CHAPTER - IV

Molecular Structure and Vibrational Spectra of 3-amino-5-hydroxypyrazole by Density Functional Method

Abstract

A combined experimental and theoretical study on the molecular and vibrational structure of 3-amino-5-hydroxypyrazole (3A5HP) has been reported in this Chapter. The Fourier transform infrared and Fourier transform Raman spectra of 3A5HP were recorded in the solid phase. The molecular geometry and vibrational frequencies of 3A5HP in the ground state have been calculated by using the density functional method B3LYP with basis sets, 6-311++G(d,p), 6-311+G(3df, 2p), 6-311+G(3df, 2pd), cc-pVDZ, aug-cc-pVDZ and cc-pVTZ. The optimized geometrical parameters obtained by B3LYP show best agreement with the experimental values. Intermolecular Hydrogen bonding of 3A5HP has also been studied by taking dimer and reference molecules. The theoretical spectrograms for FT-IR and FT-Raman spectra of the title molecule have been constructed.
4.1 Introduction

Pyrazole is an important heterocyclic molecule which is strongly hydrogen bonded in the solid. It is a small, five membered ring for which the vibrational spectra are not yet fully studied. Pyrazole and its derivatives have received a great deal of attention. They have a very versatile chemistry and constitute the active moieties of several biochemical systems as well as the ligands of many organometallic compounds [1]. 3-amino-5-hydroxypyrazole (3A5HP) has previously been identified as biologically active. For example, urea derivatives of 5-aminopyrazoles have recently been reported as potent inhibitors of p38 kinase [2], TNF-production [3] and cholesterol acyl transferase [4].

There have been several recently reported [5-9] vibrational studies on pyrazole. In most of these studies [5-8] only the infrared spectra of the normal and the deuterated species were presented. In some of the more recently reported [8-9] Raman studies, the spectral data in the gaseous phase were reported with particular emphasis on the N-H and C-H stretching regions. Majoube [5] utilized infrared spectra of the vapour, dilute solutions in CCl₄ and polycrystalline solids of seven N- and C-deuterated isotopic species of pyrazole to address the assignments of several bands which remained questionable from the earlier study [8].

The microwave spectra of the complete set of monosubstituted isotopic pyrazoles were recorded and a complete $r_s$ structure determined [10]. An estimated $r_s$ structure was then compared with crystal structures derived by X-ray [11-12] and neutron diffraction [13] studies. These data indicated little differences between the structural parameters obtained for the isolated molecule and those for the molecule in the crystal, except for the elongation of the N-H bond in the crystal because of hydrogen bonds and possibly one of the C-N distances.
Durig et al [14] investigated the FT-Raman spectrum of polycrystalline pyrazole with the expectation that these new data would help to address some of the questionable assignments. Recently, theoretical study on 3,5-dimethylpyrazole was reported by Orza et al [15,16]. These authors performed RHF/6-31(d) calculations and applied scale factors to correct the harmonic force field (scaled quantum mechanical method). Tentative band assignments were also made by assuming C\textsubscript{s} point group symmetry. It should be emphasized that in this calculations p-polarization function on hydrogen atoms, which are known to be very important for reproducing the out-of-plane vibrations involving hydrogen atoms have been included. It is anticipated that both ab initio HF and DFT (B3LYP and BLYP) level of theories are reliable for predicting the vibrational spectra of 3A5HP. Density functional theory calculations are also reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [17, 18].

Literature survey reveals that so far there is no complete theoretical study for 3A5HP. So in this work, the vibrational frequencies of 3A5HP in the ground state have been calculated to distinguish the fundamentals from the experimental vibrational frequencies and geometric parameters at B3LYP/ 6-311++G(d,p), 6-311+G(3df,2p), 6-311+G(3df, 2pd), cc-pVDZ, aug-cc-pVDZ and cc-pVTZ basis sets. These calculations are valuable for providing insight into the vibrational spectrum and molecular parameters.
4.2 Experimental Details

The compound 3A5HP in the light yellow powder form was obtained from Sigma-Aldrich Chemical Company, USA with a stated purity of greater than 99% and it was used as such without further purification. The FT-Raman spectrum of 3A5HP has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50-3500 cm\(^{-1}\) on a Bruker model IFS 66 V spectrophotometer. The FT-IR spectrum of this compound was recorded in the region 4000-400 cm\(^{-1}\) on Bruker IFS 66V spectrophotometer using KBr pellet technique. Spectra were collected for samples with 1000 scan accumulated for over 30 min duration. The spectral resolution after apodization was 2 cm\(^{-1}\). The observed experimental FT-IR and FT-Raman spectra of the title compound and scaled FT-IR spectra by B3LYP/6-311+G(3df, 2pd), B3LYP/6-311+G(3df, 2p) and B3LYP/aug-cc-pVDZ methods are shown in Figs. 1-3. The spectral measurements were carried out at Central Electrochemical Research Institute (CECRI), Karaikudi, Tamil Nadu.
Fig. 1 FT-IR SPECTRUM OF 3A5HP

Fig. 2 FT-RAMAN SPECTRUM OF 3A5HP
Fig. 3 Comparison of observed and computed FT-IR Spectra of 3ASHP
4.3 Computational details

DFT calculations were performed using GAUSSIAN 03W [19] program package on a Pentium IV processor personal computer without any constraint on the geometry [20]. Geometries of the monomer, dimer and model monomers and model dimers have been first optimized with full relaxation on the potential energy surfaces at HF/6-31G and the resultant geometries have been used as inputs for further calculations at DFT level. The 6-311++G(d,p), 6-311+G(3df,2p) and 6-311+G(3df,2pd) have been invoked in all the calculations. Polarization functions have been added for the better treatment of the amino group. The geometries were obtained from all-electron calculations using the B3LYP hybrid functional and Dunning’s cc-pVDZ and aug-cc-pVDZ basis sets [21], which have been found to be an accurate and computationally affordable combination [22, 23]. Additional calculations with iterative CC methods were performed with the correlation consistent polarized valence triple-zeta (cc-pVTZ) [24] basis set. Harmonic vibrational analyses have been done to determine the stationary points as minima.

4.4 Results and discussion

4.4.1 Molecular geometry

The numbering system adopted for 3A5HP is shown in Fig.4. The geometrical parameters calculated at B3LYP invoking various basis functions have been collected in Table-1. Irrespective of the type of basis set, the N1-N2 bond length of 1.372 Å is only 1.4% higher than that obtained from XRD or microwave spectroscopy. This infinitesimally higher value may be attributed to inter molecular interaction in the solid state which is obviously absent in the calculation. This noticeable variation is prevalent in other bond length values also. Comparison of calculated bond angles using different basis sets shows consistency among themselves and they do not vary appreciably from microwave results. But bond angles from crystal data vary to an extent of ~10°. The calculated dihedral angles are not more basis set sensitive. Thermodynamic properties of 3A5HP have been collected in Table-2. The dipole moment values obtained around -2.6 D further confirms the basis set independence of the calculations.
An attempt has been made to evaluate the hydrogen bond strength. For that, the
dimer shown in Fig 5 has been constructed and fully optimized and the energy difference
between the monomer and dimer has been taken to be the hydrogen bond strength, shown
in Table 3. Except B3LYP/cc-pVDZ other calculations estimate the hydrogen bond
strength around 45 kJ/mol. Attempts have been made to model this dimer for hydrogen
bond strength choosing two models, Fig 6 and Fig 7. The various geometrical parameters
of the hydrogen bond frame work are also shown. The result obtained is very low with a
hydrogen bond strength around \(\sim 28\) kJ/mol and \(\sim 22\) kJ/mol. This low value may be
attributed to the absence of resonance assisted hydrogen bonding (RAHB) [25].

Fig. 4 Numbering system adopted in 3A5HP – Monomer
Table 1 Geometrical parameters of 3A5HP (at B3LYP method)

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<th>cc-pVDZ</th>
<th>cc-pVTZ</th>
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<th>6-311+G (3df,2pd)</th>
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<td>1.330</td>
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## Table 2  Thermodynamic properties of 3A5HP (at B3LYP)

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<th>cc-pVTZ</th>
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## Table 3  Intermolecular hydrogen bond strength (kJ/mole) (at B3LYP)

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<th></th>
<th>6-311++G(d,p)</th>
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<th>cc-pVDZ</th>
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Fig. 5 3A5HP – dimer

Fig. 6 Methylenehydrazine - Model 1

Fig. 7 (E)-formohydrasonamide – Model 2
4.4.2 Vibrational assignments

The title molecule 3A5HP has 12 atoms. It has 30 normal vibrational modes. Assuming that the pyrazole ring defines a symmetry plane, i.e. that the molecule belongs to the $C_s$ point group, 21 of these modes should be symmetric, $A'$ and 9 antisymmetric, $A''$, with respect to reflection on the symmetry plane. For the atoms located in the plane of molecule, the $A'$ vibrational displacements take place in the plane of the molecule, the $A''$ modes correspond to displacement out of the plane of the molecule. All the 30 fundamental vibrations are active in both IR and Raman. The $C_s$ structure was the lowest in energy at all levels. Therefore the symmetry point group for this molecule is $C_s$, because the two of the H atoms of the NH$_2$ group are slightly out of the molecular plane.

The assignments shown in Table 4 for several of pyrazole ring modes along with substituents are briefly discussed in this chapter. The harmonic vibrational frequencies calculated for 3A5HP at B3LYP levels using basis sets cc-pVDZ, cc-pVTZ, 6-311++G(d,p), 6-311+G(3df, 2p), 6-311+G(3df, 2pd) and aug-cc-pVDZ have been collected in Table 5. However, vibrational frequencies predicted (normally overestimated) from quantum chemistry models seldom agree with the corresponding experimental frequencies due to neglect of anharmonicity in real systems. So it is customary to scale down the calculated harmonic frequencies in order to improve the agreement with the experimental data. Different scaling factors have been adopted for each basis set, shown in the note of Table 5. On the basis of calculations and recorded experimental data, it is made a reliable one to one correspondence between the fundamentals and any of the frequencies calculated by the B3LYP method. The assignments are based on the vibrational animations of fundamentals using the Gauss-View package programme [26] in all the calculations.
Table 4  Experimental FT-IR and FT-Raman frequencies and assignments for 3A5HP (cm\(^{-1}\))

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<tr>
<td>1693w</td>
<td></td>
<td>Overtone combination</td>
</tr>
<tr>
<td>1649s</td>
<td></td>
<td>C-O vibration</td>
</tr>
<tr>
<td>1604w</td>
<td>1597ms</td>
<td>NH(_2) scissoring</td>
</tr>
<tr>
<td>1565vw</td>
<td></td>
<td>C-C stretch</td>
</tr>
<tr>
<td>1554w</td>
<td></td>
<td>C-NH(_2) stretch</td>
</tr>
<tr>
<td>1532w</td>
<td></td>
<td>Overtone combination</td>
</tr>
<tr>
<td>1512s</td>
<td></td>
<td>C-N stretch</td>
</tr>
<tr>
<td>1450w</td>
<td>1456vw</td>
<td>N-H bend</td>
</tr>
<tr>
<td></td>
<td>1379m</td>
<td>C-C stretch</td>
</tr>
<tr>
<td>1317w</td>
<td>1303w</td>
<td>NH deform</td>
</tr>
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</table>

vs-very strong, s-strong, ms-medium strong, m-medium, w-weak, vw-very weak; ipb- in plane bending; opb- out of plane bending.
Table 4 (cond.,) Experimental FT-IR and FT-Raman frequencies and assignments for 3A5HP (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>FT-IR</th>
<th>FT-Raman</th>
<th>Vibrational Assignments</th>
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<tbody>
<tr>
<td>1231(\text{m})</td>
<td>C-O stretch</td>
<td></td>
</tr>
<tr>
<td>1209(\text{s})</td>
<td>(OH + NH) (\text{ipb})</td>
<td></td>
</tr>
<tr>
<td>1177(\text{w})</td>
<td>CH (\text{ipb})</td>
<td></td>
</tr>
<tr>
<td>1090(\text{vs})</td>
<td>NNC (\text{ipb})</td>
<td></td>
</tr>
<tr>
<td>1013(\text{w})</td>
<td>NH(_2) rocking</td>
<td></td>
</tr>
<tr>
<td>910(\text{vw})</td>
<td>CNN (\text{ipb})</td>
<td></td>
</tr>
<tr>
<td>840(\text{w})</td>
<td>CH (\text{opb})</td>
<td></td>
</tr>
<tr>
<td>797(\text{vs})</td>
<td>NH(_2) twisting</td>
<td></td>
</tr>
<tr>
<td>765(\text{w})</td>
<td>NH(_2) wagging</td>
<td></td>
</tr>
<tr>
<td>675(\text{m})</td>
<td>CH (\text{opb})</td>
<td></td>
</tr>
<tr>
<td>635(\text{ms})</td>
<td>Ring twist</td>
<td></td>
</tr>
<tr>
<td>515(\text{w})</td>
<td>Ring twist</td>
<td></td>
</tr>
<tr>
<td>456(\text{w})</td>
<td>C-NH(_2) (\text{ipb+ OH ipb})</td>
<td></td>
</tr>
<tr>
<td>420(\text{ms})</td>
<td>NH (\text{opb})</td>
<td></td>
</tr>
<tr>
<td>378(\text{vs})</td>
<td>NH(_2) torsion</td>
<td></td>
</tr>
<tr>
<td>306(\text{m})</td>
<td>OH (\text{opb + NH}_2) deform</td>
<td></td>
</tr>
<tr>
<td>168(\text{vw})</td>
<td>C-NH(_2) (\text{opb+ NH opb})</td>
<td></td>
</tr>
<tr>
<td>132(\text{vw})</td>
<td>Lattice vibration</td>
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</tbody>
</table>

vs-very strong, s-strong, ms-medium strong, m-medium, w-weak, vw-very weak; \(\text{ipb}\)-in plane bending; \(\text{opb}\)-out of plane bending
<table>
<thead>
<tr>
<th>Mode No.</th>
<th>cc-pVDZ</th>
<th>cc-pVTZ</th>
<th>6-311++G(d, p)</th>
<th>6-311+G(3df,2p)</th>
<th>6-311+G(3df,2pd)</th>
<th>aug-cc-pVDZ</th>
<th>Vibrational assignments</th>
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<td>1</td>
<td>203</td>
<td>201</td>
<td>168</td>
<td>198</td>
<td>207</td>
<td>202</td>
<td>γ C-NH₂ + γ C-OH</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
<td>217</td>
<td>187</td>
<td>216</td>
<td>226</td>
<td>236</td>
<td>γ O–H</td>
</tr>
<tr>
<td>3</td>
<td>248</td>
<td>253</td>
<td>228</td>
<td>246</td>
<td>260</td>
<td>244</td>
<td>γ O–H + τ NH₂</td>
</tr>
<tr>
<td>4</td>
<td>292</td>
<td>283</td>
<td>260</td>
<td>279</td>
<td>294</td>
<td>305</td>
<td>γ N-H + τ NH₂ + γ Ring</td>
</tr>
<tr>
<td>5</td>
<td>315</td>
<td>312</td>
<td>292</td>
<td>311</td>
<td>324</td>
<td>313</td>
<td>τ NH₂ + γ N-H + β CCO</td>
</tr>
<tr>
<td>6</td>
<td>431</td>
<td>422</td>
<td>394</td>
<td>418</td>
<td>436</td>
<td>428</td>
<td>γ N-H + γ Ring</td>
</tr>
<tr>
<td>7</td>
<td>461</td>
<td>460</td>
<td>432</td>
<td>459</td>
<td>478</td>
<td>457</td>
<td>β CCN + β CCO</td>
</tr>
<tr>
<td>8</td>
<td>596</td>
<td>593</td>
<td>558</td>
<td>591</td>
<td>615</td>
<td>593</td>
<td>Ring Breathing</td>
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<tr>
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<td>642</td>
<td>639</td>
<td>592</td>
<td>621</td>
<td>649</td>
<td>628</td>
<td>γ NH₂ + γ CH</td>
</tr>
<tr>
<td>10</td>
<td>659</td>
<td>652</td>
<td>605</td>
<td>644</td>
<td>671</td>
<td>647</td>
<td>γ CH + γ Ring deformation</td>
</tr>
<tr>
<td>11</td>
<td>689</td>
<td>687</td>
<td>640</td>
<td>674</td>
<td>702</td>
<td>674</td>
<td>γ CH + ω NH₂</td>
</tr>
<tr>
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<td>751</td>
<td>738</td>
<td>683</td>
<td>727</td>
<td>756</td>
<td>728</td>
<td>ω NH₂ + γ Ring deformation</td>
</tr>
<tr>
<td>13</td>
<td>780</td>
<td>763</td>
<td>714</td>
<td>757</td>
<td>787</td>
<td>759</td>
<td>β CH + Ring deformation</td>
</tr>
<tr>
<td>14</td>
<td>960</td>
<td>954</td>
<td>889</td>
<td>951</td>
<td>989</td>
<td>958</td>
<td>v CC + β NH + β Ring deformation</td>
</tr>
<tr>
<td>15</td>
<td>1020</td>
<td>1014</td>
<td>945</td>
<td>1011</td>
<td>1052</td>
<td>1017</td>
<td>β CCN + β Ring deformation</td>
</tr>
<tr>
<td>16</td>
<td>1057</td>
<td>1043</td>
<td>971</td>
<td>1035</td>
<td>1078</td>
<td>1046</td>
<td>ρ NH₂ + Ring breathing</td>
</tr>
<tr>
<td>17</td>
<td>1130</td>
<td>1117</td>
<td>1041</td>
<td>1112</td>
<td>1157</td>
<td>1124</td>
<td>β OH + β CH</td>
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<tr>
<td>18</td>
<td>1160</td>
<td>1144</td>
<td>1067</td>
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<td>1185</td>
<td>1153</td>
<td>β OH + β NH</td>
</tr>
<tr>
<td>19</td>
<td>1163</td>
<td>1160</td>
<td>1076</td>
<td>1156</td>
<td>1203</td>
<td>1158</td>
<td>β CH + ρ NH₂</td>
</tr>
<tr>
<td>20</td>
<td>1308</td>
<td>1304</td>
<td>1213</td>
<td>1297</td>
<td>1350</td>
<td>1307</td>
<td>β NH + β OH</td>
</tr>
<tr>
<td>21</td>
<td>1427</td>
<td>1405</td>
<td>1308</td>
<td>1396</td>
<td>1452</td>
<td>1417</td>
<td>β NH + υ Ring</td>
</tr>
</tbody>
</table>
Table 5 (Contd.) Vibrational wavenumbers obtained for 3A5HP at B3LYP with proper scaling factor

<table>
<thead>
<tr>
<th>Mode No.</th>
<th>cc-pVDZ</th>
<th>cc-pVTZ</th>
<th>6-311++G(d, p)</th>
<th>6-311+G(3df,2p)</th>
<th>6-311+G(3df,2pd)</th>
<th>aug-cc-pVDZ</th>
<th>Vibrational assignments</th>
</tr>
</thead>
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<tr>
<td>22</td>
<td>1492</td>
<td>1474</td>
<td>1371</td>
<td>1466</td>
<td>1525</td>
<td>1527</td>
<td>v CN + δ NH2 + β CH</td>
</tr>
<tr>
<td>23</td>
<td>1551</td>
<td>1536</td>
<td>1427</td>
<td>1528</td>
<td>1590</td>
<td>1589</td>
<td>v CN + v CC + δ NH2</td>
</tr>
<tr>
<td>24</td>
<td>1576</td>
<td>1563</td>
<td>1455</td>
<td>1555</td>
<td>1617</td>
<td>1616</td>
<td>v CC + δ NH2 + β NH</td>
</tr>
<tr>
<td>25</td>
<td>1594</td>
<td>1592</td>
<td>1486</td>
<td>1584</td>
<td>1647</td>
<td>1637</td>
<td>δ NH2</td>
</tr>
<tr>
<td>26</td>
<td>3158</td>
<td>3137</td>
<td>2923</td>
<td>3125</td>
<td>3252</td>
<td>3260</td>
<td>v CH</td>
</tr>
<tr>
<td>27</td>
<td>3395</td>
<td>3413</td>
<td>3190</td>
<td>3415</td>
<td>3547</td>
<td>3532</td>
<td>υ₃ NH₂</td>
</tr>
<tr>
<td>28</td>
<td>3485</td>
<td>3504</td>
<td>3275</td>
<td>3507</td>
<td>3645</td>
<td>3633</td>
<td>υ₄ NH₂</td>
</tr>
<tr>
<td>29</td>
<td>3556</td>
<td>3555</td>
<td>3312</td>
<td>3547</td>
<td>3686</td>
<td>3678</td>
<td>υ NH</td>
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<tr>
<td>30</td>
<td>3689</td>
<td>3706</td>
<td>3467</td>
<td>3709</td>
<td>3859</td>
<td>3836</td>
<td>υ OH</td>
</tr>
</tbody>
</table>

Scale Factors

B3LYP/cc-pVDZ = 0.97; B3LYP/aug-cc-pVDZ = 0.9704; B3LYP/cc-pVTZ = 0.9651; B3LYP/6-311++g(d,p) = 0.9089 upto 800 cm⁻¹ and 0.8992. 800 cm⁻¹ onwards: B3LYP/6-311+g(3df, 2p) = 0.9614; B3LYP/6-311+g(3df,2pd) = 1.00.

υ - stretching; υᵣ-symmetric stretching; υₐ-asymmetric stretching; β-in-plane bending; γ - out-of-plane bending; ω- wagging; ρ - rocking; t - twisting; δ - scissoring; τ - torsion.
4.4.3 N-H vibrations

Heteroaromatic molecule containing an N-H group shows its stretching absorption in the region 3500 - 3220 cm\(^{-1}\). The position of absorption in this region depends upon the degree of hydrogen bonding, and hence upon the physical state of the sample or the polarity of the solvent [27]. Primary amines examined in dilute solution display two weak absorption bands, one near 3500 cm\(^{-1}\) and the other around 3400 cm\(^{-1}\). These bands represent, respectively, the asymmetrical and symmetrical N-H stretching modes [28]. In the present work, the FT-IR band observed at 3560 cm\(^{-1}\) in 3A5HP have been assigned to N-H stretching vibrations. The theoretical calculation indicates the scaled frequency value at 3555 cm\(^{-1}\) by B3LYP/cc-pVTZ method gives an excellent agreement with this experimental observation. However the theoretically scaled value by other methods such as B3LYP/cc-pVQZ, B3LYP/aug-cc-pVQZ, B3LYP/6-311++G(d, p), B3LYP/6-311+G(3df, 2p) and B3LYP/6-311+G(3df, 2pd) deviates by about 4 cm\(^{-1}\), 118 cm\(^{-1}\) and 248 cm\(^{-1}\), 13 cm\(^{-1}\) and 126 cm\(^{-1}\) respectively for N-H stretching vibration. The vibrational assignment of this mode (no. 29) shows that they are pure stretching modes. The N-H deformation vibration calculated by B3LYP/cc-pVTZ 1304 cm\(^{-1}\) (mode no. 20) also exactly coincides with the experimental observations at 1303 cm\(^{-1}\) as a weak FT-Raman band, and the same vibration in FT-IR at 1317 cm\(^{-1}\). Calculated N-H stretching frequencies for dimer are 3337 cm\(^{-1}\) (Raman intensity 713) and 3362 cm\(^{-1}\) (IR intensity 2227), whereas for monomer is 3556 cm\(^{-1}\) in B3LYP/cc-pVDZ.

4.4.4 Phenyl ring vibrations

Many ring modes are affected by the substitution to pyrazole and pyridine rings. Due to the different substituents, pyridine ring absorbs strongly in the region 1630- 1300 cm\(^{-1}\) [29]. Pyrazole ring has several bands of variable intensities in the range of 1530-1013 cm\(^{-1}\) due to ring stretching vibrations [30]. In the present study, the FT-IR peaks observed at 1565 cm\(^{-1}\) is assigned to ring (C-C stretch) stretching vibration. The theoretically scaled value at (mode no. 24) 1555 cm\(^{-1}\) by B3LYP/6-311+G(3df,2p) and 1617 cm\(^{-1}\) by B3LYP/6-311+G(3df,2pd) methods correspond to the symmetrical stretching of the C-C double bonds of the 3A5HP ring. The pyrazole in-plane ring
deformations are observed in the region below 1000 cm⁻¹ and out-of-plane ring deformation modes in the region below 700 cm⁻¹. Again in this region it is observed that some of the modes are mixed vibrational modes as evident from calculated vibrational assignments results and also in agreement with the reported results on the present compound [31].

4.4.5 C-H vibrations

In the infrared spectrum of 3A5HP, in the region of the aromatic C-H stretchings, only one band is observed with absorption maxima at 3153 cm⁻¹. This absorption is in good agreement as far as frequencies are concerned, with the calculated ones. The same behaviour was also found in N-methylpyrazole [31]. It has to be emphasized that frequencies predicted by B3LYP/cc-pVTZ at 3137 cm⁻¹ and B3LYP/6-311+G(3df, 2p) at 3125 cm⁻¹ give excellent agreement with the experimental observations. The band corresponding to both out-of-plane and in-plane C-H deformations are observed in the region 1300-750 cm⁻¹. In 3A5HP, the FT-Raman band observed at 1177 cm⁻¹ exactly correlates with the theoretically scaled value at 1163 cm⁻¹ (mode no. 19) by B3LYP/cc-pVDZ method for C-H in-plane bending mode. The C-H out-of-plane bending mode calculated by B3LYP/6-311+G(3df,2p) method at 674 cm⁻¹ (mode no. 11) is also in excellent agreement with FT-IR experimental observations at 675 cm⁻¹.

4.4.6 NH₂ vibrations

The NH₂ group has two (N-H) stretching vibrations, one being asymmetric and other symmetric. The frequency of asymmetric vibration is higher than that of symmetric one. In the region 3700 - 3300 cm⁻¹, it is observed only two bands. The higher wavenumber band which is very intense in the IR spectrum of 3449 cm⁻¹ has been assigned to asymmetric stretch in amino group vibration. The relatively lower wavenumber band in the IR spectrum of 3326 cm⁻¹ which is also intense has been assigned to symmetric stretch amino group vibrations. These assignments find support from the work of other researchers in the case of related molecules [30]. These frequencies and ratio of intensities of the two bands are characteristic of NH₂ stretching modes.
If the two NH bonds of the NH$_2$ group are symmetric, the NH modes of vibrations satisfy an empirical relation as suggested by Bellamy and Williams [32] as

$$v_s = 345.5 + 0.876 \, v_{as}$$

where $v_s$ and $v_{as}$ are in wavenumbers. In the present case, the wavenumbers 3326 cm$^{-1}$ and 3449 cm$^{-1}$ are assigned to $v_s$ NH$_2$ and $v_{as}$ NH$_2$ stretchings respectively. It is to be noted that the validity of the empirical relationship of Bellamy and Williams suggests the symmetry nature of the two NH bonds of the NH$_2$ group in 3A5HP. The asymmetric frequency calculated at B3LYP level using cc-pVDZ basis set at 3485 cm$^{-1}$ (mode no. 28) is in satisfactory agreement with FT-IR value of 3449 cm$^{-1}$ and it is very nearer to the reported value of 3500 cm$^{-1}$ for phenylamine [33]. The symmetric frequency calculated at B3LYP level using the same basis set at 3395 cm$^{-1}$ (mode no. 27) is also in satisfactory agreement with medium FT-IR band value of 3326 cm$^{-1}$.

In addition, the NH$_2$ group has scissoring $\delta$(NH$_2$), rocking $\rho$(NH$_2$), wagging $\omega$(NH$_2$) and torsion $\tau$(NH$_2$) modes. The internal deformation vibrations known as NH$_2$ scissoring frequency obtained at B3LYP level using 6-311+G(3df, 2pd) basis sets at 1647 cm$^{-1}$ (mode no. 25) is well within the range (1650 - 1590 cm$^{-1}$) reported for aniline by Jesson and Thompson [34] and this observation is in conforming with the experimental value of 1649 cm$^{-1}$ in FT-IR spectrum. The -NH$_2$ wagging mode has been identified with the frequency at 765 cm$^{-1}$ in FT-Raman and this is in excellent agreement with the reported range of 909 - 666 cm$^{-1}$. The theoretical scaled value at 756 cm$^{-1}$ (mode no. 12) by B3LYP/6-311+G(3df, 2pd) shows an excellent agreement with the experimental data. The rocking mode predicted at 1035 cm$^{-1}$ (mode no.16) by B3LYP/6-311+G(3df, 2p) method also shows an excellent agreement with the experimental observation at 1013 cm$^{-1}$ in FT-IR. The torsional mode of NH$_2$ with frequencies at 324 cm$^{-1}$ (mode no. 5) by B3LYP/6-311+G(3df, 2pd) method satisfactorily agree with experimental data of 378 cm$^{-1}$ in FT-Raman spectra.

**4.4.7 O-H vibrations**

The O-H group gives rise to three vibrations namely stretching, in-plane bending and out-of-plane bending. The C-O group vibrations are likely to be the most sensitive to
the environment, so they show pronounced shifts in the spectra of the hydrogen-bonded species. In the case of unsubstituted phenol it has been shown that the frequency of the OH stretching vibration in the gas phase is $3657 \text{ cm}^{-1}$ [35]. In 3A5HP also a strong and broad FT-IR band observed at $3745 \text{ cm}^{-1}$ is assigned to OH stretching vibration. However scaled wavenumber by B3LYP/6-311+G(3df, 2p) method predict at $3709 \text{ cm}^{-1}$ deviating by about $36 \text{ cm}^{-1}$. The absence of broad and intense absorption in FT-IR around $3700 \text{ cm}^{-1}$ shows the presence of hydrogen bond free O-H vibration. The O-H in-plane bending vibration in phenols, in general, lies in the region $1250 - 1150 \text{ cm}^{-1}$ and is not much affected due to hydrogen bonding unlike the stretching and out-of-plane bending frequencies. In almost all 1,2,3,5-tetrasubstituted benzene derivatives with one OH and two halogen substituents, this vibration was found in a very narrow region of $1252 - 1225 \text{ cm}^{-1}$ [36]. The strong FT-Raman frequency at $1209 \text{ cm}^{-1}$ is attributed to this vibration. The theoretically computed value at $1185 \text{ cm}^{-1}$ (mode no. 18) by B3LYP/6-311+G(3df, 2pd) method satisfactorily agrees with the experimental observation.

The OH out-of-plane deformation vibration in phenol lies in the region $320 - 290 \text{ cm}^{-1}$ for the free OH and in the region $710 - 517 \text{ cm}^{-1}$ for associated OH [35]. In both intermolecular and intramolecular associations, the frequency is at a higher value than in free OH. The frequency increase with hydrogen bond strength because of the larger amount of energy required to twist the OH bond out-of-plane [37]. In the IR spectrum of solid p-nitrophenol this band is shifted to higher wavenumber ($668 \text{ cm}^{-1}$) due to intermolecular hydrogen bonding [38-40]. In 3A5HP, the FT-Raman band at $306 \text{ cm}^{-1}$ is assigned for OH out-of-plane deformation. The theoretically computed value at $240 \text{ cm}^{-1}$ by B3LYP/cc-pVDZ method deviates negatively by $66 \text{ cm}^{-1}$ with the experimental data.

### 4.4.8 Other molecular properties

Several calculated geometrical parameters for various basis sets are presented in Table – 1. Scale factors have been recommended [41] for an accurate prediction in determining the zero-point vibration energies (ZPVE), and the entropy, $S_{\text{ vib}}(T)$. The variations in the ZPVEs using different basis sets seem to be insignificant. The thermodynamic parameters viz., ZPVE, dipole moment and the change in the total entropy of 3A5HP at room temperature at different methods are also presented in Table.
Chapter IV

4.5 Conclusions

The calculated geometrical parameters were found to be in good agreement with the reported experimental data. Comparison of the observed fundamental vibrational frequencies of 3A5HP and the results calculated by density functional theory using the basis sets 6-311++G(d,p), 6-311+G(3df, 2p), 6-311+G(3df, 2pd), cc-pVDZ, aug-cc-pVDZ and cc-pVTZ shows satisfactory agreement between the experimental and theoretical values after scaling down. On the basis of the calculated results, assignments of the fundamental vibrational frequencies have been proposed. The good agreement between frequencies calculated by B3LYP/6-311+G(3df,2p) and experimental results indicate that the density functional methods are reliable and provide valuable information and understanding of the vibrational spectra of the title molecule.
References


