1. Abstract

3-Amino Pyrazole (3AP) is used as the remedial agent for the cure of cancer and cell proliferative disorders. In the present communication vibrational frequencies and the structural properties of 3AP have been investigated using Density Functional Theory (DFT) employing B3LYP exchange-correlation with high level basis set 6-311++G (d, p). The FT-IR Liquid phase (4000-400cm⁻¹) and FT-Raman spectra (4000-400cm⁻¹) of 3AP was recorded at room temperature. By following the Scaled Quantum Mechanical Force Field method (SQMFF) the task of assigning the vibrational spectra by means of Normal Coordinate Analysis (NCA) was obtained and compared with experimental FT-IR and FT-Raman spectra. The NLO properties of 3AP have been computed using quantum mechanical calculations. The Natural Bond Orbital and HOMO, LUMO analysis has also been carried out for the title compound. Thermal properties of 3AP at different temperatures have been calculated on the basis of vibrational analysis. UV-visible spectrum of the compound was recorded in the region 200-800 nm.

2. Key words

3-Amino pyrazole; DFT; FT-IR; FT-RAMAN; UV-V is Spectrum; NBO; HOMO and LUMO

3. Introduction

Pyrazole refers to a 5-membered Heterocyclic compound distinguished through three carbon atoms and two adjacent nitrogen atoms. In recent years Pyrazoles have attracted the interest of researchers in the field of medicine and agriculture. Pyrazole is a biologically active compound having the wide range of applications in pharmacological industries such as anti-inflammatory [1], antitumor [2], anticonvulsant [3], antidepressant [4] and antimicrobial [5,6] activities. It is also found Pyrazoles have widespread applications in the fields of supramolecular chemistry, crystal engineering, material sciences, sensors, biochemistry, catalysis etc. [7-14]. Pyrazole derivatives are well known fluorescent compounds with high quantum yields and are used as optical brightening agents for textiles, fabrics, plastics and papers. There have been several studies reported [15-17] for the vibrational analysis of pyrazole.

Recently Meryem Evecen et al. [18] was reported theoretical investigations on 1-(2-nitrobenzoyl) 3, 5-bis (4-methoxyphenyl)-4, 5-dihydro-¹ H-pyrazole. Vibrational spectral studies of 3, 5-dimethyl pyrazole based on density functional calculations have been done by Krishna kumar et al. [19]. Literature investigation specifies there is no absolute study of both experimental and theoretical study of 3AP compound. In the present study, we have elucidated the optimized geometrical parameters, different normal modes of 3AP. The vibrational frequencies of the compound 3AP are allotted to normal modes based on Potential Energy Distribution (PED). By Natural Bonding Orbital (NBO) analysis hyper conjugative interaction and Intermolecular Charge Transfers (ICT) are interpreted. The first order hyperpolarizability, dipole moment, HOMO and LUMO Energies of 3AP are calculated using DFT/B3LYP method using 6-311++G* basis set. Different thermodynamic properties were theoretically calculated using harmonic vibrations.

4. Experimental Details

The liquid sample of commercially available 3-Aminopyrazole was procured from sigma Aldrich chemical company (USA).
was used as such in the spectroscopic investigations. Fourier transform-infrared spectra (FT-IR) of 3AP was recorded using KBr pellet method in the region 400–4000 cm⁻¹ using a Nicolet 6700 FTIR spectrometer at a resolution of ±1 cm⁻¹ with UV or visible laser excitation with a Thermo Nicolet Continuum IR microscope. FT-Raman spectrum of the 3AP with a Nicolet Magna 750 Raman spectrometer at a resolution of 4 cm⁻¹ in spectrum range (stokes region) 4000–50 cm⁻¹ using the 1064 nm line of an Nd: YAG laser for excitation operating at 500 mW. Power operated with an InGaAs (Indium gallium arsenide) detector. UV-Vis spectrum of the compound has been using a Perkin Elmer Lambda 35 UV-Vis spectrometer. All the data were recorded after 1 cycle, with a Period of 1 nm slit width of 2 nm and a scan rate of 240 nm-min⁻¹ with the spectral resolution of 0.05–0.4 nm. The UV-V is spectrum was recorded using dimethyl sulphuric acid as solvent.

4.1. Computational details

Density functional computations were carried out using Gaussian 09 W Revision- A.02 SMP [20] using Becke’s Three-Parameter (B3LYP) hybrid DFT level applied with the typical 6-311++G** basis set to optimize the molecular geometry. The harmonic vibrational frequencies were calculated by taking the second order derivative of the energy and the predicted frequencies were scaled according to Scaled Quantum Mechanical (SQM) procedure [21–23] followed by the Potential Energy Distribution (PED) matrix. The characterization of the normal modes of 3AP was carried out through with the MOLVIB -7.0 Program using Potential Energy Distribution (PED) written by Sundius [24,25]. In order to know the intra-molecular delocalization or hyper conjugation the NBO calculations [26] were executed using NBO 3.1 program as implemented in the Gaussian 09W [20] package at the DFT/B3LYP level.

5. Results and Discussion

5.1. Molecular geometry

According to theoretical calculations the molecule 3AP has a nonplanar structure of C1 symmetry consists of 11 atoms so it has 27 normal modes of internal vibrations. The optimized structure parameters of the compound were calculated by DFT/B3LYP level with 6-311G** basis set shown in Table 1 in accordance with the atom numbering Scheme given in Figure 1.

<table>
<thead>
<tr>
<th>Bond Length</th>
<th>Value(A°)</th>
<th>Bond Angle</th>
<th>Value(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2</td>
<td>1.422</td>
<td>C1-C2-C3</td>
<td>104.422</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.380</td>
<td>C2-C3-N4</td>
<td>106.622</td>
</tr>
<tr>
<td>C3-N4</td>
<td>1.354</td>
<td>C3-N4-N5</td>
<td>113.034</td>
</tr>
<tr>
<td>N4-N5</td>
<td>1.361</td>
<td>N4-N5-C1</td>
<td>104.01</td>
</tr>
<tr>
<td>N5-C1</td>
<td>1.333</td>
<td>N5-C1-C2</td>
<td>111.907</td>
</tr>
<tr>
<td>C2-H7</td>
<td>1.079</td>
<td>N5-N4-H9</td>
<td>118.848</td>
</tr>
<tr>
<td>C3-H8</td>
<td>1.080</td>
<td>C3-N4-H9</td>
<td>128.117</td>
</tr>
<tr>
<td>N4-H9</td>
<td>1.006</td>
<td>N4-C3-H8</td>
<td>121.955</td>
</tr>
<tr>
<td>C1-N6</td>
<td>1.398</td>
<td>C1-C2-H7</td>
<td>128.067</td>
</tr>
<tr>
<td>N6-H10</td>
<td>1.013</td>
<td>C2-C1-N6</td>
<td>127.307</td>
</tr>
<tr>
<td>N6-H11</td>
<td>1.013</td>
<td>N5-C1-N6</td>
<td>120.709</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C1-N6-H10</td>
<td>123.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C1-N6-H11</td>
<td>111.231</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H10-N6-H11</td>
<td>110.476</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C3-C2-H7</td>
<td>127.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C2-C3-H8</td>
<td>131.42</td>
</tr>
</tbody>
</table>

Table 1: Optimized geometrical parameters of 3-amino Pyrazole obtained by B3LYP/6–311+G** density functional calculations.

For numbering of atoms refer to Figure 1.

The C1-N6 bond length is a longer bond length of about 1.39 Å since these bonds play a bridge role between the carbon and amino group. The density functional calculation gives shortening of angles C3-C2-C1, N4-N5-C1, N4-C3-C2 and increasing of angles, C2-C1-N5 and N5-N4-C3 from 110° exactly at the substitution and other parts of ring respectively. This asymmetry of angles reveals the conjugation with the Pyrazole ring and N-N group through a C-N double bond.

5.2. Vibrational analysis

The maximum number of active noticeable fundamental frequencies of a non-linear molecule (contains N atoms) is equal to 3N - 6 excluding three translational and three rotational degrees of freedom. Accordingly 3AP has 27 normal modes of vibrations. The 27 normal modes of the title compound is distributed amongst the symmetry Species as

Γ3N-6 = 15 (in - plane) + 12 (out - of - plane)

i.e., all the vibrations were active both in Raman scattering and infrared absorption. The A' vibration are totally symmetric and
gives rise to polarized Raman lines whereas $A'$ vibrations are antisymmetric and gives rise to depolarized Raman lines.

For the entire assignment of fundamental vibrational modes of frequencies Normal Coordinate Analyses (NCA) were carried out to the compound 3AP. For this reason, the full set of 38 typical internal coordinates (containing 11 redundancies) of the compound was presented in Table 2.

Table 2: Definition of internal coordinates of 3-aminopyrazole.

<table>
<thead>
<tr>
<th>No.(i)</th>
<th>Symbol</th>
<th>Type</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Jan</td>
<td>$R_1$</td>
<td>CN</td>
<td>C3-N4, C1-N5, C1-N6.</td>
</tr>
<tr>
<td>5-Apr</td>
<td>$P_1$</td>
<td>CC</td>
<td>C1-C2, C2-C3</td>
</tr>
<tr>
<td>7-Jun</td>
<td>$Q_1$</td>
<td>CH</td>
<td>C3-H8, C2-H7.</td>
</tr>
<tr>
<td>8</td>
<td>$r_{1}$</td>
<td>NH</td>
<td>N6-H10, N5-N6-H9</td>
</tr>
<tr>
<td>10-Sep</td>
<td>$r_{1}$</td>
<td>NH</td>
<td>N6-H10, N6-H11.</td>
</tr>
<tr>
<td>11</td>
<td>$T_1$</td>
<td>NN</td>
<td>N4-N5.</td>
</tr>
<tr>
<td>In-Plane bending</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16-Dec</td>
<td>$\beta_{ij}$</td>
<td>Ring1</td>
<td>C1-C2-C3, C2-C3-N4, C3-N4-N5, N4-N5-C1, N5-C1-C2.</td>
</tr>
<tr>
<td>17-20</td>
<td>$\sigma_{ij}$</td>
<td>CCH</td>
<td>C1-C2-H7, C3-C2-H7, C2-C3-H8, N4-C3-H8.</td>
</tr>
<tr>
<td>21-22</td>
<td>$\delta_{ij}$</td>
<td>CCN</td>
<td>C2-C1-N6, N5-C1-N6.</td>
</tr>
<tr>
<td>23-24</td>
<td>$\sigma_{ij}$</td>
<td>CNH</td>
<td>C1-N6-H10, C1-N6-H11.</td>
</tr>
<tr>
<td>25</td>
<td>$\delta_{ij}$</td>
<td>HNH</td>
<td>H10-N6-H11.</td>
</tr>
<tr>
<td>26-27</td>
<td>$r_{ij}$</td>
<td>NHN</td>
<td>N5-N4-H9, C3-N4-H9.</td>
</tr>
<tr>
<td>Out-of-plane bending</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>$\omega_{ij}$</td>
<td>CN</td>
<td>N6-C1-N5-C2.</td>
</tr>
<tr>
<td>29-30</td>
<td>$\eta_{ij}$</td>
<td>CH</td>
<td>H7-C2-C1-C3, H8-C3-C2-N4.</td>
</tr>
<tr>
<td>31</td>
<td>$\rho_{ij}$</td>
<td>NH</td>
<td>H9-N4-C3-N5.</td>
</tr>
<tr>
<td>Torsion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32-36</td>
<td>$\tau_{ij}$</td>
<td>ring1</td>
<td>C1-C2-C3-N4, C2-C3-N4-N5, C3-N4-N5-C1, C1-N6-C1-C2, C2-C3-N1-C2.</td>
</tr>
<tr>
<td>37-38</td>
<td>$\tau_{ij}$</td>
<td>NH2</td>
<td>C2-C1-N6-H10, N5-C1-N6-H11.</td>
</tr>
</tbody>
</table>

For numbering of atom refer Figure 1.

As of these, a non-redundant set of local symmetry coordinates were created by appropriate linear combinations of internal coordinates subsequent the recommendations of Fogarasi and co-workers [27] are reviewed in Table 3. The theoretically calculated DFT force fields were changed to the latter set of vibrational coordinates and used in all subsequent calculations.

The detailed fundamental vibrational modes of 3AP along with the calculated IR and Raman intensities and normal mode descriptions (characterized by PED) are reported in Table 4. By Selective scaling, the visual comparison of simulated IR and Raman spectra has shown in Figures 2 and 3, respectively.

### Table 3: Definition of local-symmetry coordinates and the values of corresponding scale factors Used to correct the B3LYP/6-31G (d,p) (refined) force field of 3-Amino Pyrazole.

<table>
<thead>
<tr>
<th>No.(i)</th>
<th>Symbol</th>
<th>Definition</th>
<th>Scale factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretching</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Jan</td>
<td>$v(C-H)$</td>
<td>R1, R2, R3</td>
<td>0.922</td>
</tr>
<tr>
<td>5-Apr</td>
<td>$v(C-C)$</td>
<td>P4, P5</td>
<td>0.922</td>
</tr>
<tr>
<td>7-Jun</td>
<td>$v(C-H)$</td>
<td>Q6, Q7</td>
<td>0.911</td>
</tr>
<tr>
<td>8</td>
<td>$v(N-H)$</td>
<td>q8</td>
<td>0.911</td>
</tr>
<tr>
<td>9</td>
<td>$v(NH2ss)$</td>
<td>(q9+q10)/2</td>
<td>0.934</td>
</tr>
<tr>
<td>10</td>
<td>$v(NH2ass)$</td>
<td>(q9+q10)/2</td>
<td>0.934</td>
</tr>
<tr>
<td>11</td>
<td>v N-N</td>
<td>T11</td>
<td>0.944</td>
</tr>
<tr>
<td>In-Plane bending</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>R2 bend1</td>
<td>$\beta_{ij} = a \times (\beta_{ij} + \beta_{ij} + \beta_{ij} + \beta_{ij})$</td>
<td>0.945</td>
</tr>
<tr>
<td>13</td>
<td>R2 bend2</td>
<td>(a - b) $\times (\beta_{ij} + \beta_{ij} + \beta_{ij} + \beta_{ij})$</td>
<td>0.945</td>
</tr>
<tr>
<td>14-15</td>
<td>bCH</td>
<td>$\sigma_{17} \times \sigma_{18}$</td>
<td>0.95</td>
</tr>
<tr>
<td>16</td>
<td>bCN</td>
<td>$\sigma_{17} \times \sigma_{18}$</td>
<td>0.964</td>
</tr>
<tr>
<td>17</td>
<td>NH2rock</td>
<td>(a-23-a 24)/2</td>
<td>0.975</td>
</tr>
<tr>
<td>18</td>
<td>NH2twist</td>
<td>(a-23-a 24)/2</td>
<td>0.975</td>
</tr>
<tr>
<td>19</td>
<td>NH2sciss</td>
<td>(2625-a 23-a 24)/2</td>
<td>0.975</td>
</tr>
<tr>
<td>20</td>
<td>bNH</td>
<td>(a-26-a 27)/2</td>
<td>0.95</td>
</tr>
<tr>
<td>Out of plane bending</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>$\omega_{CN}$</td>
<td>$\omega_{28}$</td>
<td>0.9744</td>
</tr>
<tr>
<td>22-23</td>
<td>$\omega_{CH}$</td>
<td>$\omega_{29}, \omega_{30}$</td>
<td>0.9744</td>
</tr>
<tr>
<td>24</td>
<td>$\omega_{N-H}$</td>
<td>$\omega_{31}$</td>
<td>0.9744</td>
</tr>
<tr>
<td>Torsion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>R2torsion1</td>
<td>$\rho_{32} \times \rho_{33}$</td>
<td>0.97</td>
</tr>
<tr>
<td>26</td>
<td>R2torsion2</td>
<td>$\rho_{32} \times \rho_{33}$</td>
<td>0.975</td>
</tr>
<tr>
<td>27</td>
<td>rNH2</td>
<td>$\tau_{37} + \tau_{38}$</td>
<td>0.974</td>
</tr>
</tbody>
</table>

For numbering of atom refer Figure 1.

Abbreviations: $v$, stretching; $b$, in plane bending; $\omega$, out of plane bending; $\tau$, torsion, sym, symmetric deformation, asy, asymmetric deformation, twist, twisting, rock, rocking, sciss, scissoring, ss, symmetrical stretching, ass, asymmetrical stretching.

a The symbols used for description of the normal modes by PED in Table 4.

b The internal coordinates used here are defined in Table 2.

### Table 4: Selective scaling factors of 3-Amino Pyrazole.

<table>
<thead>
<tr>
<th>s. no.</th>
<th>Experimental (cm$^{-1}$)</th>
<th>Scale factors(cm$^{-1}$)</th>
<th>Intensity</th>
<th>Characterization of normal modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-IR</td>
<td>FT-Raman</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>3451</td>
<td>0.0405</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>3404</td>
<td>0.0025</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>-</td>
<td>3327</td>
<td>0.483</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>2995w</td>
<td>3071</td>
<td>0.00026</td>
</tr>
<tr>
<td>5</td>
<td>2940w</td>
<td>2913s</td>
<td>2851</td>
<td>0.00991</td>
</tr>
<tr>
<td>6</td>
<td>2300s</td>
<td>-</td>
<td>2361</td>
<td>0.00009</td>
</tr>
<tr>
<td>7</td>
<td>1734</td>
<td>1734</td>
<td>0.0006</td>
<td>0.05</td>
</tr>
</tbody>
</table>

a = cos 144° and b = cos 72°.

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Table 4: Detailed assignments of fundamental vibrations of 3-Amino Pyrazole by normal mode analysis based on SQM force field calculations using B3LYP/6-311G**.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Wavenumber (cm⁻¹)</th>
<th>IR Intensity (Arb. Units)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(υCN)</td>
<td>2266</td>
<td>1.8</td>
<td>C-H out-of-plane bending</td>
</tr>
<tr>
<td>β(CH)</td>
<td>1382</td>
<td>1.1</td>
<td>C-H in-plane bending</td>
</tr>
<tr>
<td>ν(NH2)</td>
<td>3327</td>
<td>1.0</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>β(NH2)</td>
<td>3327</td>
<td>1.0</td>
<td>N-H in-plane bending</td>
</tr>
<tr>
<td>υ(NH)</td>
<td>3327</td>
<td>1.0</td>
<td>N-H out-of-plane bending</td>
</tr>
</tbody>
</table>

Figure 2: Potential energy surface scan for dihedral angle of 3-Amino Pyrazole.

5.2.1. RMS values of frequencies were evaluated using the following expression:

\[ \text{RMS} = \sqrt{\frac{1}{(n-1)} \sum_{i=1}^{n} (\nu_i^{\text{calc}} - \nu_i^{\text{exp}})^2} \]

The RMS error of the frequencies between the unscaled and experimental values was found to be 81.08 cm⁻¹. After scaling, the RMS error among the observed and scaled frequencies of 3AP by B3LYP/6-311+G** basis set is found to be 2.19 cm⁻¹.

5.2.2. C-H vibrations: The task of assigning carbon–hydrogen stretching mode is straightforward on the basis of the scaled ab initio predicted frequencies as well known “group frequencies”. The aromatic structure shows the presence of C-H stretching vibration in the Characteristic region of 3100–3000 cm⁻¹. In the present molecule, the expected C-H stretching vibrations observed at 3071 cm⁻¹ scaled frequency and 2995 cm⁻¹ in the FT-Raman spectrum are assigned to C2-H7 and C3-H8 Respectively. The in-plane C-H bending vibrations of benzene moreover its derivatives are examined in the region 1300–1000 cm⁻¹. The calculated frequency 1291 cm⁻¹ is assigned to C-H in-plane bending vibration and this is in good agreement with the recorded FT-IR spectrum at 1272 cm⁻¹. The computed frequency at 826 cm⁻¹ is allocated to C-H out-of-plane bending vibration. All the above assigned C-H vibrations are in good agreement with the previous literature [28].

5.2.3. N-H vibrations: The aromatic molecule containing an N-H group shows its stretching absorption in the region 3500–3200 cm⁻¹. The scaled frequency observed at 3327 cm⁻¹ is assigned to N-H stretching vibration. The strong band observed at 1272 cm⁻¹ in the FT-IR assigned to N-H in plane bending vibration.

5.2.4. Amino group vibrations: The frequencies of amino group appear around 3500-3300 cm⁻¹ for NH2 stretching, 1700-1600 cm⁻¹ for scissoring and 1150-900 cm⁻¹ for rocking deformations. The antisymmetric and symmetric stretching modes of NH2 group scaled frequencies are found at 3451 cm⁻¹, 3404 cm⁻¹ in 3AP. The weak IR bands for twisting NH2 modes of 3AP is identified at 668 cm⁻¹ and very weak Raman bands for twisting NH2 mode is identified at 667 cm⁻¹. The Experimental bands are good
agreement with the scaled frequency 667 cm$^{-1}$.

5.2.5. C-C vibrations: The ring C=C and C-C stretching vibrations known as semicircle stretching usually occurs in the region 1625–650 cm$^{-1}$ [29-31]. Pyrazole ring has several bands of variable intensities in the range of 1530-1013 cm$^{-1}$ due to ring stretching vibration [32]. In the present study 1507 cm$^{-1}$ strong band observed in the FT-IR spectrum assigned to C-C vibration and another scaled frequency 1202 cm$^{-1}$ is assigned to another C-C vibration. The calculated frequencies have 25-43% contribution to the C-C stretching vibration from PED data. These vibrations may be assigned to C2=C3 and C1-C2 bonds.

5.2.6. C-N Vibrations: The task of C-N vibrations is a difficult because the mixing of vibrations is probable in the region. Through the force field calculations, the C-N vibrations are identified and assigned in this study. The position and intensity of the C-N stretching vibrations involving the nitrogen atom of the amino group will also help to identify the availability of the C-N vibrations.

6. Polarizability and Hyperpolarizability

Investigation of organic compounds possessing conjugated p-electron structures as well as large hyperpolarizability using infrared and Raman spectroscopy has been evolved as a focus of research [33]. In the present molecule the first hyperpolarizability $\beta$, dipole moment $\mu$ and polarizability $\alpha$ was calculated using HF/6-311G (d, p) basis set on the basis of the finite-field approach. The total static dipole moment $\mu$, the mean polarizability $\alpha_0$, the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability $\beta_0$, using the x, y, z components are defined as

$$\mu = \mu_x^2 + \mu_y^2 + \mu_z^2$$  \hspace{1cm} (3)

$$\alpha_0 = \frac{\alpha_x + \alpha_y + \alpha_z}{3}$$  \hspace{1cm} (4)

$$\Delta\alpha = 2 \left[ \frac{1}{2} (\alpha_x - \alpha_y)^2 + (\alpha_y - \alpha_z)^2 + 6\alpha_z^2 \right]^{1/2}$$  \hspace{1cm} (5)

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)$$  \hspace{1cm} (6)

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$  \hspace{1cm} (7)

$$\beta_y = \beta_{yxy} + \beta_{xyy} + \beta_{yzz}$$  \hspace{1cm} (8)

$$\beta_z = \beta_{zzz} + \beta_{zzx} + \beta_{zzy}$$  \hspace{1cm} (9)

The HF/6-311G (d) calculated first hyperpolarizability of 3AP is $1.124122236\times10^{30}$ esu and the dipole moment is 0.5625 Debye are shown in Table 5. The calculated first hyperpolarizability of 3AP is about 14 times greater than that of urea. The above results show that title compound is best material for NLO applications.

<table>
<thead>
<tr>
<th>$\mu$ and $\alpha$ components</th>
<th>$\beta$ components</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_x$</td>
<td>$\beta_x$</td>
</tr>
<tr>
<td>$\mu_y$</td>
<td>$\beta_y$</td>
</tr>
<tr>
<td>$\mu_z$</td>
<td>$\beta_z$</td>
</tr>
<tr>
<td>$\mu$ (D)</td>
<td>$\beta$ tot value</td>
</tr>
<tr>
<td>$\alpha_x$</td>
<td>$\mu_x$</td>
</tr>
<tr>
<td>$\alpha_y$</td>
<td>$\mu_y$</td>
</tr>
<tr>
<td>$\alpha_z$</td>
<td>$\mu_z$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$\mu$ tot value</td>
</tr>
<tr>
<td>$\beta_0$</td>
<td>$\alpha$ tot value</td>
</tr>
</tbody>
</table>

Table 5: Calculated all $\beta$ components and $\beta$ tot value of 3-Amino Pyrazole by HF/6-31G (d, p) method.

7. NBO Analysis

The Natural Bond Orbital (NBO) computations were carried out so as to understand different second-order interactions amongst the filled orbital's of one subsystem and unfilled orbital's of a different subsystem, which is a measure of the delocalization or hyper conjugation. The interactive hyperconjugative energy is deduced from the second-order perturbation approach. For the molecule 3AP the orbital overlap between (C-C), (N-H), (C-H), (N-N) and (C-C), (N-H), (C-H), (N-N) antibond orbital are formed due to intramolecular hyper conjugative interactions. Moreover intramolecular charge transfer (ICT) happens which causes the stabilization of the system. For every donor (i) also acceptor (j), the stabilization energy $E (2)$ joined through the delocalization $i\rightarrow j$ is predictable as

$$E^{(2)} = \Delta E_j = [q_i (F_j^2)] \ [\epsilon_i - \epsilon_j]$$  \hspace{1cm} (10)

Where $q_i$ is the $i^{th}$ donor orbital occupancy, $\epsilon_i$, $\epsilon_j$ are diagonal elements and $F_j$ is the off diagonal elements of the NBO matrix.

The interactions among the lone-pair orbital's and their C-C and C-N filled orbital's are the large energetic repulsions. From the Table 6, the interaction among the lone pair N4 (1) and the antibond C2-C3 is seen to present the strongest stabilization, 44.34kcal/mol. This larger energy proves the hyper conjugation among the electron donating groups and the Pyrazole ring.
Table 6: Second order perturbation theory analysis of fock matrix in NBO basis for 3-Amino Pyrazole.

<table>
<thead>
<tr>
<th>Donor(i)</th>
<th>Type</th>
<th>E(d)</th>
<th>Acceptor(j)</th>
<th>Type</th>
<th>E(d)</th>
<th>E(2) E(2) kJ mol⁻¹</th>
<th>E(i)-E(j) a.u</th>
<th>f(i,j) a.u</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-C2</td>
<td>σ</td>
<td>1.97663</td>
<td>C2-C3</td>
<td>σ'</td>
<td>0.0993</td>
<td>1.69</td>
<td>1.25</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.97663</td>
<td>C3-H8</td>
<td>σ'</td>
<td>0.01355</td>
<td>5.17</td>
<td>1.14</td>
<td>0.069</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.97663</td>
<td>N6-H11</td>
<td>σ'</td>
<td>0.00804</td>
<td>1.9</td>
<td>1.14</td>
<td>0.042</td>
</tr>
<tr>
<td>C1-N5</td>
<td>σ</td>
<td>1.98471</td>
<td>C1-C2</td>
<td>σ'</td>
<td>0.02919</td>
<td>1.66</td>
<td>1.35</td>
<td>0.042</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.98471</td>
<td>C2-H7</td>
<td>σ'</td>
<td>0.01104</td>
<td>2.04</td>
<td>1.31</td>
<td>0.046</td>
</tr>
<tr>
<td>C1-N5</td>
<td>σ</td>
<td>1.8811</td>
<td>C2-C3</td>
<td>σ'</td>
<td>0.36541</td>
<td>11.49</td>
<td>0.32</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.8811</td>
<td>N6-H10</td>
<td>σ'</td>
<td>0.00717</td>
<td>1.23</td>
<td>0.76</td>
<td>0.028</td>
</tr>
<tr>
<td>C2-C3</td>
<td>σ</td>
<td>1.97548</td>
<td>C1-C2</td>
<td>σ'</td>
<td>0.02919</td>
<td>1.72</td>
<td>1.23</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>σ</td>
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<td>C1-N6</td>
<td>σ'</td>
<td>0.02366</td>
<td>6.45</td>
<td>1.14</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.97548</td>
<td>N4-H9</td>
<td>σ'</td>
<td>0.01673</td>
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<td>1.16</td>
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</tr>
<tr>
<td>C2-C3</td>
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<td>1.8262</td>
<td>C1-N5</td>
<td>σ'</td>
<td>0.44246</td>
<td>27.91</td>
<td>0.28</td>
<td>0.084</td>
</tr>
<tr>
<td>C2-H7</td>
<td>σ</td>
<td>1.98384</td>
<td>C1-N5</td>
<td>σ'</td>
<td>0.01963</td>
<td>2.45</td>
<td>1.08</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>σ</td>
<td>1.98384</td>
<td>C3-N4</td>
<td>σ'</td>
<td>0.0295</td>
<td>1.85</td>
<td>1.02</td>
<td>0.039</td>
</tr>
<tr>
<td>C3-N4</td>
<td>σ</td>
<td>1.9918</td>
<td>C2-H7</td>
<td>σ'</td>
<td>0.01104</td>
<td>3.17</td>
<td>1.32</td>
<td>0.058</td>
</tr>
<tr>
<td>C3-H8</td>
<td>σ</td>
<td>1.98504</td>
<td>C1-C2</td>
<td>σ'</td>
<td>0.02919</td>
<td>1.44</td>
<td>1.1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>N4-N5</td>
<td>σ'</td>
<td>0.01457</td>
<td>3.57</td>
<td>0.95</td>
<td>0.052</td>
</tr>
<tr>
<td>N4-N5</td>
<td>σ</td>
<td>1.88411</td>
<td>C1-N6</td>
<td>σ'</td>
<td>0.02366</td>
<td>6</td>
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<td>0.076</td>
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<tr>
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<td>σ</td>
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<td>C3-H8</td>
<td>σ'</td>
<td>0.01355</td>
<td>2.27</td>
<td>1.3</td>
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</tr>
<tr>
<td>N4-H9</td>
<td>σ</td>
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<td>C1-N5</td>
<td>σ'</td>
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<td>1.24</td>
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<tr>
<td></td>
<td>σ</td>
<td>1.99106</td>
<td>C2-C3</td>
<td>σ'</td>
<td>0.00913</td>
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<tr>
<td>N6-H10</td>
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<td>1.98338</td>
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<td>0.01963</td>
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<td>1.17</td>
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<tr>
<td></td>
<td>σ</td>
<td>1.98338</td>
<td>C1-N5</td>
<td>σ'</td>
<td>0.44246</td>
<td>1.94</td>
<td>0.65</td>
<td>0.036</td>
</tr>
<tr>
<td>N6-H11</td>
<td>σ</td>
<td>1.98749</td>
<td>C1-C2</td>
<td>σ'</td>
<td>0.02919</td>
<td>5.38</td>
<td>1.16</td>
<td>0.071</td>
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<td>LP</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N4(1)</td>
<td></td>
<td>1.58956</td>
<td>C1-N5</td>
<td>σ'</td>
<td>0.44246</td>
<td>24.99</td>
<td>0.28</td>
<td>0.076</td>
</tr>
<tr>
<td>N5(1)</td>
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<td>1.94369</td>
<td>C1-C2</td>
<td>σ'</td>
<td>0.36541</td>
<td>44.34</td>
<td>0.29</td>
<td>0.102</td>
</tr>
<tr>
<td>N6(1)</td>
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<td>C1-N5</td>
<td>σ'</td>
<td>0.44246</td>
<td>26.48</td>
<td>0.32</td>
<td>0.089</td>
</tr>
</tbody>
</table>

8. HOMO-LUMO Energy Gap and UV-Vis Spectrum

Several organic molecules having conjugated π electron are expressed by huge values of first order hyperpolarizabilities are investigated by means of vibrational spectroscopy [34].The molecules are described by a small highest occupied molecular orbital-lowest unoccupied molecular orbital separation. The HOMO and LUMO topologies gives definite overlap of two orbital's in the middle region of the π -conjugated systems, this is a requirement to allow an efficient charge transfer transition. The HOMO-LUMO energy gap determined by B3LYP/6-311++G** method are shown in Table 7. The HOMO-LUMO gap has been calculated as6.36284143eV and is shown in figure 5. The Visualization of the molecular orbital's [MO: 15-MO: 30] of 3-Amino Pyrazole under C1 symmetry is shown in figure 6. The experimental UV-Vis spectrum is shown in figure 7 and value of λ maxis 257.65 nm.

Table 7: The calculated quantum chemical parameters for 3-aminopyrazole obtained by B3LYP/6-311G** calculations.

<table>
<thead>
<tr>
<th>Property</th>
<th>3-aminopyrazole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy (a.u)</td>
<td>-1</td>
</tr>
<tr>
<td>EHOMO(eV)</td>
<td>-5.446089</td>
</tr>
<tr>
<td>ELUMO(eV)</td>
<td>0.916752</td>
</tr>
<tr>
<td>EHOMO-ELUMO(eV)</td>
<td>-6.362841</td>
</tr>
<tr>
<td>Electronagativity (eV)</td>
<td>2.264668</td>
</tr>
<tr>
<td>Chemical hardness(eV)</td>
<td>-3.18142</td>
</tr>
<tr>
<td>Electorofility index(eV)</td>
<td>-0.806043</td>
</tr>
<tr>
<td>Global Softness(eV)</td>
<td>-0.314324</td>
</tr>
<tr>
<td>Total energy change(ΔET)</td>
<td>0.759355</td>
</tr>
<tr>
<td>Dipole moment(D)</td>
<td>0.5625</td>
</tr>
</tbody>
</table>
9. Thermo Dynamic Properties

On the basis of vibrational analyses and statistical thermodynamics, the standard thermodynamic functions such as heat capacity, internal energy, entropy and enthalpy are calculated and are listed in Table 8. As observed from Table 8, the values of CP, CV, U, H and S all increase with the increase of temperature from 50 to 500 K, which is attributed to the enhancement of the molecular vibration as the temperature increases.

10. Molecular Electrostatic Potential

The Molecular Electrostatic Potential (MEP) is determined over the entire accessible surface of the molecules (this corresponds with the Van der Waals contact surface). The positive electrostatic potential regions indicate an excess of positive charge, while the negative potential regions indicate areas with an excess of negative charge. The MEP of 3-amino pyrazole is obtained based on the DFT optimized result and shown in Figure 8.

Table 8: Thermo dynamical parameters of 3-Amino Pyrazole.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CV (J/K/mol)</th>
<th>CP (J/K/mol)</th>
<th>U (kJ/mol)</th>
<th>H (kJ/mol)</th>
<th>S (J/K/mol)</th>
<th>G (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>63.226</td>
<td>73.8415</td>
<td>552.495</td>
<td>549.795</td>
<td>362.458</td>
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<td>105.344</td>
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<td>560.265</td>
<td>353.094</td>
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<td>566.362</td>
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<td>574.238</td>
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<td>484.812</td>
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<td>664.476</td>
<td>666.823</td>
<td>688.903</td>
<td>314.287</td>
</tr>
</tbody>
</table>

References


6. Kumar S, Meenakshi, Kumar S, Kumar P. Synthesis and antimicrobial activity of some (3-phenyl-5-(1-phenyl-3-aryl-1H-pyrazol-4-yl)-4,5-


