Investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of Diphenylacetylene Molecule

C. C. SANGEETHA 1, R. MADIVANANE 2, V. POUCHANAME 3

1* Department of Physics, Manonmaniyam Sundaranar University, Tirunelveli, Tamilnadu, India.
2 Department of Physics, Bharathidasan Government College for Women, Puducherry, India.
3 Department of Chemistry, Bharathidasan Government College for Women, Puducherry, India.

Corresponding author: carosangee@gmail.com

Abstract

FT-IR and FT-Raman spectra of Diphenylacetylene were recorded and analyzed in the region 3700–0 cm⁻¹. Molecular modeling of the compound was completed by the density functional theoretical (DFT) method using Becke’s three parameter exchange functional combined with the Lee–Yang–Parr correlation functional with 6-311++G(d,p) as basis set. The computed values of frequencies were scaled using a suitable scale factor to yield good coherence with the observed values. The linear polarizability (α) and the first order hyperpolarizability (β) values and its related properties (α₀, µ and Δα) of the investigated molecule have been computed using DFT quantum mechanical calculations. The energy and oscillator strength calculated by time-dependent density functional theory (TD-DFT) results complements with the experimental findings. The ¹H nuclear magnetic resonance (NMR) chemical shifts of the molecule were calculated by GIAO method. The thermodynamic functions of the title compound have been performed.

Introduction

Diphenylacetylene is the molecule consists of phenyl groups attached to both ends of alkyne [1]. It is a colorless crystalline material with molecular weight 178.23g/mol. This molecule is widely used as a building block in organic and as a ligand in organo metallic chemistry and in the pharmaceutical field. Jim et.al., were study the Production of 6-Phenylacetylene Picolinic Acid from Diphenylacetylene by a Toluene-Degrading Acinetobacter Strain[2]. Their result shows the potential for using the normal growth substrate to provide energy and to maintain induction of the enzymes involved in biotransformation during preliminary stages of biocatalyst development. Rahmat Hidayat et al., were studied the Photoluminescence and Electroluminescence in Polymer Mixture of Poly (alkylphenylacetylene) and Poly (Diphenylacetylene) Derivatives [3]. Han, Dong Cheul et al., were reported the Improvement of Operation Lifetime in Organic Solar Cell Coated with Diphenylacetylene Polymer Film. The Diphenylacetylene polymer film significantly improved the operation lifetime of the Organic Solar Cell by efficiently absorbing the UV light, while reducing the UV-light energy loss to a minimum by converting the UV light to visible light through a down-conversion process [4].

To the best of our knowledge, neither quantum chemical calculation, nor the vibrational spectra of Diphenylacetylene (DPA) have been reported. Therefore, the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various modes with greater wavenumber accuracy. Density functional theory (DFT) and Hartree Fock (HF) calculations have been performed to support our wavenumber assignments. Hence, in the present work, a detailed vibrational analysis,
Investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of Diphenylacetylene Molecule

SANGEETHA C. C., R. MADIVANANE, V. POUCHANAME

Chemical shifts, HOMO–LUMO, Mulliken atomic charge, thermodynamic studies, NMR spectral analysis and UV-Visible spectral analysis has been attempted using DFT/B3LYP and HF methods at 6-311++G(d,p) basis set. FT-IR and FT-Raman spectra of the compound.

**Experimental details**

The samples Diphenylacetylene was purchased from Sigma–Aldrich Company (USA) with a stated purity 98% and it was used as such without further purification. The FTIR spectrum of Diphenylacetylene was recorded in the region 3700–0 cm\(^{-1}\) recorded by KBr pellet on a Burkerr 1 FS 66 v Spectrometer equipped with a global source, Ge/KBr beam splitter and a TGs detector. The FT–Raman spectrum of the compound also recorded in the range 0-3700 cm\(^{-1}\) using the same instrument with FRA 106 Raman module equipped with Nd: YAG laser source. The frequencies of all sharp bands are accurate to 2 cm\(^{-1}\). The ultraviolet absorption spectrum of the tested molecule has been examined in the range 200–400 nm using Shimadzu UV-1800 PC, UV–Vis recording Spectrometer. Data are analyzed by UV PC personal spectroscopy software, version 3.91. NMR experiments were performed in Bruker DPX 400 MHz at 300 K. The compound was dissolved in CDCl\(_3\). Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) for \(^1\)H NMR spectra of Diphenylacetylene.

**Quantum chemical calculations**

The density functional theory [5] treated according to hybrid Becke’s three parameter and the Lee–Yang–Parr functional (B3LYP) [6-8] functional were used to carry out ab initio analysis with the standard 6-311++G (d,p) basis sets to study the molecule Diphenylacetylene. All calculations were carried out using Gaussian 09 package [9]. Using the version 8 of Gaussian 09W (revision B.01) program, the DFT calculation of the title compound was carried out on Intel Core2Duo/2.20 GHz processor. For the simulated IR and Raman spectra pure Lorentzian band shapes with the band width of 10 cm\(^{-1}\) was employed using the Gabedit Version 2.32 [10]. The animation option of the Gauss view 05 graphical interface for Gaussian program was employed for the proper assignment of the title compound and it was also used to visualize vibrational modes of the title compound and to check whether the mode was pure or mixed [11-14]. An empirical uniform scaling factor of 0.98 and 0.97 [15, 16] were used to offset the systematic errors caused by basis set incompleteness, neglect of electron correlation and vibrational anharmonicity [17]. After scaled with scaling factor, the deviation from the experiments is less than 10cm\(^{-1}\) with a few exceptions. The mean polarizability properties of tested molecules were obtained from the theoretical calculations to show the NLO property of the molecules. The thermodynamic properties of tested molecules, such as heat capacity, entropy, and enthalpy were investigated for the different terms from the vibrational frequency calculations of title molecule. The energy of highest occupied molecular orbit (\(E_{\text{HOMO}}\)) and the energy of Lowest unoccupied Molecular Orbital (\(E_{\text{LUMO}}\)) the dipole moment (\(\mu\)), the ionization potential (I), the electron affinity (A), the electro negativity (X), the global hardness (\(\eta\)) were calculated for both the molecules and the comparison also discussed. The electronic absorption spectrum requires calculation of the allowed excitations and oscillator strengths. The theoretical UV–vis spectra have been compared with the experimental spectra for the molecule. These calculations are based on both TD-DFT methods with 6-311++G (d,p) basis set. \(^1\)H NMR chemical shifts are calculated with gauge included atomic orbital (GIAO) approach [18, 19] by applying B3LYP/6-
311++G(d,p) method and compared with the experimental NMR spectra of DPA molecule.

Results and Discussion

Molecular geometry

The geometrical structure along with numbering of atoms of Diphenylacetylene is obtained from Gaussian 03W and GAUSSVIEW programs are shown in Fig.1.

The optimized geometrical parameters of DPA obtained by DFT–B3LYP/6-311++G (d,p) and HF/6-311++G(d,p) levels are listed in Table 1. From the structural data given in Table 3, it is observed that the various bond lengths are found to be almost same at HF and B3LYP levels. However, the B3LYP/6-31++G (d,p) level of theory, in general slightly over estimates bond lengths but it yields bond angles in excellent agreement with the HF method. The calculated geometric parameters can be used as origin to calculate the other parameters for the compound. The calculated C–C bond lengths of the ring vary from 1.39 to 1.42 Å. In this study the C-H bond lengths were studied as 1.08 Å. The density functional calculation gives almost same bond angles in tested molecule. The dihedral angles of our title molecule show that our tested molecule was planar. In generally the optimized bond length and bond angles are slightly smaller than the experimental values. This is due to the fact that all the theoretical calculations belongs to isolated molecule were done in gaseous state and the experimental results were belongs to molecule is in solid state.

![Fig. 1: Optimized molecular structure of Diphenylacetaline.](image)

Table 1 (a): Comparison of the geometrical parameter bond lengths (in angstrom) of Diphenylacetaline

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DFT(B3LYP) 6-311++G (d-p)</th>
<th>HF 6-311++G (d-p)</th>
<th>Parameters</th>
<th>DFT(B3LYP) 6-311++G (d-p)</th>
<th>HF 6-311++G (d-p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOND LENGTH</td>
<td></td>
<td></td>
<td>BOND LENGTH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1C-2C</td>
<td>1.4073</td>
<td>1.3926</td>
<td>8C-9C</td>
<td>1.4233</td>
<td>1.4391</td>
</tr>
<tr>
<td>1C-6C</td>
<td>1.4073</td>
<td>1.3928</td>
<td>9C-10C</td>
<td>1.4073</td>
<td>1.3929</td>
</tr>
<tr>
<td>1C-7C</td>
<td>1.4233</td>
<td>1.4391</td>
<td>9C-14C</td>
<td>1.4073</td>
<td>1.3924</td>
</tr>
<tr>
<td>2C-3C</td>
<td>1.3902</td>
<td>1.3832</td>
<td>10C-11C</td>
<td>1.3902</td>
<td>1.3828</td>
</tr>
<tr>
<td>2C-15H</td>
<td>1.0834</td>
<td>1.0744</td>
<td>10C-23H</td>
<td>1.0833</td>
<td>1.0745</td>
</tr>
<tr>
<td>3C-4C</td>
<td>1.3951</td>
<td>1.3858</td>
<td>11C-12C</td>
<td>1.395</td>
<td>1.3862</td>
</tr>
<tr>
<td>3C-17H</td>
<td>1.0842</td>
<td>1.0754</td>
<td>11C-21H</td>
<td>1.0842</td>
<td>1.0754</td>
</tr>
<tr>
<td>4C-5C</td>
<td>1.395</td>
<td>1.3859</td>
<td>12C-13C</td>
<td>1.3951</td>
<td>1.3855</td>
</tr>
</tbody>
</table>
Vibrational analysis

The vibrational spectrum is mainly determined by the modes of free molecule observed at higher wavenumbers, together with the lattice (translational and vibrational) modes in the low wavenumber region. In our present study, we have performed a frequency calculation analysis to obtain the spectroscopic signature of Diphienyacylene. The DPA molecule consists of 24 atoms therefore they have 66 vibrational normal modes. All the frequencies are assigned. The measured (FTIR and FT-Raman) wavenumbers and assigned wavenumbers of the some selected intense vibrational modes

Table 1 (b): Comparison of the geometrical parameter bond angles (in degrees) of Diphenylacetaline.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DFT (B3LYP) 6-311++G (d-p)</th>
<th>HF 6-311++G (d-p)</th>
<th>Parameters</th>
<th>DFT (B3LYP) 6-311++G (d-p)</th>
<th>HF 6-311++G (d-p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2C-1C-6C</td>
<td>118.7344</td>
<td>119.2529</td>
<td>10C-9C-14C</td>
<td>118.7338</td>
<td>119.2539</td>
</tr>
<tr>
<td>2C-1C-7C</td>
<td>120.638</td>
<td>120.365</td>
<td>9C-10C-11C</td>
<td>120.4424</td>
<td>120.2644</td>
</tr>
<tr>
<td>6C-1C-7C</td>
<td>120.6276</td>
<td>120.3822</td>
<td>9C-10C-23H</td>
<td>119.1666</td>
<td>119.4379</td>
</tr>
<tr>
<td>1C-2C-3C</td>
<td>120.4249</td>
<td>120.2644</td>
<td>11C-10C-23H</td>
<td>120.3909</td>
<td>120.2977</td>
</tr>
<tr>
<td>1C-2C-15H</td>
<td>119.166</td>
<td>119.4447</td>
<td>10C-11C-12C</td>
<td>120.3413</td>
<td>120.2164</td>
</tr>
<tr>
<td>3C-2C-15H</td>
<td>120.3911</td>
<td>120.2908</td>
<td>10C-11C-21H</td>
<td>119.6121</td>
<td>119.6891</td>
</tr>
<tr>
<td>2C-3C-4C</td>
<td>120.3412</td>
<td>120.2167</td>
<td>12C-11C-21H</td>
<td>120.0466</td>
<td>120.0945</td>
</tr>
<tr>
<td>2C-3C-17H</td>
<td>119.613</td>
<td>119.6818</td>
<td>11C-12C-13C</td>
<td>119.6982</td>
<td>119.7866</td>
</tr>
<tr>
<td>4C-3C-17H</td>
<td>120.0459</td>
<td>120.1014</td>
<td>11C-12C-20H</td>
<td>120.1513</td>
<td>120.1014</td>
</tr>
<tr>
<td>3C-4C-5C</td>
<td>119.6988</td>
<td>119.7871</td>
<td>13C-12C-20H</td>
<td>120.1505</td>
<td>120.1121</td>
</tr>
<tr>
<td>3C-4C-19H</td>
<td>120.1504</td>
<td>120.1078</td>
<td>12C-13C-14C</td>
<td>120.3414</td>
<td>120.2149</td>
</tr>
<tr>
<td>5C-4C-19H</td>
<td>120.1508</td>
<td>120.1051</td>
<td>12C-13C-22H</td>
<td>120.0466</td>
<td>120.1057</td>
</tr>
<tr>
<td>4C-5C-6C</td>
<td>120.3413</td>
<td>120.2143</td>
<td>14C-13C-22H</td>
<td>119.612</td>
<td>119.6793</td>
</tr>
<tr>
<td>4C-5C-18H</td>
<td>120.0477</td>
<td>120.1005</td>
<td>9C-14C-13C</td>
<td>120.4429</td>
<td>120.2637</td>
</tr>
<tr>
<td>6C-5C-18H</td>
<td>119.611</td>
<td>119.6852</td>
<td>9C-14C-24H</td>
<td>119.1653</td>
<td>119.4488</td>
</tr>
<tr>
<td>1C-6C-5C</td>
<td>120.4414</td>
<td>120.2646</td>
<td>13C-14C-24H</td>
<td>120.3918</td>
<td>120.2874</td>
</tr>
<tr>
<td>1C-6C-16H</td>
<td>119.1665</td>
<td>119.4434</td>
<td>&quot;1C-7C-8C-6C—1C&quot;</td>
<td>179.9991</td>
<td>180.0277</td>
</tr>
<tr>
<td>5C-6C-16H</td>
<td>120.3921</td>
<td>120.292</td>
<td>&quot;7C-8C-9C-14C-1C&quot;</td>
<td>179.9945</td>
<td>179.9884</td>
</tr>
<tr>
<td>8C-9C-10C</td>
<td>120.6332</td>
<td>120.3648</td>
<td>&quot;1C-7C-8C-6C—2C&quot;</td>
<td>180.004</td>
<td>180</td>
</tr>
<tr>
<td>8C-9C-14C</td>
<td>120.6331</td>
<td>120.3814</td>
<td>&quot;7C-8C-9C-14C—2C&quot;</td>
<td>179.9889</td>
<td>180</td>
</tr>
</tbody>
</table>
calculated at the B3LYP and HF levels using basis set 6-311++G(d,p) basis set and they are listed in Table 2. For B3LYP and HF with 6-311++G(d,p) basis set, the wavenumbers are scaled with 0.99 and 0.98 respectively\cite{20}. This reveals good correspondence between theory and experiment in main spectral features. The experimental and theoretical FTIR and FT-Raman spectra are shown in Figs. 2 and 3.

The C–C stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm\(^{-1}\). The aromatic ring modes are influenced more C-C bands \cite{21-23}. Therefore, the C–C stretching vibrations of the title compound are found at 1602, 1575, 1456, 1386, 1288, 1243 cm\(^{-1}\) in FTIR and 1572, 1460, 1382, 1290, 1240 cm\(^{-1}\) in the FT-Raman spectrum and these modes are confirmed by their TED values. The theoretically computed values for C–C vibrational modes by B3LYP/6-31+G(d,p) method gives excellent agreement with experimental data. In the present work the bands occurring at 1007 and 720 cm\(^{-1}\) in Raman spectrum are assigned to the CCC in-plane trigonal bending and ring breathing vibrations, respectively. These frequencies appear in the respective range \cite{24-26}. The C–C–C trigonal bending and ring breathing modes of benzene ring are attributed to the strong bands 923 and 848 cm\(^{-1}\). The normal coordinate analysis predicts that the C–C–C in plane bending vibrations significantly mixed with the C–H in-plane bending modes \cite{27}. The ring C=C stretching vibrations, known as semicircle stretching usually occur in the region 1400–1625 cm\(^{-1}\)\cite{28, 29}.

The C–C stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm\(^{-1}\). The aromatic ring modes are influenced more C-C bands \cite{21-23}. Therefore, the C–C stretching vibrations of the title compound are found at 1602, 1575, 1456, 1386, 1288, 1243 cm\(^{-1}\) in FTIR and 1572, 1460, 1382, 1290, 1240 cm\(^{-1}\) in the FT-Raman spectrum and these modes are confirmed by their TED values. The theoretically computed values for C–C vibrational modes by B3LYP/6-31+G(d,p) method gives excellent agreement with experimental data. In the present work the bands occurring at 1007 and 720 cm\(^{-1}\) in Raman spectrum are assigned to the CCC in-plane trigonal bending and ring breathing vibrations, respectively. These frequencies appear in the respective range \cite{24-26}. The C–C–C trigonal bending and ring breathing modes of benzene ring are attributed to the strong bands 923 and 848 cm\(^{-1}\). The normal coordinate analysis predicts that the C–C–C in plane bending vibrations significantly mixed with the C–H in-plane bending modes \cite{27}. The ring C=C stretching vibrations, known as semicircle stretching usually occur in the region 1400–1625 cm\(^{-1}\)\cite{28, 29}.

![Fig. 2: Experimental (top) and theoretical (bottom) FTIR spectra of Diphenylacetaline.](image1)

![Fig. 3: Experimental (top) and theoretical (bottom) FT-Raman spectra of Diphenylacetaline](image2)
Table 2: Comparison of the experimental and calculated vibrational wavenumbers and proposed assignments of Diphenylacetaline

<table>
<thead>
<tr>
<th>S. no</th>
<th>Experimental wavenumber</th>
<th>B3LYP/6-311++G** Calculated wavenumber</th>
<th>IR Intensity</th>
<th>Raman Activity</th>
<th>HF/6-311++G** Calculated wavenumber</th>
<th>IR Intensity</th>
<th>Raman Activity</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
<td>Raman</td>
<td>Unscaled</td>
<td>scaled</td>
<td>unscaled</td>
<td>scaled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>26</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>15</td>
<td>15</td>
<td></td>
<td>Lattice Vibration + Ring twisting</td>
</tr>
<tr>
<td>2</td>
<td>47</td>
<td>47</td>
<td>0.5562</td>
<td>0</td>
<td>51</td>
<td>51</td>
<td>0.6383</td>
<td>Lattice Vibration</td>
</tr>
<tr>
<td>3</td>
<td>81</td>
<td>51</td>
<td>1.1608</td>
<td>0</td>
<td>56</td>
<td>56</td>
<td>1.4769</td>
<td>Lattice Vibration + Ring butterfly</td>
</tr>
<tr>
<td>4</td>
<td>140</td>
<td>0</td>
<td>2.3553</td>
<td>158</td>
<td>153</td>
<td>153</td>
<td>2.0831</td>
<td>CCCβ+ring scissoring</td>
</tr>
<tr>
<td>5</td>
<td>153</td>
<td>516</td>
<td>0</td>
<td>5.5692</td>
<td>177</td>
<td>177</td>
<td>177</td>
<td>CCCγ+ring rocking</td>
</tr>
<tr>
<td>6</td>
<td>260</td>
<td>260</td>
<td>0.2709</td>
<td>272</td>
<td>272</td>
<td>272</td>
<td>0</td>
<td>Ring scissoring</td>
</tr>
<tr>
<td>7</td>
<td>286</td>
<td>286</td>
<td>0.1135</td>
<td>0</td>
<td>319</td>
<td>283</td>
<td>0.1647</td>
<td>Ring butterfly</td>
</tr>
<tr>
<td>8</td>
<td>410</td>
<td>410</td>
<td>0</td>
<td>0.0048</td>
<td>448</td>
<td>420</td>
<td>0</td>
<td>Ring breathing</td>
</tr>
<tr>
<td>9</td>
<td>448</td>
<td>448</td>
<td>0</td>
<td>8.3621</td>
<td>450</td>
<td>422</td>
<td>0.0001</td>
<td>Ring breathing</td>
</tr>
<tr>
<td>10</td>
<td>465</td>
<td>478</td>
<td>1.5379</td>
<td>0</td>
<td>461</td>
<td>461</td>
<td>0</td>
<td>7.374</td>
</tr>
<tr>
<td>11</td>
<td>507</td>
<td>526</td>
<td>16.275</td>
<td>0</td>
<td>510</td>
<td>505</td>
<td>2.2254</td>
<td>CCCCβ+ CCH γ</td>
</tr>
<tr>
<td>12</td>
<td>534</td>
<td>539</td>
<td>11.3885</td>
<td>576</td>
<td>541</td>
<td>17.6349</td>
<td>0</td>
<td>0.00000</td>
</tr>
<tr>
<td>13</td>
<td>577</td>
<td>577</td>
<td>20.644</td>
<td>584</td>
<td>549</td>
<td>11.0368</td>
<td>0</td>
<td>0.00000</td>
</tr>
<tr>
<td>14</td>
<td>635</td>
<td>635</td>
<td>0.0031</td>
<td>646</td>
<td>646</td>
<td>24.1964</td>
<td></td>
<td>0.00000</td>
</tr>
<tr>
<td>15</td>
<td>641</td>
<td>641</td>
<td>5.6451</td>
<td>648</td>
<td>648</td>
<td>32.6691</td>
<td></td>
<td>0.00000</td>
</tr>
<tr>
<td>16</td>
<td>689</td>
<td>691</td>
<td>70.733</td>
<td>678</td>
<td>678</td>
<td>0</td>
<td>0</td>
<td>CCHβ+CH OPB</td>
</tr>
<tr>
<td>17</td>
<td>715</td>
<td>694</td>
<td>0.0014</td>
<td>695</td>
<td>681</td>
<td>0</td>
<td>0</td>
<td>0.1708</td>
</tr>
<tr>
<td>18</td>
<td>755</td>
<td>755</td>
<td>14.4242</td>
<td>759</td>
<td>751</td>
<td>14.255</td>
<td></td>
<td>0.01590</td>
</tr>
<tr>
<td>19</td>
<td>771</td>
<td>771</td>
<td>0.0032</td>
<td>10.5645</td>
<td>762</td>
<td>762</td>
<td>0.9472</td>
<td>1.1252</td>
</tr>
<tr>
<td>20</td>
<td>849</td>
<td>849</td>
<td>96.133</td>
<td>763</td>
<td>763</td>
<td>74.241</td>
<td>0.01590</td>
<td>CH OPB+CCC bending</td>
</tr>
<tr>
<td>21</td>
<td>850</td>
<td>850</td>
<td>0</td>
<td>0.0011</td>
<td>848</td>
<td>848</td>
<td>71.551</td>
<td>9.63450</td>
</tr>
<tr>
<td>22</td>
<td>856</td>
<td>856</td>
<td>0</td>
<td>0.098</td>
<td>849</td>
<td>849</td>
<td>57.96</td>
<td>11.9076</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>916</td>
<td>927</td>
<td>918</td>
<td>1.2995</td>
<td>0</td>
<td>904</td>
<td>904</td>
<td>4.1552</td>
</tr>
<tr>
<td></td>
<td>930</td>
<td>930</td>
<td>0.0003</td>
<td>0.2487</td>
<td>946</td>
<td>918</td>
<td>0</td>
<td>0.0019</td>
</tr>
<tr>
<td>25</td>
<td>980</td>
<td>980</td>
<td>7.0251</td>
<td>0</td>
<td>947</td>
<td>947</td>
<td>0.001</td>
<td>1.04</td>
</tr>
<tr>
<td>26</td>
<td>981</td>
<td>981</td>
<td>0</td>
<td>0.0002</td>
<td>CH( ^{\gamma} + CH ) OPB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>995</td>
<td>995</td>
<td>0</td>
<td>0</td>
<td>HCCC( ^{\gamma} + CH ) OPB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>997</td>
<td>996</td>
<td>996</td>
<td>0.167</td>
<td>0.0048</td>
<td>CCC( ^{\beta} + CH ) OPB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>1012</td>
<td>1012</td>
<td>0.0004</td>
<td>1.6088</td>
<td>CH ( \beta^{\gamma} + CH ) IPB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1025</td>
<td>1026</td>
<td>1013</td>
<td>0</td>
<td>439.412</td>
<td>CH ( \gamma^{\gamma} + CH ) IPB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>1048</td>
<td>1048</td>
<td>0.0003</td>
<td>38.7087</td>
<td>1039</td>
<td>1039</td>
<td>8.5217</td>
<td>0.005</td>
</tr>
<tr>
<td>32</td>
<td>1080</td>
<td>1070</td>
<td>0</td>
<td>259.371</td>
<td>Ring Sym.Deform +CH IPB</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>1099</td>
<td>1066</td>
<td>9.6909</td>
<td>0.001</td>
<td>1081</td>
<td>1081</td>
<td>0.1981</td>
<td>0.041</td>
</tr>
<tr>
<td>34</td>
<td>1101</td>
<td>1080</td>
<td>1078</td>
<td>0.0002</td>
<td>0.012</td>
<td>1101</td>
<td>1101</td>
<td>0.0004</td>
</tr>
<tr>
<td>35</td>
<td>1114</td>
<td>1103</td>
<td>12.216</td>
<td>0.00000</td>
<td>1114</td>
<td>1113</td>
<td>0.0198</td>
<td>2.6656</td>
</tr>
<tr>
<td>36</td>
<td>1115</td>
<td>1115</td>
<td>0</td>
<td>1210.74</td>
<td>1115</td>
<td>1115</td>
<td>0.0825</td>
<td>0.6768</td>
</tr>
<tr>
<td>37</td>
<td>1118</td>
<td>1118</td>
<td>0.0044</td>
<td>1119</td>
<td>1118</td>
<td>0.0001</td>
<td>26.9084</td>
<td>CH ( \beta^{\gamma} + CH ) IPB</td>
</tr>
<tr>
<td>38</td>
<td>1156</td>
<td>1159</td>
<td>1148</td>
<td>16.4968</td>
<td>1168</td>
<td>1168</td>
<td>7.5725</td>
<td>0.0003</td>
</tr>
<tr>
<td>39</td>
<td>1141</td>
<td>1164</td>
<td>1150</td>
<td>0.0075</td>
<td>10.0018</td>
<td>1169</td>
<td>1146</td>
<td>0.0076</td>
</tr>
<tr>
<td>40</td>
<td>1178</td>
<td>1182</td>
<td>1159</td>
<td>0.0653</td>
<td>0.001</td>
<td>1199</td>
<td>1175</td>
<td>4.8249</td>
</tr>
<tr>
<td>41</td>
<td>1202</td>
<td>1202</td>
<td>0.1435</td>
<td>0.0003</td>
<td>1238</td>
<td>1238</td>
<td>6.8645</td>
<td>0.0739</td>
</tr>
<tr>
<td>42</td>
<td>1280</td>
<td>1309</td>
<td>1282</td>
<td>4.8597</td>
<td>0</td>
<td>1285</td>
<td>1285</td>
<td>0.0095</td>
</tr>
<tr>
<td>43</td>
<td>1311</td>
<td>1312</td>
<td>1312</td>
<td>0.0003</td>
<td>25.871</td>
<td>1286</td>
<td>1286</td>
<td>0</td>
</tr>
<tr>
<td>44</td>
<td>1330</td>
<td>1340</td>
<td>1326</td>
<td>0.5422</td>
<td>0.0106</td>
<td>1318</td>
<td>1318</td>
<td>0.8497</td>
</tr>
<tr>
<td>45</td>
<td>1386</td>
<td>1352</td>
<td>1352</td>
<td>0.0002</td>
<td>26.2704</td>
<td>CC ( v + CH ) IPB</td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>1441</td>
<td>1442</td>
<td>1470</td>
<td>8.4232</td>
<td>0.0006</td>
<td>C=C str</td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>1492</td>
<td>1482</td>
<td>1472</td>
<td>0</td>
<td>235.754</td>
<td>CC ( v + C=C )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>1514</td>
<td>1483</td>
<td>46.917</td>
<td>0.00010</td>
<td>1403</td>
<td>1333</td>
<td>0</td>
<td>55.0115</td>
</tr>
<tr>
<td>49</td>
<td>1532</td>
<td>1533</td>
<td>1533</td>
<td>0.0001</td>
<td>0.4318</td>
<td>1452</td>
<td>1394</td>
<td>0.0186</td>
</tr>
<tr>
<td>50</td>
<td>1571</td>
<td>1604</td>
<td>1572</td>
<td>3.2794</td>
<td>0.0007</td>
<td>1454</td>
<td>1440</td>
<td>1.4086</td>
</tr>
<tr>
<td>51</td>
<td>1598</td>
<td>1592</td>
<td>1605</td>
<td>1582</td>
<td>0.0001</td>
<td>239.54</td>
<td>1589</td>
<td>1542</td>
</tr>
<tr>
<td>52</td>
<td>1633</td>
<td>1600</td>
<td>32.364</td>
<td>0.00140</td>
<td>1641</td>
<td>1575</td>
<td>0.5643</td>
<td>0.0023</td>
</tr>
<tr>
<td>53</td>
<td>1673</td>
<td>1643</td>
<td>1643</td>
<td>0</td>
<td>9459.75</td>
<td>1655</td>
<td>1588</td>
<td>0.0052</td>
</tr>
</tbody>
</table>
Aromatic compounds commonly exhibit multiple weak bands in the region 3100–3000 cm\(^{-1}\) due to aromatic C-H stretching vibrations\[^{30}\]. The bands due to the C-H in-plane deformation vibrations, which usually occurs in the region 1390–990 cm\(^{-1}\) are very useful for characterization and are very strong indeed\[^{31}\]. When there is in-plane interaction above 1200 cm\(^{-1}\), a carbon and its hydrogen usually move in opposite direction \[^{32}\]. All the C-H stretching vibrations are very weak in intensity. The bands due to C-H in-plane bending vibrations are observed in the region 1000–1300 cm\(^{-1}\)\[^{33}\]. The C-H out-of-plane bending or wagging vibrations are appeared within the region 980–717 cm\(^{-1}\) in naphthalene \[^{34}\]. After scaling procedure, the theoretical C-H vibrations are in good agreement with the experimental values and literature \[^{35}\]. The assignments for the tested molecule are listed in table 2 which shows analogous with the data from the above literature survey.

### Frontier molecular orbital analysis

The highest occupied molecular orbital (HOMO) and the lowest-lying unoccupied molecular orbital (LUMO) are named as frontier molecular orbitals (FMO). The FMO play an important role in the optical and electric properties, as well as in quantum chemistry and UV–Vis. spectrum \[^{41}\]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to the LUMO \[^{36, 37}\]. Chemical hardness (\(\eta\)) and softness (\(s\)) can be used as harmonizing tools to describe the thermodynamic aspects of chemical reactivity. The Frontier orbital gap helps to characterize the chemical reactivity kinetic stability, chemical reactivity, optical polarizability, chemical hardness, softness of a molecule \[^{38}\]. The
calculated HOMO and LUMO energy and the energy values of the frontier orbitals by B3LYP/6-311++G (d,p) are presented in Table 3. The ionization potential (I.P) values suggest how tightly an electron is bound within the nuclear attractive field of the systems. It is linearly related with the chemical hardness (\(g\)). By using HOMO and LUMO energy values for a molecule, the Ionization potential and chemical hardness of the molecule were calculated using Koopmans’ theorem[39] and are given by \(\eta = (I_P - E_A)/2\) where \(I_P\)~E(HOMO), \(E_A\)~E(LUMO), \(I_P\) = Ionization potential (eV), \(E_A\) = electron affinity (eV)

\[\eta = \frac{1}{2} (\epsilon_{LUMO} - \epsilon_{HOMO}).\]

The hardness has been associated with the stability of chemical system. Considering the chemical hardness, large HOMO–LUMO gap means a hard molecule and small HOMO–LUMO gap means a soft molecule. One can also relate the stability of molecule to hardness, which means that the molecule with least HOMO–LUMO gap means, it is more reactive. The hard molecules are not more polarizable than soft ones because they need big energy to excitation 3D plots of the HOMO, LUMO, orbitals computed at the B3LYP/6-311++G (d,p) level for the tested molecule are illustrated in Fig 4. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, \(\mu = \frac{1}{2} (\epsilon_{LUMO} + \epsilon_{HOMO}).\) Chemical softness(S) = \(1/\eta\) describes the capacity of an atom or group of atoms to receive electrons and is the inverse of the global hardness [40]. The soft molecules are more polarizable than the hard ones because they need small energy to excitation. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule [41]. A hard molecule has a large energy gap and a soft molecule has a small energy gap [42]. It is shown from the calculations that Diphenylacetylene has the least value of global hardness (0.063305eV) and the highest value of global softness (15.796540 eV) is expected to have the highest inhibition efficiency. The global electrophilicity index, \(\omega = \mu^2/2 \eta\) is also calculated and these values are listed in Table 3.

**NLO properties**

Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields [43]. The first hyperpolarizability (\(\beta_0\)) of this novel molecular system and related properties (\(\beta_{tot}, \alpha, \Delta\alpha\)) of Diphenylacetylene are calculated using DFT/B3LYP method at 6-311G++ (d,p) basis set based on the finite field approach. NLO is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical inter connections [44-46].

In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyperpolarizability is a third rank tensor that can be described by \(3 \times 3 \times 3\) matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [37]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the \(3 \times 3 \times 3\) matrices is a tetrahedral. The components of \(\beta\) are defined as the coefficients in the Taylor series expansion of the energy in the external electric field.
When the external electric field is weak and homogeneous, this expansion becomes:

\[ E = E_0^2 - \mu \alpha F + 1/6 \beta \alpha \beta \alpha + \ldots \]

Where \( E_0 \) is the energy of the unperturbed molecules, \( F_0 \) is the field at the origin, \( \mu \), \( \alpha \) and \( \beta \) are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively.

DFT has been extensively used as an effective method to investigate the organic NLO materials [47-51]. The total static dipole moment (\( \mu \)), the mean polarizability (\( \alpha_0 \)), the anisotropy of the polarizability (\( \Delta \alpha \)) and the mean first order hyperpolarizability (\( \beta_0 \)), using the x, y, z components they are defined as:

\[
\alpha_{\text{total}} = \alpha_0 = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
\]

\[
\Delta \alpha = \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \alpha_{xy}^2 + 6 \alpha_{xz}^2 + 6 \alpha_{yz}^2 \right]^{1/2}
\]

\[
\beta_0 = (\beta_{xx}^2 + \beta_{yy}^2 + \beta_{zz}^2)^{1/2}
\]

\[
(\beta_{xx} + \beta_{xy} + \beta_{xz})^2 + (\beta_{yy} + \beta_{xy} + \beta_{yz})^2 + (\beta_{zz} + \beta_{xz} + \beta_{yz})^2)^{1/2}
\]

\[
\Delta \alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2)^{1/2}
\]

Polarizability is the property of a species and it is minimum for most stable species and is maximum for least stable species like transition state. The \( \alpha \) and \( \beta \) values of the Gaussian 05 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u) (\( \alpha \): 1 a.u = 0.1482x10^-24 esu; for \( \beta \): 1 a.u = 8.639x10^-33 esu) and these above polarizability values of Diphenylacetylene are listed in Table 4. The total dipole moment can be calculated using the following equation.

\[
\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}
\]
Table 3: Calculated energy values of Diphenylacetaline in its ground state.

<table>
<thead>
<tr>
<th>Molecular properties</th>
<th>B3LYP/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{LUMO}+1}$ (eV)</td>
<td>-0.17641</td>
</tr>
<tr>
<td>$E_{\text{LUMO}}$ (eV)</td>
<td>-0.21409</td>
</tr>
<tr>
<td>$E_{\text{HOMO}}$ (eV)</td>
<td>-0.34070</td>
</tr>
<tr>
<td>$E_{\text{HOMO}-1}$ (eV)</td>
<td>-0.3738</td>
</tr>
<tr>
<td>$\Delta E_{\text{HOMO-LUMO}}$ (eV)</td>
<td>0.12661</td>
</tr>
<tr>
<td>$\Delta E_{\text{HOMO-LUMO}+1}$ (eV)</td>
<td>0.16429</td>
</tr>
<tr>
<td>$\Delta E_{\text{HOMO}-1 - \text{LUMO}}$ (eV)</td>
<td>0.15971</td>
</tr>
<tr>
<td>$\Delta E_{\text{HOMO}-1 - \text{LUMO}+1}$ (eV)</td>
<td>0.19739</td>
</tr>
<tr>
<td>Global hardness($\eta$)</td>
<td>0.063305</td>
</tr>
<tr>
<td>Chemical softness(S)</td>
<td>15.796540</td>
</tr>
<tr>
<td>Electronic chemical potential($\mu$)</td>
<td>0.277395</td>
</tr>
<tr>
<td>Global electrophilicity index($\omega$)</td>
<td>0.607755991</td>
</tr>
</tbody>
</table>

To study the NLO properties of molecule the value of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison. The total molecular dipole moment of Diphenylacetaline from DFT–B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) basis sets are 9.2096 and 4.4375 Debye which are greater than that of urea and the first order hyperpolarizability DFT and HF with the same basis sets are 0.0118 and 0.0627 are lesser than that of urea ($\mu$ and $\beta$ of urea are 1.3732 Debye and 0.3728 x10-30 cm5/esu obtained by HF/6-311G(d,p) method[52]. These results indicate that the title compound is a good candidate of NLO material. The calculated dipole moment and hyperpolarizability values obtained from B3LYP/6-311G (d,p) and HF/6-31++G (d,p) methods are collected in Table 4. These results indicate that the title compound is a good candidate of NLO material. The theoretical calculation of $\beta$ components is very useful as this clearly indicates the direction of charge delocalization. In $\beta_{xyz}$ direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction. The maximum $\beta$ value may be due to $\pi$ electron cloud movement from donor to acceptor which makes the molecule highly polarized and the intra molecular charge transfer possible.

Table 4: The electric dipole moment, polarizability and first order hyperpolarizability of Diphenyl acetaline.

<table>
<thead>
<tr>
<th>Parameters (a.u)</th>
<th>DFT B3LYP/6-311++G(d,p)</th>
<th>HF/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{xx}$</td>
<td>324.649023</td>
<td>147.763424</td>
</tr>
<tr>
<td>$\alpha_{xy}$</td>
<td>-0.00187608745</td>
<td>0.160182117</td>
</tr>
<tr>
<td>$\alpha_{yx}$</td>
<td>155.525453</td>
<td>266.581938</td>
</tr>
<tr>
<td>$\alpha_{xz}$</td>
<td>-0.000938377337</td>
<td>0.0221625953x10^{-30}</td>
</tr>
<tr>
<td>$\alpha_{zx}$</td>
<td>-0.000004235011055</td>
<td>-2.42340920x10^{-30}</td>
</tr>
<tr>
<td>$\alpha_{yy}$</td>
<td>84.3612923</td>
<td>83.9905152</td>
</tr>
<tr>
<td>$\alpha_{zz}$</td>
<td>188.178</td>
<td>166.1119591</td>
</tr>
<tr>
<td>$\Delta \alpha$</td>
<td>213.7817967</td>
<td>160.5061538</td>
</tr>
</tbody>
</table>
Investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of Diphenylacetylene Molecule

SANGEETHA C. C., R. MADIVANANE, V. POUCHANAME

&

\[ \begin{array}{ccc}
\beta_{xx} & 0.00329884618 & -0.0929418325 \\
\beta_{xy} & 0.0207528357 & -0.00306912782 \\
\beta_{yy} & 0.00318870607 & 0.0380264257 \\
\beta_{yy} & -0.0145490038 & 0.0505090201 \\
\beta_{xx} & 0.00443534185 & -9.0248532 \times 10^{-29} \\
\beta_{xy} & 0.07209402843 & 1.7616305 \times 10^{-28} \\
\beta_{yy} & 0.00146952131 & 4.24573960 \times 10^{-29} \\
\beta_{xy} & -0.00397387105 & 0.00221151415 \\
\beta_{yy} & 0.00461365515 & -0.0134852216 \\
\beta_{yy} & 0.00265002629 & 1.22531942 \times 10^{-18} \\
\beta_{x} & 0.011763718 & 0.062694655 \\
\mu_{x} & -0.0000237661383 & 0.000122452807 \\
\mu_{y} & 0.0000867565483 & -0.0000426523936 \\
\mu_{z} & 0.0000197539515 & 0.00306710389 \times 10^{-30} \\
\mu_{\text{total (Debye)}} & 9.209639842 \times 10^{-5} & 4.43753713 \times 10^{-31} \\
\end{array} \]

**Mulliken charge analysis:**

The charge distribution on a molecule has a significant influence on the vibrational spectra. The atomic charge in molecules is fundamental to chemistry. For instance, atomic charge has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions. Mulliken net charges calculated at the HF and DFT level with the 6-311++G(d,p) atomic basis set in gas phase using Gaussian 09. The results are given in Table 5. The magnitudes of the carbon atomic charges, found to be either positive or negative, were noted to change from -1.092 to 1.236. All the hydrogen atoms have positive charges.

Table 5: Mulliken atomic charges of Diphenylacetone calculated by DFT/B3LYP/6-311++G(d,p).

<table>
<thead>
<tr>
<th>S.NO</th>
<th>ATOMS</th>
<th>B3LYP/6-311++G(d,p)</th>
<th>HF/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C</td>
<td>0.666426</td>
<td>0.758363</td>
</tr>
<tr>
<td>2</td>
<td>C</td>
<td>-1.09158</td>
<td>-1.31522</td>
</tr>
<tr>
<td>3</td>
<td>C</td>
<td>0.081044</td>
<td>0.142072</td>
</tr>
<tr>
<td>4</td>
<td>C</td>
<td>-0.61569</td>
<td>-0.77597</td>
</tr>
<tr>
<td>5</td>
<td>C</td>
<td>0.08105</td>
<td>0.141518</td>
</tr>
<tr>
<td>6</td>
<td>C</td>
<td>-1.0921</td>
<td>-1.31119</td>
</tr>
<tr>
<td>7</td>
<td>C</td>
<td>1.23643</td>
<td>1.464231</td>
</tr>
<tr>
<td>8</td>
<td>C</td>
<td>1.23647</td>
<td>1.464321</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>0.666385</td>
<td>0.758289</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>-1.09164</td>
<td>-1.31342</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
<td>0.081001</td>
<td>0.141999</td>
</tr>
<tr>
<td>12</td>
<td>C</td>
<td>-0.61569</td>
<td>-0.77625</td>
</tr>
<tr>
<td>13</td>
<td>C</td>
<td>0.081057</td>
<td>0.142071</td>
</tr>
</tbody>
</table>
Investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of Diphenylacetylene Molecule

Thermodynamic properties:

The values of some thermodynamic parameters (such as zeropoint vibrational energy, specific heat capacity, rotational constants, entropy and dipole moment) of title molecule by B3LYP/6-311G (d,p) and HF/6-31++G (d,p) methods in ground state are listed in Table 6. On the basis of vibrational analysis, the statically thermodynamic functions: heat capacity (C), enthalpy changes (H) and entropy (S) for the title molecule were obtained from the theoretical harmonic frequencies and listed in Table 6. All the thermodynamic data supply helpful information for the further study on the Diphenylacetylene. They can be used to compute the other thermodynamic energies according to relationships of thermodynamic functions and estimate directions of chemical reactions according to the second law of thermodynamics.

Table 6: The calculated thermodynamic parameters of Diphenylacetaline employing B3LYP/ 6–311++G(d,p) methods

<table>
<thead>
<tr>
<th>Parameters</th>
<th>B3LYP/6-311++G(d,p)</th>
<th>HF/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero point energy</td>
<td>500579.4 (Joules/Mol)</td>
<td>534635.2 (Joules/Mol)</td>
</tr>
<tr>
<td></td>
<td>119.64134 (Kcal/Mol)</td>
<td>127.78088 (Kcal/Mol)</td>
</tr>
<tr>
<td>Rotational temperature (Kelvin)</td>
<td>0.13672</td>
<td>0.13867</td>
</tr>
<tr>
<td></td>
<td>0.01195</td>
<td>0.01203</td>
</tr>
<tr>
<td></td>
<td>0.01099</td>
<td>0.01107</td>
</tr>
<tr>
<td>Rotational constants (GHZ)</td>
<td>2.84875</td>
<td>2.88935</td>
</tr>
<tr>
<td></td>
<td>0.24891</td>
<td>0.25067</td>
</tr>
<tr>
<td></td>
<td>0.22891</td>
<td>0.23066</td>
</tr>
<tr>
<td>Entropy (Cal/Mol-Kelvin)</td>
<td>Total</td>
<td>107.629</td>
</tr>
<tr>
<td></td>
<td>Translational</td>
<td>41.438</td>
</tr>
<tr>
<td></td>
<td>Rotational</td>
<td>31.960</td>
</tr>
<tr>
<td></td>
<td>Vibrational</td>
<td>34.231</td>
</tr>
<tr>
<td>Thermal Energy (KCal/Mol)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
UV–Visible studies and electronic properties:

Ultraviolet spectral analyses of Diphenylacetylene have been investigated by theoretical calculation. On the basis of fully optimized ground-state structure, TD-DFT/B3LYP/6-311++G(d,p) calculations have been used to determine the low-lying excited states of Diphenylacetylene. The electronic absorption spectrum of the title compound was recorded within the 200–400 nm range and representative spectra are shown in Fig. 6.

Table 7: Theoretical and experimental electronic absorption spectra values of Diphenylacetaline.

<table>
<thead>
<tr>
<th>Experimental States</th>
<th>Calculated by B3LYP/6-311++G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ (nm)</td>
<td>Absorbance</td>
</tr>
<tr>
<td>377.20</td>
<td>0.003</td>
</tr>
<tr>
<td>320.60</td>
<td>0.006</td>
</tr>
<tr>
<td>315.00</td>
<td>0.007</td>
</tr>
</tbody>
</table>

From the table, the calculated absorption maxima values have been found to be 377, 320 and 315 nm at TD-DFT/B3LYP/6-311++G(d,p) method. These values may be slightly shifted by solvent effects. The broad absorption bands associated to a strong π→π*and a weak σ→σ* transition characterize the UV–Vis absorption spectra. Natural bond orbital analysis indicates that molecular orbitals are mainly composed of σ and π atomic orbitals. The absorption bands at the longer wave lengths 377 and 320 nm of Diphenylacetylene are caused by the n→π* transition. The absorption band at 315 nm is caused by π→π* transition. The λ$_{max}$ is a function of substitution, the stronger the donor character substitution, the more electrons pushed into the molecules, the larger λ$_{max}$. These values may be slightly shifted by solvent effects. The role of substituents and solvent influences the UV-spectrum [55]. The theoretical electronic excitation energies, oscillator strengths and wavelength of the excitations were calculated and listed in Table 7.

NMR studies

NMR spectroscopy is currently used to study the structure of organic molecules. The combined use of experimental and computer simulation methods offer a powerful way to interpret and predict the
structure of large molecules. The optimized structure of Diphenylacetylene is used to calculate the NMR spectra at the DFT (B3LYP) method with 6-311++G(d,p) level using the GIAO(Gauge-Including Atomic Orbital) method. The NMR spectra calculations were performed by using the Gaussian03 program package. The theoretical $^1\text{H}$ NMR chemical shifts of Diphenylacetylene have been compared with the experimental data and listed in Table 8.

Chemical shifts are reported in ppm relative to TMS for $^1\text{H}$ NMR spectrum. The $^1\text{H}$ 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. The calculated and experimental chemical shift values are given in Table 8 shows a good agreement between the experimental and theoretical approaches. The theoretical and experimental $^1\text{H}$ and NMR spectra are shown in Figure 6.
Table 8: The observed (in CDCl₃) and predicted ¹H and ¹³C NMR isotropic chemical shifts (with respect to TMS, all values in ppm) for Diphenylacetaline.

<table>
<thead>
<tr>
<th>S.NO</th>
<th>ATOMS</th>
<th>Experimental NMR Chemical shift</th>
<th>Calculated chemical shift by B3LYP method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15 H</td>
<td>7.652</td>
<td>7.66427</td>
</tr>
<tr>
<td>2</td>
<td>16 H</td>
<td>7.668</td>
<td>7.66427</td>
</tr>
<tr>
<td>3</td>
<td>17 H</td>
<td>7.646</td>
<td>7.3875</td>
</tr>
<tr>
<td>4</td>
<td>18 H</td>
<td>7.004</td>
<td>7.3875</td>
</tr>
<tr>
<td>5</td>
<td>19 H</td>
<td>6.498</td>
<td>7.3875</td>
</tr>
<tr>
<td>6</td>
<td>20 H</td>
<td>6.476</td>
<td>7.3875</td>
</tr>
<tr>
<td>7</td>
<td>21 H</td>
<td>6.498</td>
<td>7.3875</td>
</tr>
<tr>
<td>8</td>
<td>22 H</td>
<td>6.498</td>
<td>7.3875</td>
</tr>
<tr>
<td>9</td>
<td>23 H</td>
<td>7.673</td>
<td>7.66427</td>
</tr>
<tr>
<td>10</td>
<td>24 H</td>
<td>8.307</td>
<td>7.66427</td>
</tr>
</tbody>
</table>

Conclusions

The FTIR, FT-Raman, ¹H NMR spectra, UV–Vis spectral measurements have been made for the Diphenylacetylene molecule. The complete vibrational analysis and first order hyperpolarizability, NBO analysis, HOMO and LUMO analysis and thermodynamic properties of the title compound was performed on the basis of DFT and HF calculations at the 6-311++G(d,p) basis set. The consistency between the calculated and experimental FTIR and FT-Raman data indicates that the B3LYP and HF methods can generate reliable geometry and related properties of the title compound. The difference between the observed and scaled wave number values of most of the fundamentals is very small. The theoretically constructed FTIR and FT-Raman spectra exactly coincide with experimentally observed counterparts. The Mulliken atomic charges and the natural atomic charges obtained are tabulated that gives a proper understanding of the atomic theory. The calculated dipole moment and first order hyperpolarizability results indicate that the title compound is a good candidate of NLO material. The calculated normal-mode vibrational frequencies provide thermodynamic properties by the way of statistical mechanics. The ¹H NMR chemical shift was calculated and compared with experimental one. The UV spectrum was measured experimentally and compared with the theoretical values by using TD-DFT/ 6-311++G(d,p) basis set. The energies of important MOs and the $\lambda_{max}$ of the compounds were also evaluated from TD-DFT method.

Reference:
4. Han, Dong Cheul; Kwak, Giseop; Kim, Yong Bae; Bae, Jin Ju; Lee, Wang Hoon; Seo, Yoon-Sik; Byun, Jae Hyuk; Kang, Shin Won., Journal of Nanoscience and Nanotechnology, Volume 14, Number 8, August 2014, pp. 5937-5941.


32. A. Srivastava, V.B. Singh, Indian J. Pure.
33. D. Lin–Vien, N.B. Colthup, W.G. Fateley,
J.G. Grasselli, The Handbook of Infrared
Raman Characteristic Frequencies of Organic
Molecules, Academic Press, Boston, MA,
34. Fleming, Frontier Orbitals and Organic
35. A.M. Asiri, M. Karabacak, M. Kurt, K.A.
455.
36. B. Kosar, C. Albayrak, Spectrochim. Acta A
1979.
40. I. Fleming, Frontier Orbitals and Organic
Chemical Reactions, (John Wiley and Sons),
NewYork, 1976
41. Obi-Egbedi N O, Obot I B, El-Khaiary M I,
Umoren S A and Ebenso E E, Int J Electro
Chem Sci., 2011; 6:5649-5675
42. Y.X. Sun, Q.L. Hao, W.X. Wei, Z.X. Yu,
Struct.:Theochem. 904 (2009) 74–82.
43. C. Andraud, T. Brotin, C. Garcia, F. Pelle, P.
Goldner, B. Bigot, A. Collet, J. Am.
44. V.M. Geskin, C. Lambert, J.L. Bredas, J. Am.
9648–9655.
47. D. Sajan, I.H. Joe, V.S. Jayakumar, J. Zaleski,
48. Y.X. Sun, Q.L. Hao, Z.X. Yu, W.X. Wei,
223.
49. A.B. Ahmed, H. Feki, Y. Abid, H. Bouhazala,
C. Minot, A. Mlayah, J. Mol. Struct. 920
50. J.P. Abraham, D. Sajan, V. Shettigar, S.M.
Dharmaparaksh, N.I.H. Joe, V.S. Jayakumar,
51. S.G. Sagdinc, A. Esme, Spectrochim. Acta A
52. A.B. Ahamed, H. Feki, Y. Abid, H.
Bouhazala, C. Monit, Spectrochim. Acta A 75
Theoretical Model of Chemical Bonding,Part
54. S. Fliszar, Charge Distributions and
55. S. Sebastian, N. Sundaraganesan, B.
Karthikeyan, V. Srinivasan, Spectrochim.
Acta Part A Mol. Biomol. Spectrosc. 78
(2011) 590–600.
5692