-5-phenylthiazol-4-yl)-3-aryl quinazolinone derivatives as anticancer agents. Hatnapure et al. [4] reported the synthesis and biological evaluation of novel piperazine derivatives of flavones as potent anti-inflammatory and antimicrobial agents. Additionally, some piperazine derivatives were proven to possess a high biological activity for multidrug resistance in cancer and malaria [5]. Piperazine is a potent anthelmintic used in the therapy of ascariasis (roundworms) and oxyuriasis (threadworms/pinworms) infestations [6]. Piperazines have been reported in gene transfer reactions [7] and quaternary piperazinium salts have shown spasmolytic, anthelmintic and germicidal activity. 1-(2-methoxyphenyl)piperazine is used as intermediate of Naftopidil [8]. A Complete vibrational analysis of 2-[4-(1H-benzo[d]imidazol-2-yl)-phenyl]piperazine has been reported [9]. DFT investigations on 1-cyclobutylpiperazine have been done [10]. Gunasekaran and Anita [11] reported the spectral investigation and normal coordinate analysis of piperazine. Krishnakumar et al. reported the spectroscopic investigations of 2-methyl piperazine [12].

Sheena Mary et al. had conducted the spectroscopic investigation on opipramol, a piperazine based compound [13]. Kesan et al. [14] reported the spectroscopic and quantum chemical investigations of some halide complexes of 1-phenylpiperazine. The vibrational analysis of 1-(m-trifluoromethyl)phenyl)piperazine has also been done [15]. Considering the pharmaceutical significance of the parent ring, a systematic study on the molecular structure and vibrational spectra of 1-(2-methoxyphenyl)piperazine (MPP) and 1-(2-chlorophenyl) piperazine (CPP) has been carried out.

Experimental Details

The compounds under investigation 1-(2-methoxyphenyl)piperazine and 1-(2-chlorophenyl) piperazine are purchased from Aldrich chemicals, USA. The room temperature FTIR spectrum of the compounds is measured in the 4000-400 cm⁻¹ region at a resolution of ±1 cm⁻¹, using a perkin elmer spectrum RX1, vacuum Fourier transform spectrometer, equipped with mercury cadmiumtelluride (MCT) detector, KBr beam splitter and globar source. The FT-Raman spectrum of MPP and CPP is recorded on a BRUKER RFS 27 model.

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interferometer. The spectrum is recorded in the 4000-50 cm-1 Stokes region using the 1064 nm line of an Nd:YAG laser for excitation, operating at 200 mW power. The reported wavenumbers are expected to be accurate within ± 1 cm⁻¹.

1H and 13C nuclear magnetic resonance (NMR) (300 MHz; CDCl3) spectra are recorded on a BRUKER instrument. Chemical shifts for protons are reported in parts per million scale (δ scale) downfield from tetramethylsilane. The ultraviolet absorption spectra, in the region 200-1100 nm are recorded on a Lambda 35 spectrophotometer in 1.00 cm cells at 25 ± 0.1°C.

Computational details

The quantum chemical calculations of MPP and CPP are performed using the Gaussian 09 program [16] with the B3LYP level of theory, supplemented with the standard 6-311++G(d,p) basis set. The optimized geometries corresponding to the minimum on the potential energy surface are obtained by solving self-consistent field equation iteratively. Harmonic vibrational wavenumbers are calculated using analytic second derivatives to confirm the convergence to minima on the potential energy surface and to evaluate the zero-point vibrational energy [17]. Normal coordinate analysis on MPP and CPP is performed using the Molvib-7.0 program [18,19]. Multiple scaling of the force field is carried through the SQM procedure [20,21], to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity [22]. The calculated analytic force constants are used by Molvib in the calculation of vibrational frequencies by diagonalization of dynamical matrix. The natural bonding orbitals (NBO) calculations [23] are performed using NBO 3.1 program in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, which is a measure of the intermolecular delocalization or hyper conjugation. The hyper conjugative interaction energy was deduced from the second-order perturbation approach [24]. 1H and 13C chemical shifts are computed by adopting the standard GIAO/B3LYP/6-311++G (d,p) (Gauge-Independent Atomic Orbital) approach [25,26].

Results and Discussion

Molecular geometry

Both the titled molecules MPP and CPP are phenyl substituted, except that MPP has methoxy group substituted in its 12th position whereas CPP is substituted with chlorine atom in the same position. First, conformational analysis of MPP is performed to find the most stable conformer. So, the potential energy surface (PES) scan is performed on the dihedral angle O26-C12-C7-N1 first and then on H28-C27-O26-C12. The Structure optimization has been carried out for the minimum energy conformer. In the case of CPP, its input geometry is optimized without imposing any external constraints on the geometrical parameters and the resultant optimized geometry has been used as input for vibrational frequency calculations. The labeled optimized structure of MPP and CPP is given in Figure 1. The molecules under investigation belong to C1 point group symmetry. The optimized structural parameters including bond length, bond angle and dihedral angle, for MPP and CPP are listed in Table 1. Their global minimum energy, zero-point vibrational energies, rotational constants, entropies and dipole moments obtained for optimized geometry are presented in Table 2.

Piperazine can have different conformations such as chair, half-chair, boat, twist boat and envelope forms. Chair conformation was found to be the most stable conformer and Hendrickson proposed that for chair-chair interconversion the most stable transition state would be one of the possible chair forms [27,28]. The chair conformation of MPP and CPP is confirmed by the dihedral angles C6-N1-C7-C8 and C2-N1-C7-C12. Since oxygen atom is more electronegative than the chlorine atom, the methoxy group substituted to C12 atom pulls the piperazine ring to a greater extent than the chlorine atom of CPP. The dihedral angle C12-C7-N1-C6 for MPP is 63.9° and for CPP is 70° which makes the above statement tangible. The C12-C26 bond length value in CPP is 1.76 Å which agrees the C-C bond length of piperazine compounds [29]. The N1-C7 bond length is found to be 1.41 Å which is comparatively shorter than other N-C bond lengths. This is due to the conjugation of the phenyl group and also by the contribution of its electronegativity character [15]. The resonance effect between C and N atoms and Coulomb repulsive interaction between CH2 groups makes the other N-C bond lengths to be shorter than the C-C bond lengths in the piperazine ring (Table 1). The C-O bond lengths in MPP average to 1.4 Å.

Hyperpolarizability

The static first hyperpolarizability (β₀) of MPP and CPP is calculated based on the finite-field approach and reported in Table 3. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyperpolarizability is a third rank tensor that can be described by a 3×3×3 matrix. The 27 components of the 3D matrix can be reduced to ten components due to the Kleinman symmetry [30]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3×3×3 matrices is a tetrahedral. The components of β are defined as the coefficients in the Taylor series of expansion of energy in the external electric field. The total static dipole moment μ, the mean polarizability α₀, the anisotropy of the polarizability β₀, the x, y, z components are defined as given in the literature [31]. Since the values of the polarizabilities (α) and hyperpolarizability (β) of the Gaussian 09 output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu).

The total molecular dipole moment of MPP and CPP are 1.0691 and 1.3538 Debye, respectively and the total static first hyperpolarizability values are 4.4582×10⁻³⁰ cm⁵/esu (MPP) and 4.4124×10⁻³⁰ cm⁵/esu (CPP). If equilibrium geometries are noncentrosymmetric, the dipole moments, as well as first hyperpolarizabilities, are nonzero [32]. The highest value of dipole moment is observed for components μx and μy for MPP and CPP, respectively. In these directions, the dipole moment value is equal to 0.5059 D (MPP) and 0.7361 D (CPP). DFT has been extensively used as an effective method to investigate the organic non-linear optical (NLO) materials [33]. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Therefore it was used frequently as a threshold value for

**Figure 1:** Molecular structure of MPP and CPP with atom numbering scheme.
comparative purposes. The $\beta$ total of urea is found to be 0.5883*10^{-30} cm^5/esu obtained at B3LYP/6-311++G(d,p) level [34]. Theoretically, the total static first hyperpolarizability of the title compounds is of eight times the magnitude of urea. Hence, the titled molecules are said to be good NLO materials.

The theoretical calculation of $\beta$ component is very useful as it clearly indicates the direction of charge delocalization. Domination of particular component indicates the substantial delocalization of charges in a direction. The large value of hyperpolarizability ($\beta$), which is a measure of the non-linear optical activity of the molecular system, is associated with the intramolecular charge transfer, resulting from the electron cloud movement, through the $\pi$ conjugated frame work of electron [35]. In both MPP and CPP, the $\pi$ – electron delocalization has been extended towards $\beta$ xxx direction. The comparison of MPP and CPP had inferred that the substituents do not affect the hyperpolarizability value of the molecules to a greater extent. Hence it is evident that both MPP and CPP are enhanced for SHG (second harmonic generation) along $\beta$xxx direction. So, $\beta$xxx is an active direction for SHG and is suitable for growing crystals along this direction for NLO applications.

### Thermodynamic analysis

Several calculated thermodynamic parameters, rotational constants, rotational temperature, vibrational temperature and dipole moment for MPP and CPP are presented in Table 2. The standard thermodynamic functions such as heat capacity at constant pressure (Cp), entropy (S) and enthalpy change ($\Delta H_{0\to T}$) are calculated on the basis of vibrational analysis and statistical thermodynamics. They are listed in Table 4. The graph showing the correlation of heat capacity at constant pressure (Cp), entropy (S) and enthalpy change ($\Delta H_{0\to T}$) with temperature is delineated in Figures 2 and 3. All the computed thermodynamic functions of MPP and CPP, increases steadily with temperature, ranging from 100 to 1000 K, due to the enhancement of the molecular vibration with increase in temperature. Here, all the mentioned thermodynamic calculations were done in gas phase.

#### Table 1: Optimized geometrical parameters of MPP and CPP.

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Value (Å)</th>
<th>Bond angle</th>
<th>Value (°)</th>
<th>Torsional angle</th>
<th>Value (°)</th>
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<td>N1-C2</td>
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<td>C3-C2-N1</td>
<td>109.84</td>
<td>109.79</td>
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<tr>
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<td>111.09</td>
<td>111.34</td>
<td>C3 - N4 - C5 - C6</td>
</tr>
<tr>
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<td>1.46</td>
<td>C6-C5-N4</td>
<td>113.90</td>
<td>109.21</td>
<td>N4-C5-C6-N1</td>
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<td>109.70</td>
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<td>N1-C7</td>
<td>1.42</td>
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<td>111.52</td>
<td>111.33</td>
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<td>117.16</td>
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<td>122.22</td>
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<td>121.96</td>
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<td>120.31</td>
<td>120.20</td>
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<td>108.78</td>
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<td>109.18</td>
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<td>H16-C3-C2</td>
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<td>108.59</td>
<td>H16-C3-C2-N1</td>
</tr>
<tr>
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<td>H17-N4-C3</td>
<td>109.91</td>
<td>110.86</td>
<td>H17-N4-C3-C2</td>
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<tr>
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<td>1.10</td>
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<td>109.14</td>
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<td>108.66</td>
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<tr>
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<td>1.08</td>
<td>H20-C6-N1</td>
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<td>110.04</td>
<td>H20-C6-N1-C7</td>
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<td>C10-H24</td>
<td>1.08</td>
<td>H21-C6-N1</td>
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<td>109.49</td>
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<td>C11-H25</td>
<td>1.08</td>
<td>H22-C8-C9</td>
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<td>119.15</td>
<td>H22-C8-C9-C10</td>
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<td>C12-C26</td>
<td>1.38</td>
<td>H23-C9-C10</td>
<td>120.30</td>
<td>120.80</td>
<td>H23-C9-C10-C11</td>
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<tr>
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<td>O27-C126-C12-C7</td>
<td>116.44</td>
<td>-</td>
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<tr>
<td>N1-C6</td>
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<td>O29-C27-C26</td>
<td>110.84</td>
<td>-</td>
<td>H29-C27-O26-C12-C7</td>
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<tr>
<td>-</td>
<td>-</td>
<td>O30-C27-C26</td>
<td>110.58</td>
<td>-</td>
<td>H30-C27-O26-C12-C7</td>
</tr>
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</table>
the second law of thermodynamics in thermo chemical field [36], these calculations can be used to compute the other thermodynamic energies and help to estimate the directions of chemical reactions.

**Spectral analysis**

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the full set of 109 standard internal coordinates of MPP (containing 25 redundancies) and 93 standard internal coordinates of CPP (containing 21 redundancies) are defined in Tables 5 and 6, respectively. The non-redundant set of local symmetry coordinates are constructed for both the molecules, by suitable linear combinations of internal coordinates following the recommendation of Fogarasi et al. [37,38]. They are summarized in Tables 7 and 8. In agreement with the C1 symmetry, the 84 normal modes of MPP and 72 normal modes of CPP are distributed among the symmetry species as follows

For MPP, \( \Gamma_{3N-6} = 57 \) (in-plane) + 27 (out-of-plane).

For CPP, \( \Gamma_{3N-6} = 49 \) (in-plane) + 23 (out-of-plane).

In order to reproduce the observed frequencies, the refinement of scaling factors are applied and optimized via least square refinement algorithm. This results in a weighted RMS deviation between the experimental and scaled frequencies as 4.8 cm\(^{-1}\) for MPP and 3.7 cm\(^{-1}\) for CPP. The detailed vibrational assignments of fundamental modes of the titled compounds along with calculated IR, Raman intensities and normal mode description (characterized by PED) are reported in Tables 9 and 10. For visual comparison, the observed and simulated FT-Raman and FT-IR spectra of the compounds are produced in common frequency scales in Figures 4-7.

**Table 2: Calculated thermodynamic parameters of MPP and CPP.**

<table>
<thead>
<tr>
<th>Structural parameters</th>
<th>DMP</th>
<th>DPC</th>
</tr>
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<tbody>
<tr>
<td>SCF energy (Hartrees)</td>
<td>-613.665</td>
<td>-958.735</td>
</tr>
<tr>
<td>Total energy (thermal), ( E_{\text{total}} ) (kcal mol(^{-1}))</td>
<td>170.819</td>
<td>143.746</td>
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<tr>
<td>Heat capacity at const. volume, ( C_v ) (cal mol(^{-1}) K(^{-1}))</td>
<td>49.823</td>
<td>44.301</td>
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<td>Entropy, ( S ) (cal mol(^{-1}) K(^{-1}))</td>
<td>110.425</td>
<td>104.168</td>
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<tr>
<td>Vibrational energy, ( E_{\nu,\text{vib}} ) (kcal mol(^{-1}))</td>
<td>169.042</td>
<td>141.999</td>
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<tr>
<td>Zero-point vibrational energy, ( E_0 ) (kcal mol(^{-1}))</td>
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<td>136.775</td>
</tr>
<tr>
<td>Electron negativity (( \chi ))</td>
<td>6.7234</td>
<td>6.5588</td>
</tr>
<tr>
<td>Chemical potential (( \mu ))</td>
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<td>-6.5588</td>
</tr>
<tr>
<td>Hardness (( \eta ))</td>
<td>1.8152</td>
<td>1.6693</td>
</tr>
<tr>
<td>softness (( S ))</td>
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<td>0.30</td>
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<tr>
<td>Electrophilicity index (( \omega ))</td>
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<td>12.885</td>
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<td>Rotational constants (GHz)</td>
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<td></td>
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<td>A</td>
<td>1.23635</td>
<td>1.22054</td>
</tr>
<tr>
<td>B</td>
<td>0.49138</td>
<td>0.50116</td>
</tr>
<tr>
<td>C</td>
<td>0.39461</td>
<td>0.38465</td>
</tr>
<tr>
<td>Dipole moment (Debye)</td>
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<tr>
<td>( \mu_x )</td>
<td>-0.0516</td>
<td>0.7361</td>
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<tr>
<td>( \mu_y )</td>
<td>-0.9404</td>
<td>-1.1326</td>
</tr>
<tr>
<td>( \mu_z )</td>
<td>0.5059</td>
<td>-0.0901</td>
</tr>
<tr>
<td>( \mu_{\text{total}} )</td>
<td>1.0691</td>
<td>1.3538</td>
</tr>
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</table>

**Table 3: Calculated \( \beta \) components and \( \beta_{\text{total}} \) (×10\(^{-30}\)) value of MPP and CPP.**

<table>
<thead>
<tr>
<th>( \beta ) - components</th>
<th>MPP</th>
<th>CPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta_{xx} )</td>
<td>361.944</td>
<td>-434.173</td>
</tr>
<tr>
<td>( \beta_{yy} )</td>
<td>-150.103</td>
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<td>( \beta_{zz} )</td>
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<tr>
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**Methoxy group vibrations of MPP:** One of the titled molecule MPP is a methoxyphenyl substituted compound. For the assignments of CH3 group frequencies, one can expect that nine fundamentals can be associated to CH3 group, namely CH3ss, symmetric stretch; CH3ips, in-plane stretch (i.e. in-plane hydrogen stretching mode); CH3ipb, in-plane bending, (i.e. hydrogen deformation mode); CH3sb, symmetric bending; CH3ipr, in-plane rocking; CH3opr, out-of-plane rocking; CH3ops, out-of-plane stretch; CH3opb, out-of plane bending modes and CH3 twisting modes. Among which the CH3ops, out-of-plane stretch and CH3opb, out-of plane bending modes of CH3 group would be expected to be depolarized for A* symmetry species. In addition to this TOC wagging and C–O–C in-plane bending also exist. The CH3...
symmetric and asymmetric stretching vibrations generally occur at lower frequency region 2850-3000 cm$^{-1}$. The out-of-plane stretching mode of CH$_3$ group is expected around 2980 cm$^{-1}$ and symmetric one is expected around 2870 cm$^{-1}$ [39]. For the title compound the peaks simulated at 2955, 2915 and 2879 cm$^{-1}$ are attributed to OCH$_3$ops, OCH$_3$ips, and OCH$_3$s vibrations respectively, for which only two peaks are identified in IR at 2915 cm$^{-1}$ and FT-IR at 2955 cm$^{-1}$.

The antisymmetric and symmetric deformation vibrations of methyl group normally appear in the region 1465-1440 cm$^{-1}$ and 1390-1370 cm$^{-1}$, respectively and the rocking vibrations of CH$_3$ modes usually appear in the region 1070-1010 cm$^{-1}$ [38]. Based on the above data the vibrations calculated at 1164, 1250, 1318, 1440 and 1500 cm$^{-1}$ are assigned for the vibrations OCH$_3$op, OCH$_3$ip, OCH$_3$s, OCH$_3$opb and OCH$_3$ipb, respectively. Except OCH$_3$s, all other vibrations are found in FT-Raman spectra. The torsional vibration (tOCH$_3$) evaluated at 135 cm$^{-1}$ is found in Raman spectrum at 136 cm$^{-1}$. All the experimental values agree well the simulated values.

**N-H vibrations:** Heteroaromatics containing an N-H group show N-H stretching absorption in the region of 3500–3220 cm$^{-1}$. The position of absorption within this general region depends on the degree of hydrogen bonding and hence upon the physical state of the sample or the polarity of the solvent [40]. The nitrogen and hydrogen bond present in both MPP and CPP will give rise to N–H stretching, in-plane and out-of-plane bending vibrations. In the present work, the IR band appearing at 3300 cm$^{-1}$ is designated to N–H stretching vibration of MPP. In the case of CPP, the same vibration falls at 3340 cm$^{-1}$ in Raman spectrum. Both of these assignments agree well with the simulated values. The out-of-plane mode of N–H bending vibration is calculated at 783 cm$^{-1}$ for MPP and at 788 cm$^{-1}$ for CPP, whereas the in-plane mode of N–H is determined at 1443 cm$^{-1}$ (MPP) and 1480 cm$^{-1}$ (CPP).

**C-C group vibrations:** The ring carbon–carbon stretching vibrations occur in the region 1625-1430 cm$^{-1}$. In general, these bands are of variable intensity from the wavenumber ranges given by Varsanyi [41]. The experimental and theoretical skeletal (ring CC) vibrations were assigned in the region 915-1591 cm$^{-1}$ and 941-1626 cm$^{-1}$ and are observed at 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1280 cm$^{-1}$ [42]. In the present study the C-C stretching vibrations are simulated at 1632, 1596, 1509, 1476, 1317, 1237, 981 and 915 cm$^{-1}$ for MPP and 1631, 1595, 1517, 1453, 1123, 1041, 942 and 869 cm$^{-1}$ for CPP. These vibrations are active in MPP’s IR spectrum at 1630, 1591, 1318, 1236 and 925 cm$^{-1}$ and CPP’s IR spectrum at 1590, 1452, 1120, 1040, 942 and 875 cm$^{-1}$. The computed values show good agreement with the experimental values.

**C-N and C-Cl vibrations:** The identification of C–N vibrations is a very difficult task since mixing of several bands is possible in this region [43]. However, with the help of theoretical calculations, the C–N stretching vibrations are identified and assigned in this study. Silverstein et al. [44] assigned C–N stretching absorption in the region 1382-1266 cm$^{-1}$ for aromatic amines. Pyrimidine absorb strongly in the region 1600-1500 cm$^{-1}$ due to the C=C and C=N ring stretching vibrations. Absorbance is also absorbed at 1640-1620 cm$^{-1}$, 1580-1520 cm$^{-1}$, 1000-960 cm$^{-1}$ and 825-775 cm$^{-1}$ [44]. Both the chosen molecules have five C–N stretching vibrations and they are appeared at 1177(Raman), 1155, 1136, 1031 and 945 cm$^{-1}$ (IR) for MPP. The same vibrations are found for CPP in IR at 1260, 1140 and 1054 cm$^{-1}$ and in Raman at 1130 cm$^{-1}$. One peak is absent in both the spectra of CPP. The C–N in-plane and out-of-plane bending modes are predicted at 410, 473 cm$^{-1}$ (MPP), 561, 499 cm$^{-1}$ (CPP) and 330, 303 cm$^{-1}$ (MPP), 328, 315 cm$^{-1}$ (CPP). These assignments agree well with the literature values [15].

Aliphatic C-Cl absorption is observed in the broad region between 850 and 550 cm$^{-1}$ [44]. The C-Cl stretching vibrations give generally strong bands in the region 730–580 cm$^{-1}$ [45]. Mooney [46] assigned vibrations of C–X group (X = Cl, Br, I) in the frequency range of 1129–480 cm$^{-1}$. The C–Cl deformation vibrations are expected around 460–175 cm$^{-1}$ [47]. V. Arjuman et al. [48] have assigned C–Cl in-plane bending mode at 414 cm$^{-1}$ and C–Cl out of plane bending vibration at a low frequency region of the Raman spectrum at 214 cm$^{-1}$. Accordingly, the computed vibrations at 688, 436 and 174 cm$^{-1}$ are assigned for C–Cl stretching, in-plane and out-of-plane bending vibrations. The experimental counterparts of these vibrations are found in Raman at 685, 429 and 185 cm$^{-1}$. These assignments are also supported by the literature [49-51].

**Ring vibrations:** The ring in-plane and out-of-plane bending vibrations of both MPP and CPP are assigned unambiguously with the help of PED output and Gauss view program. The small changes in frequencies observed for these modes are due to the changes in force constant/reduced mass ratio resulting mainly due to the extent of mixing between ring and substituent group.

**C-H vibrations:** The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3100–3000 cm$^{-1}$, which is the characteristic region for the ready identification of C-H stretching vibrations. In this region, the bands are not affected appreciably by the nature of the substituent [52]. In the present investigation, the FT-IR bands at 2993, 3060 cm$^{-1}$ and Raman bands at 3000, 3071 cm$^{-1}$ have been assigned to C-H stretching vibration of MPP. The theoretically computed frequency, after scaling down, coincides exactly with the observed values. In the case of CPP, for the same vibration, the bands at 3270 cm$^{-1}$ in IR and 3170, 3130 and 3070 cm$^{-1}$ in Raman are assigned. In general the C-H vibrations of MPP and CPP, calculated theoretically are in good agreement in the experimentally reported values [53,54]. In-plane aromatic C-H deformation vibrations occur in the region 1300–1000 cm$^{-1}$ [14]. The C-H in-plane bending vibrations of MPP and CPP are simulated at 1294, 1270, 1174, 1054 cm$^{-1}$ and 1162, 1183, 1245, 1378 cm$^{-1}$, respectively. The corresponding observed frequencies are tabulated in Tables 9 and 10. The C-H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm$^{-1}$ [40,54-55]. For CPP, the peaks predicted at 946, 868, 856 and 762 cm$^{-1}$ is due to C-H out-of-plane bending vibrations, which coincides well with the observed values. In MPP, the bands observed at 940 and 870 cm$^{-1}$ in Raman are assigned to C-H out-of-plane bending vibration. The two values 860 and 758 cm$^{-1}$ calculated for gCH vibrations are not found experimental spectra.

**CH$_2$ group vibrations:** The vibrational frequencies and IR intensities of CH$_2$ group are sensitive to conformational changes and nature of substituent [56]. Among the four CH$_2$ asymmetric stretching vibrations of MPP and CPP, only one is identified at 2940 cm$^{-1}$ in IR of MPP, whereas in CPP three peaks are identified in IR at 3030, 2950 and 2909 cm$^{-1}$. In MPP, the CH$_2$ symmetric stretching vibrations appears in FT-IR spectrum at 2680, 2742, 2829 cm$^{-1}$ and in FT-Raman at 2835 cm$^{-1}$. Their corresponding calculated values are predicted at 2680, 2742, 2829 and 2835 cm$^{-1}$. For CPP, the IR peaks at 2880, 2824 and 2740 cm$^{-1}$ and the Raman peak at 2780 cm$^{-1}$ are allotted for CH2SS vibration. The calculated values for the same vibration are at 2880, 2780 and 2750 cm$^{-1}$. These values match well with the literature [57-61].

The fundamental CH$_2$ vibrations due to scissoring, wagging, twisting and rocking appear in the frequency region 1500–800 cm$^{-1}$. The shift in wavenumber of these bands is due to the nature of atom and molecule groups linked to CH$_2$ [44]. Four scissoring vibrations
Temperature (K) & Entropy (J mol⁻¹ K⁻¹) & Heat capacity (C_p, J mol⁻¹ K⁻¹) & Enthalpy (KJ mol⁻¹) \\ 
MPP & CPP & MPP & CPP & MPP & CPP \\ 
100 & 310.01 & 301.71 & 89.51 & 77.27 & 5.83 & 5.26 \\ 
200 & 390.19 & 371.85 & 149.44 & 132.43 & 17.74 & 15.69 \\ 
300 & 463.47 & 437.15 & 218.11 & 194.86 & 36.04 & 32.01 \\ 
400 & 536.01 & 501.92 & 288.89 & 257.61 & 51.33 & 45.57 \\ 
500 & 607.42 & 565.48 & 351.72 & 312.40 & 93.54 & 83.25 \\ 
600 & 676.32 & 626.56 & 404.01 & 357.48 & 131.42 & 116.82 \\ 
700 & 741.94 & 684.52 & 447.09 & 394.30 & 174.04 & 154.47 \\ 
800 & 804.05 & 739.22 & 482.88 & 424.66 & 220.59 & 195.47 \\ 
900 & 862.71 & 790.75 & 512.97 & 450.04 & 270.43 & 239.24 \\ 
1000 & 918.11 & 839.30 & 538.48 & 471.47 & 323.03 & 323.03 \\ 

Table 4: The temperature dependence of thermodynamic parameters of MPP and CPP.

No (i) & Type & Definitionb \\ 
Stretching & & \\ 
1 – 5 & C – N & N1-C2, N1-C6, N4-C3, N4-C5, N1-C7. \\ 
6-13 & C – C & C2-C3, C6-C5, C7-C8, C8-C9, C9-C10, C10-C11, C11-C12, C12-C7. \\ 
18-20 & CH (Methyl) & C27-H28, C27-H29, C27-H30. \\ 
21 & N - H & N4-H17. \\ 
22-23 & C-O & C12-O26, C27-O26. \\ 
Bending & & \\ 
32-37 & bRing 1 & N1-C2-C3, C3-N4-C5, C5-C6-N1, C2-C3-N4,N4-C5-C6,C6-N1-C2 \\ 
38-43 & bRing 2 & C7-C8-C9, C8-C9-C10, C9-C10-C11, C10-C11-C12, C11-C12-C7, C12-C7-C8. \\ 
52,53 & bNH & H17-N4-C3, H17-N4-C5. \\ 
54 - 57 & bCN & C7-N1-C6, C7-N1-C2, N1-C7-C12, N1-C7-C8. \\ 
58,59 & bCO & C7-C12-O26, C11-C12-O26. \\ 
60 & bCOC & C27-O26-C12. \\ 
67 - 82 & bCH2 & N1-C2-H13, N1-C2-H14, C2-C3-H15, C2-C3-H16, C3-C2-H13, C3-C2-H14, N4-C3-H15, N4-C3-H16, N4-C5-H18, N4-C5-H19, C5-C6-H20, C5-C6-H21, C6-C5-H18, C6-C5-H19, N1-C6-H20, N1-C6-H21. \\ 
Out-of-plane bending & & \\ 
87 & gNH & H17-N4-C3-C5. \\ 
88,89 & gCN & C7-N1-C2-C6,N1-C7-C8-C12. \\ 
90 & gOCO & O26-C12-C7-C11. \\ 
Torsion & & \\ 
91-96 & fRing1 & N1-C2-C3-N4, C3-N4-C5-C6, C5-C6-N1-C2, C2-C3-N4-C5, N4-C5-C6-N1, C6-N1-C2-C3. \\ 
97-102 & fRing2 & C7-C8-C9-C10, C9-C10-C11-C12, C11-C12-C7-C8, C8-C9-C10-C11, C10-C11-C12-C7, C12-C7-C8-C9. \\ 
103-104 & fCOC & C27-O26-C12-C7,C27-O26-C12-C7. \\ 
108,109 & fphil & C6-N1-C7-C12, C2-N1-C7-C8. \\ 

*b for numbering of atom refer figure1. 
Abbreviations used: b, bending; g, deformation; t, torsion. 
Table 5: Definition of internal coordinates of MPP.

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doi:10.4172/21532435.1000391
No (i) | Type | Definition^b |
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</tr>
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<td>C – C</td>
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<td>N4-H17.</td>
</tr>
</tbody>
</table>

### Bending

28-33 | bRing 1 | N1-C2-C3, C3-N4-C5, C5-C6-N1, C2-C3-N4, N4-C5-C6, C6-N1-C2. |
| 34 - 39 | bRing 2 | C7-C8-C9, C8-C9-C10, C9-C10-C11, C10-C11-C12, C11-C12-C7, C12-C7-C8. |
| 48,49 | bNH | H17-N4-C3, H17-N4-C5. |
| 50 – 53 | bCN | C7-N1-C6, C7-N1-C2, N1-C7-C12, N1-C7-C8. |
| 54,55 | bCCI | C26-C12-C7, C26-C12-C11. |
| 56-71 | bCH2 | N1-C2-H13, N1-C2-H14, C2-C3-H15, C2-C3-H16, C3-C2-H14, N4-C3-H17, N4-C3-H18, N4-C3-H19, N5-C6-H20, C5-C6-H21, C5-C5-H18, C6-C5-H19, N1-C6-H20, N1-C6-H21. |

### Out-of-Plane Bending

72-75 | gCH | H22-C8-C7-C9, H22-C8-C9-C10, H24-C10-C9-C11, H25-C11-C10-C12. |
| 76 | gNH | H17-N4-C3-C5. |
| 77,78 | gCN | C7-N1-C2-C6, N1-C7-C8-C12. |
| 79 | gCCL | C26-C12-C7-C11. |

### Torsion

80-85 | tRing1 | N1-C2-C3-N4, C3-N4-C5-C6, C6-N1-C2-C3. |
| 92,93 | tpH2 | C6-N1-C7-C12, C2-N1-C7-C8. |

^bfor numbering of atom refer figure1. 

Abbreviations used: b, bending; g, deformation; t, torsion.

**Table 6:** Definition of internal coordinates of CPP.

<table>
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<th>No (i)</th>
<th>Symbol a</th>
<th>Definition b</th>
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The internal coordinates used here are defined in Table 5.

These symbols are used for description of the normal modes by PED in Table 9.

Table 7: Definition of local symmetry coordinates and Force constants for MPP.

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These symbols are used for description of the normal modes by PED in table 10.

The internal coordinates used here are defined in table 6.

Table 8: Definition of local symmetry coordinates and Force constants for CPP.
| 33 | - | 1350 | 1360 | 1342 | 11.84 | 3.32 |
| 34 | 1336 | - | 1346 | 1318 | 3.49 | 7.02 |
| 35 | 1318 | - | 1320 | 1317 | 61.99 | 13.29 |
| 36 | 1300 | 1300 | 1301 | 1294 | 16.75 | 1.77 |
| 37 | 1282 | 1280 | 1272 | 1270 | 18.38 | 2.12 |
| 38 | - | 1250 | 1258 | 1250 | 88.18 | 26.23 |
| 39 | 1236 | - | 1234 | 1237 | 172.97 | 35.57 |
| 40 | 1200 | 1200 | 1213 | 1205 | 17.29 | 4.30 |
| 41 | - | - | 1198 | 1204 | 0.62 | 10.12 |
| 42 | 1182 | 1177 | 1184 | 1179 | 50.57 | 4.11 |
| 43 | - | - | 1175 | 1174 | 8.59 | 5.96 |
| 44 | - | 1166 | 1166 | 1164 | 3.84 | 9.08 |
| 45 | 1155 | - | 1153 | 1155 | 17.74 | 6.28 |
| 46 | 1136 | 1140 | 1140 | 1131 | 74.90 | 1.36 |
| 47 | - | 1120 | 1119 | 1120 | 85.58 | 3.61 |
| 48 | 1118 | - | 1068 | 1090 | 22.76 | 4.91 |
| 49 | 1064 | 1055 | 1054 | 1059 | 58.90 | 3.45 |
| 50 | - | - | 1039 | 1054 | 22.39 | 35.05 |
| 51 | - | 1032 | 1050 | 3.56 | 1.37 |
| 52 | 1031 | - | 1026 | 1029 | 82.94 | 9.13 |
| 53 | - | - | 982 | 981 | 0.10 | 0.16 |
| 54 | - | 940 | 951 | 946 | 33.42 | 0.24 |
| 55 | 945 | - | 949 | 942 | 25.79 | 4.48 |
| 56 | 925 | - | 926 | 915 | 11.48 | 0.48 |
| 57 | 908 | - | 880 | 874 | 39.33 | 12.45 |
| 58 | 879 | 870 | 872 | 863 | 0.43 | 0.89 |
| 59 | - | - | 847 | 860 | 0.98 | 2.27 |
| 60 | - | 790 | 806 | 791 | 70.74 | 26.94 |
| 61 | 792 | - | 791 | 783 | 1.15 | 1.80 |
| 62 | - | - | 775 | 758 | 108.90 | 1.48 |
| 63 | - | - | 763 | 740 | 6.67 | 1.19 |
| 64 | 750 | 720 | 720 | 720 | 3.24 | 28.25 |
| 65 | - | 622 | 632 | 631 | 46.90 | 10.66 |
| 66 | 625 | 575 | 594 | 588 | 34.39 | 1.26 |
| 67 | 583 | 565 | 565 | 556 | 1.06 | 6.51 |
| 68 | 542 | 542 | 550 | 547 | 33.96 | 1.81 |
| 69 | 512 | 516 | 518 | 516 | 41.39 | 3.09 |
| 70 | 488 | - | 492 | 490 | 30.50 | 0.20 |
| 71 | 471 | 470 | 481 | 473 | 20.20 | 4.05 |
| 72 | - | 420 | 407 | 410 | 14.85 | 5.41 |
| 73 | - | 355 | 365 | 357 | 2.78 | 2.91 |
| 74 | - | - | 346 | 330 | 2.94 | 0.61 |
| 75 | - | 312 | 300 | 303 | 3.60 | 3.34 |
| 76 | - | 277 | 277 | 272 | 2.96 | 3.73 |
| 77 | - | 235 | 266 | 241 | 1.96 | 0.37 |
| 78 | - | 200 | 225 | 206 | 5.84 | 0.56 |
| 79 | - | 175 | 151 | 151 | 2.32 | 0.66 |
| 80 | - | 136 | 153 | 135 | 0.60 | 2.11 |
| 81 | - | - | 113 | 108 | 0.13 | 0.64 |

Table 9: Observed and B3LYP/ 6-311++G** level calculated vibrational frequencies (in cm\(^{-1}\)) of MPP.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Observed frequencies(cm(^{-1}))</th>
<th>Calculated frequencies (cm(^{-1})) with B3LYP/ 6-311++G** level</th>
<th>PED (%) among the internal coordinates</th>
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are calculated at 1445, 1456, 1462, and 1468 cm\(^{-1}\) for MPP and at 1473, 1477, 1485 and 1500 cm\(^{-1}\) for CPP. The CH\(_2\) scissoring frequencies observed are found to be consistent with the results of piperazine [61] and 1-phenylpiperazine [62].

For MPP the two CH\(_2\) twisting vibrations are found in FT-Raman spectrum at 1350 and 1200 cm\(^{-1}\). The other two peaks simulated at 1353 and 1204 cm\(^{-1}\) are inactive in both the spectra. Similarly only three CH\(_3\) twisting vibrations are identified for CPP in IR at 1228, 1280 and 1320 cm\(^{-1}\). All the four CH\(_2\) wagging vibrations are found in IR of CPP at 1340, 1375, 1390 and 1442 cm\(^{-1}\). In the case of MPP CH\(_3\) wagging vibrations are identified at 1390(IR), 1380 and 1350 cm\(^{-1}\)(Raman). The value simulated at 1413 cm\(^{-1}\) for the same vibration is not found in the experimental spectra. The CH\(_3\) rocking vibrations were calculated at 1059, 1050, 874 and 791 cm\(^{-1}\) for MPP and at 1091, 1073, 1070 and 925 cm\(^{-1}\) for CPP. These vibrations agree with the CH\(_3\) rocking vibrations of 1-(m- trifluoromethyl)phenyl)piperazine [15]. Thus, the DFT method is proved to be efficient for computing these vibrational modes.

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*Relative absorption intensities normalized with highest peak absorption.
*Relative Raman intensities calculated and normalized to 100.

Table 10: Observed and B3LYP/6-311++G** level calculated vibrational frequencies (in cm\(^{-1}\)) of CPP.
are gathered in Table 11. The Figures 8 and 9 depict the experimental 13C and 1H NMR spectra of MPP and CPP. The linear regression between the experimental and theoretical chemical shifts (1H and 13C NMR) of the titled compounds is calculated. The correlation coefficient of proton chemical shifts is found to be 0.975 (MPP) and 0.99 (CPP) and the same for carbon chemical shifts is found to be 1.0 (MPP) and 0.99 (CPP). 1H atom is mostly localized on periphery of the molecules and their chemical shifts would be more susceptible to intermolecular interactions in the aqueous solutions as compared to that for other heavier atoms. Aromatic carbons give signals in overlapped areas of the spectrum with chemical shift values from 100 to 150 ppm [63]. From the chemical shifts of carbon atoms listed in Table 11, it is obvious that all the carbon atoms of phenyl ring in both the molecules are in accordance with the above statement, with the exception of C27 of MPP. Since C27 is a methoxy group carbon, it experience high shielding to produce a low chemical shift value of 55.4 ppm. This value shows agreement with the literature value [64]. The C7 atom in both the atoms produce a high chemical shift than the other carbons since it is directly attached to the piperazine ring. This makes the C7 atom highly deshielded. The piperazine ring carbons C3 and C5 produce an average chemical shift of about 49.6 ppm (MPP) and 46.2 ppm (CPP), whereas C2 and C6 produce an average chemical shift of about 54.3 ppm (MPP) and 52.6 ppm (CPP). In both the molecules the H17 atom, which is attached to N4 possess the low chemical shift. It is a result of high electron cloud around the H17 atom. This value agrees with the chemical shift value of H17 atom in TFM molecule [15]. The MPP’s methoxy group hydrogen atoms show a sharp singlet peak at 3.85 ppm. The theoretical values of 1H and 13C chemical shifts are in good agreement with experimental values.

**Natural atomic charges**

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculation to molecular systems [65]. The charge distribution on the molecule has an important influence on the vibrational spectra. The natural atomic charges of MPP and CPP obtained by natural bond orbital analysis are tabulated in Table 12. In both the molecules, the electronegative nitrogen atoms are found to have high negative charge. The dominance of red colour in the MEP map around the nitrogen atoms also confirms this conclusion. The phenyl ring carbons have comparatively high negative charge than the piperazine ring carbons, except C7. The carbon atom C7 in both MPP and CPP and the methoxy group carbon C27 in MPP possess positive charge, as they delocalize their electrons to the neighbouring atoms to a greater extent. For MPP and CPP, the positive charges are localized on the hydrogen atoms. Among the hydrogen atoms in both the molecules, the H17 atom, attached with N4 atom has the highest positive value. The charge on the methoxy group hydrogens averages to 0.17. The chlorine atom of CPP effectively delocalizes its electron, which is evident from the neutral charge on the CI26 atom. The oxygen atom O26 in methoxy group of MPP has the charge value equals to -0.59.

**HOMO- LUMO**

The most important orbitals in a molecule are the frontier molecular orbitals, called HOMO and LUMO. These orbitals determine the way the molecule interacts with other species. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule [66]. The frontier molecular orbitals play an important role in the electrical and optical properties [67]. The HOMO represents the ability to donate an electron and LUMO, as an electron acceptor, represents the ability to obtain an electron. While the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap, which is important for stability of structures [68] and is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity [66]. The HOMO-LUMO orbitals computed at B3LYP/6−311++G(d,p) level for the titled compounds are illustrated in Figures 10 and 11. The Frontier orbital energy gap for MPP is 3.6304 eV and CPP is 3.3386 eV.

From Figures 10 and 11, it is evident that in the case of MPP, HOMO is localized on the phenyl and piperazine ring to a greater extent with a little contribution from the methoxy group. But in CPP, the major contribution to HOMO is from the phenyl ring and the chlorine atom. For both MPP and CPP, LUMO is localized on the phenyl ring where the piperazine ring and the substituents delocalize their charges towards the phenyl ring. The energy gap between HOMO and LUMO shows that MPP and CPP have a high band gap between the frontier molecular orbitals. A high HOMO-LUMO gap implies high kinetic stability and low chemical reactivity because it is energetically unfavorable to add electron to a high-lying LUMO by extracting electrons from low-lying HOMO [69].

**Global chemical reactivity descriptors:** Global chemical reactivity descriptors of compounds such as electronegativity (χ), chemical potential (µ), hardness (η), softness (S) and electrophilicity index (ω) are deduced from ionization potential and electron affinity values. Softness (S) is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness [70].

Using Koopman's theorem [71] for closed-shell compounds η, µ and χ can be defined as, where A and I are the ionization potential and electron affinity, respectively. Electron affinity refers to the capability of an electron to accept precisely one electron from a donor. The ionization potential is determined from I=−EHOMO, while the electron affinity is calculated from A=−ELUMO. Electrophilicity index is one of the important quantum chemical descriptors in describing reactivity and biological activities of the molecules [70,71]. It is given by

The values of electronegativity, hardness (η), softness (S) and electrophilicity index (ω) that are obtained for the titled molecules are tabulated in table 2.

**Molecular electrostatic potential (MEP)**

Molecular electrostatic potential (MEP) at a point in the space around a molecule gives an indication of the net electrostatic effect produced at that point by the total charge distribution (electron + nuclei) of the molecule and correlates with dipole moments, electronegativity, partial charges and chemical reactivity of the molecules. It is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen-bonding interactions [72-74]. MEP provides a visual method to understand the relative polarity of the molecule. The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The electrostatic potential V(r), being a real physical property can be determined experimentally by diffraction or by computational methods [75]. The Figures 12 and 13 portray the visual representation of the chemically active sites and comparative reactivity of atoms in MPP and CPP.
Figure 4: Comparison of observed and calculated FT-RAMAN spectra of MPP (a) observed and (b) calculated with B3LYP/6–311++G**.

Figure 5: Comparison of observed and calculated FT-RAMAN spectra of CPP (a) observed and (b) calculated with B3LYP/6–311++G**.

Figure 6: Comparison of observed and calculated FTIR spectra of MPP (a) observed and (b) calculated with B3LYP/6–311++G**.

Figure 7: Comparison of observed and calculated FTIR spectra of CPP (a) observed and (b) calculated with B3LYP/6–311++G**.

Figure 8: Experimental 13C and 1H NMR spectrum of MPP.

Figure 9: Experimental 13C and 1H NMR spectrum of CPP.

Figure 10: The atomic orbital compositions of the frontier molecular orbital for MPP.
As can be seen from the MEP map of the titled molecules, it is obvious that the negative potential is over the electronegative nitrogen atom N4 of the parent ring. This indicates the rich electron density around the N4 atom. The phenyl ring in both the molecules is suitable for the electrophilic attack, as it is surrounded by the red colour. The dominance of blue colour around the hydrogen atoms of piperazine ring shows that the protons of this ring are more suitable for nucleophilic attack than the phenol ring hydrogen atoms. The dominance of green colour over N1 of MPP and CPP, chlorine atom of CPP and methoxy group of MPP proves the maximum charge delocalization occurred in these atoms. This is also evident from the study of natural atomic charges.

NBO analysis

The natural bond orbital (NBO) analysis provides a description of the structure of a conformer by a set of localized bond, antibonds and Rydberg extra valence orbitals. Stabilizing interactions between filled and unoccupied orbitals and destabilizing interactions between filled orbitals can also be obtained from this analysis [76,77]. NBO analysis is used to find the interaction between the bond orbitals, electron delocalization, bond bending effect, intramolecular charge transfer (ICT) and identification of hydrogen bonding. The NBO’s obtained in this fashion correspond to the widely used lewis picture, in which two-center bonds and lone pairs are localized [78]. The larger the E (2) value, the more intensive is the interaction between electron donors and acceptors, i.e. the more electrons donating tendency from electron donors to acceptors and greater the extent of conjugation of the whole system. The intramolecular hyperconjugative interactions are formed by the orbital overlap between [σ and π (C–C, C–N and C–H) and σ* and π* (C–C, C–N and C–H)] bond orbitals which results Intermolecular Charge Transfer (ICT) causing stabilization of the system. These interactions are observed as increase in electron density (ED) in C–C, C–N and C–H antibonding orbital that weakens the respective bonds [79]. A large number of stabilizing orbital interactions are calculated in MPP and CPP and they are listed in Tables 13 and 14.

In MPP, the π electron delocalization is maximum around C7-C8 distributed to π* antibonding of C9-C10, C11-C12 with a stabilization energy of about 20.82 and 19.05 kJ mol\(^{-1}\), respectively. The other maximum stabilization energies 20.59, 19.12, 19.49 and 18.78 kJ mol\(^{-1}\) are due to the π electron delocalization around N2–C3 and C11-C10 which is distributed to π* antibonding of N1–C6, C4–C5 and C7-C8, C9-C10, respectively. In CPP, the π electron delocalization is maximum around C11-C12 distributed to π* antibonding of C7-C8 and C9-C10 with a stabilization energy of about 295.58 and 224.28 kJ mol\(^{-1}\). Here, the maximum stabilization occurs for C9-C10 (π) → C11-C12 (π*), C7-C8 (π*) and C11-C12 (π) → C7-C8 (π*), C9-C10 (π*) with a stabilization energy of about 20.93, 19.49, 19.38 and 16.76 kJ mol\(^{-1}\), respectively. The magnitude of charges transferred from MPP’s and CPP’s lone pair nitrogen LP (1) N1 shows the average stabilization energy 11.41 kJ mol\(^{-1}\).

UV analysis

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The wavelengths of absorption peaks can be correlated with the types of bonds in a given molecule and are valuable in determining the functional groups within a molecule [40]. The electronic absorption spectra of MPP and CPP have been computed with the help of the time-dependent density functional theory (TD-DFT) calculation. The observed UV-V is spectra of the chosen molecules are shown in Figures 14 and 15. The observed and calculated visible absorption maxima (λ-max) values are tabulated in Table 15, along with their respective theoretical electronic excitation energies and oscillator strength. The calculated λ-max values for MPP are 221, 237, 272 nm and the same for CPP are 221 and 263 nm. The experimental counterparts for MPP fall at 206, 236 and 277 nm. For CPP, the experimental values are found at 210 and 250 nm. These values show good agreement with the theoretical values. The observed UV-Vis bands are due to the π-π* transition [40]. Ultraviolet radiation having wavelength less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis [40].

Conclusion

The FT-IR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for the title compounds. The equilibrium geometry, harmonic vibrational frequencies, IR and Raman spectra are determined and analyzed by B3LYP/6-311++G** level of theory. The difference between the observed and calculated wave numbers is very small for most of the fundamentals. Good agreement between the simulated and observed spectra is established for the investigated compounds. The comparison of MPP and CPP has inferred that the substituents do not affect the hyperpolarizability value of the molecules to a greater extent. The compounds have similar band gap energy due to similarity in their structures. Both the compounds
Table 11: Experimental and Theoretical chemical shifts of DMP and DPC.

<table>
<thead>
<tr>
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<th>Experimental</th>
<th>MPP (ppm)</th>
<th>Experimental</th>
</tr>
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<td>53.2</td>
<td>52.3</td>
<td>52.6</td>
</tr>
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<td>49.9</td>
<td>46.5</td>
<td>46.2</td>
</tr>
<tr>
<td>C5</td>
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<td>49.2</td>
<td>46.5</td>
<td>46.2</td>
</tr>
<tr>
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<td>52.3</td>
<td>52.6</td>
</tr>
<tr>
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<td>157.3</td>
<td>142.1</td>
<td>149.7</td>
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<tr>
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<td>125.2</td>
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<tr>
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<td>121.1</td>
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<tr>
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<td>120.4</td>
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<td>152.4</td>
<td>126.8</td>
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<td>3.01</td>
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<td>3.04</td>
<td>3.04</td>
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Table 12: Natural atomic charges of MPP and CPP.

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<td>C4</td>
<td>-0.667</td>
<td>-0.682</td>
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<td>C5</td>
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<td>-0.185</td>
</tr>
<tr>
<td>C6</td>
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<td>-0.171</td>
</tr>
<tr>
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<td>0.146</td>
<td>0.157</td>
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<tr>
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<td>-0.226</td>
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<tr>
<td>C9</td>
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<td>-0.193</td>
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<tr>
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<td>0.205</td>
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<td>0.194</td>
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<td>0.352</td>
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<td>0.195</td>
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<td>0.212</td>
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<td>0.205</td>
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<td>H24</td>
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<td>0.208</td>
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<td>H30</td>
<td>0.164</td>
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**Table 13:** The Second-order perturbation energies $E(2)$ (kJ/mol) corresponding to the most important charge transfer interactions (donor-acceptor) in MPP by B3LYP/6-311++G** method.

<table>
<thead>
<tr>
<th>NBO(i)</th>
<th>Type</th>
<th>ED/e</th>
<th>NBO(j)</th>
<th>Type</th>
<th>ED/e</th>
<th>$E(2)a$ (kJ/mol)</th>
<th>$E (j)–E(i)b$ (a.u.)</th>
<th>$F (i, j)c$ (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7-C8</td>
<td>σ</td>
<td>1.96610</td>
<td>C7-C12</td>
<td>σ*</td>
<td>0.03985</td>
<td>4.40</td>
<td>1.24</td>
<td>0.066</td>
</tr>
<tr>
<td>C7-C8</td>
<td>σ</td>
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<td>C12-C126</td>
<td>σ*</td>
<td>0.03277</td>
<td>5.21</td>
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<td>0.059</td>
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<tr>
<td>C7-C8</td>
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<td>C9-C10</td>
<td>π*</td>
<td>0.34725</td>
<td>21.55</td>
<td>0.29</td>
<td>0.070</td>
</tr>
<tr>
<td>C7-C8</td>
<td>π</td>
<td>1.65066</td>
<td>C11-C12</td>
<td>π*</td>
<td>0.38668</td>
<td>18.81</td>
<td>0.27</td>
<td>0.064</td>
</tr>
<tr>
<td>C8-H22</td>
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<td>1.97543</td>
<td>C7-C8</td>
<td>π*</td>
<td>0.34767</td>
<td>18.78</td>
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<td>0.067</td>
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<td>C9-C10</td>
<td>σ</td>
<td>1.66966</td>
<td>C7-C8</td>
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<td>0.37967</td>
<td>19.49</td>
<td>0.29</td>
<td>0.066</td>
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<tr>
<td>C9-C10</td>
<td>σ</td>
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<td>C11-C12</td>
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<td>22.93</td>
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<td>1.98006</td>
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<td>π*</td>
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<td>1.07</td>
<td>0.080</td>
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<tr>
<td>C10-C11</td>
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<td>1.97120</td>
<td>C12-C126</td>
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<td>0.30377</td>
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<td>0.057</td>
</tr>
<tr>
<td>C11-C12</td>
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<td>C7-C12</td>
<td>σ*</td>
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</tr>
<tr>
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</tr>
<tr>
<td>C11-H25</td>
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</table>

* $E (2)$ means energy of hyper conjugative interaction (stabilization energy); 
* $E (j)–E(i)$ is the energy difference between donor and acceptor i and j NBO orbitals; 
* $F (i, j)$ is the Fork matrix element between i and j NBO orbitals.

**Table 14:** The Second-order perturbation energies $E(2)$ (kJ/mol) corresponding to the most important charge transfer interactions (donor-acceptor) in CPP by B3LYP/6-311++G** method.

<table>
<thead>
<tr>
<th>Excited state</th>
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<th>Theoretical</th>
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<td>CPP</td>
<td>MPP</td>
<td>CPP</td>
</tr>
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<tr>
<td>S2</td>
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<tr>
<td>S3</td>
<td>277</td>
<td>272</td>
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</table>

* $E (2)$ means energy of hyper conjugative interaction (stabilization energy); 
* $E (j)–E(i)$ is the energy difference between donor and acceptor i and j NBO orbitals; 
* $F (i, j)$ is the Fork matrix element between i and j NBO orbitals.

**Table 15:** Experimental and theoretical electronic absorption spectra values of MPP and CPP.
show high kinetic stability. The compounds show (π→ n*) transitions in the UV-Visible range. NBO result reflects the charge transfer with large stabilization energies is mainly due to the bonds C7-C8, C9-C10 in MPP and C11-C12, C9-C10 in CPP. The 1H and 13C NMR chemical shifts have been calculated and compared with the experimental one. The study of MEP map and natural atomic charges complements the detections from each other. Thus, the present investigation provides complete vibrational assignments, structural information and electronic properties of the compounds chosen.

Acknowledgement

We are thankful to Sophisticated Analytical Instrumentation Facility (SAIF), IIT Madras, Chennai, and St. Joseph’s college, Tiruchirappalli, India for providing generous support in taking spectral measurements.

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