Density Functional Theory Investigations on Molecular Structure, HOMO, LUMO, NMR, NLO and Vibrational Spectra of N, N'-dibenzoylhydrazine

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ABSTRACT: In this work, the experimental and theoretical vibrational spectra of N,N'-dibenzoylhydrazine (N,N'-DBH) have been studied. FTIR and FT-Raman spectra of the title compound in the solid phase are recorded in the region 4000–400 cm⁻¹ and 4000–50 cm⁻¹, respectively. The structural and spectroscopic data of the molecules in the ground state are calculated using density functional methods (B3LYP) with 6-31G** basis set. The vibrational frequencies are calculated and scaled values are compared with experimental FTIR and FT-Raman spectra. The observed and calculated frequencies are found to be in good agreement. The complete vibrational assignments are performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanical (SQM) method. The¹H and ¹³C NMR spectra have been simulated using the gauge independent atomic orbital (GIAO) method. The electronic properties, such as HOMO, LUMO energies, absolute electro negativity Χ and absolute hardness η were performed by DFT approach. The first order hyperpolarizability (β) of these novel molecular system and related properties (β, α, and Δα) of N,N'-DBH is calculated using DFT/6-31G** method on the finite-field approach.

KEYWORDS: N,N'-dibenzoylhydrazine, FTIR; FT-Raman, Vibrational Spectra, NMR, HOMO, LUMO, Hyperpolarizability.

I. INTRODUCTION

Hydrazine is one of the most widely used in the medical and industrial fields. However, their modes of action have not yet been established and in addition, they have been shown to be potentially carcinogenic in animals. The properties of hydrazine are of interest due to their biological activities and their use as metal extracting agencies [1]. The hydrazine derivatives are used as fungicides, and in the treatment of diseases such as tuberculosis, leprosy and mental disorders. The complexes of various hydrazines are reported to act as inhibitors of as enzymes [2]. Many substituted hydrazine are employed in the treatment of psychotic and psychoneurotic conditions. Particularly, hydrogen bonding between biomolecules and water plays an important role in determining the energetics and dynamics of bioprocesses.

At present vibrational spectroscopy is used not only for the functional group identification of organic compounds, but also to investigate the molecular structure, reaction kinetics, etc. Correct frequency assignments for complex organic molecules can be done on the basis of frequency agreement between the computed harmonics and the observed fundamentals. N,N'-DBH has been taken as the object of spectral, structural and theoretical investigations because of its interesting physicochemical and biological properties. The infrared and FT-Raman spectral studies combined with quantum chemical computations are prevalently used nowadays as effective tools in the vibrational analysis of drug molecules [3], biological compounds [4] and natural products [5]. The reason is that fluorescence free Raman spectra and the computed results can help unambiguous identification of vibrational modes as well as the bonding and structural features of complex organic molecular systems. Both IR and Raman spectroscopy along with HOMO–
LUMO and hyperpolarizability analysis have been used to elucidate the information pertaining to charge transfer within the molecule. The present work deals with DFT (B3LYP) methods with 6-31G (d, p) basis sets using the Gaussian 03W program. The present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wave number accuracy.

II. MATERIALS AND METHODS

The compound N,N'-DBH in the solid form was purchased from the Sigma–Aldrich Chemical Company (USA) with a stated purity of greater than 98% and it was used as such without any further purification. The FT-Raman spectrum of N, N’-DBH has been recorded using 1064nm line of Nd:YAG laser as excitation wavelength in the region 50–4000 cm⁻¹ on a Brucker IFS66v spectrophotometer equipped with FRA 106 FT-Raman module accessory. The FTIR spectrum of this compound was recorded in the region 400–4000 cm⁻¹ on IFS 66V spectrophotometer using KBr pellet technique. Spectra were collected for samples with 1000 scans accumulated over 30 min duration. The spectral resolution after apodization was 2 cm⁻¹. ¹H and ¹³C nuclear magnetic resonance (NMR) (400 MHz; CDCl₃) spectra were recorded on a Bruker HC400 instrument.

III. QUANTUM CHEMICAL CALCULATIONS

The quantum chemical calculations have been performed by using B3 [6] exchange functional combined with the LYP [7] correlation function resulting in the B3LYP density functional method at 6-31G** basis set. All the computations were performed using Gaussian 03W program [8] and Gauss-View program package [9]. The most optimized structural parameters, energy, and vibrational frequencies of the molecule have been evaluated for the calculations of vibrational frequencies by assuming C₁ point group symmetry. At the optimized geometry for the title molecule no imaginary frequency modes were obtained, therefore there is a true minimum on the potential energy surface was found. As a result, the unscaled calculated frequencies, infrared intensities and Raman activities are obtained. In order to fit the theoretical wavenumbers to the experimental, the scaling factors have been introduced by using a least square optimization of the computed to the experimental data. The scaling of the force field was performed according to the SQMFF procedure [10], the Cartesian representation of the force constants were transferred to a nonredundant set of local symmetry coordinates, chosen in accordance to the recommendations of Pulay et al. [11]. The descriptions of the predicted frequencies during the scaling process were followed by the potential energy distribution (PED) matrix. The characterization of the normal modes using potential energy distribution (PED) was done with the MOLVIB – 7.0 programs written by Sundius [12, 13]. Furthermore, in order to show nonlinear optic (NLO) activity of title molecule, the dipole moment, linear polarizability and first hyperpolarizability were obtained.

The prediction of Raman intensities

The Raman activity (Si) calculated by Gaussian 03 and adjusted during scaling procedure with MOLVIB were converted to relative Raman intensity (Iᵢ) using the following relation from the basic theory of Raman scattering [14, 15]

\[ I_i = \frac{f (\nu_i - \nu)^4 \nu_i^2}{\nu_i \left[ 1 - \exp \left( -\frac{hc\nu_i}{kT} \right) \right]} \]

Where \( \nu \) is the exciting wavenumber (in cm⁻¹ units), \( \nu_i \) the vibrational wavenumber of the \( i \)th normal mode, \( h, c, \) and \( k \) are the universal constants and \( f \) is a suitably chosen common normalization factor for all peak intensities. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth (FWHM) of 10 cm⁻¹. The theoretically simulated spectra are more regular than the experimental ones, because many vibrations presenting in condensed phase leads to strong perturbation of infrared intensities of many other modes.
1. **Structural properties**

   The title molecule possessing C1 point group symmetry. The labeling of atoms of the title compound is shown in Fig.1.

![Fig.1: Molecular Structure of N,N'-dibenzoylhydrazine along with Numbering of atoms.](image)

The global minimum energy obtained by the DFT structure optimization for the title compound is $-800.678108$ Hartrees for B3LYP/6-31G** basis set. The optimized geometrical parameters are presented in Table 1.

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Value (Å)</th>
<th>Bond Angle</th>
<th>Value (°)</th>
</tr>
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<td>C1-C2-C3</td>
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<td>C4-C5</td>
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<td>C4-C5-C6</td>
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<td>C2-C1-H7</td>
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The 84 fundamental modes of vibrations of N,N'-dibenzoylhydrazine are distributed into the irreducible representations as 57 in-plane vibrations and 27 out of plane vibrations, i.e., $\Gamma_{\text{vib}} = 57(\text{in-plane}) + 27(\text{out-of-plane})$. All vibrations are active in both the Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations give rise to polarized bands while the out-of-plane vibrations lead to depolarized bands. The internal coordinates and local symmetry coordinates are presented in Table 2 and 3.

**Table 2: Definition of internal coordinates of N, N'-DBH**

<table>
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<tr>
<th>No</th>
<th>Symbol</th>
<th>Type</th>
<th>Definition</th>
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<td><strong>Stretching</strong></td>
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<td>Pi</td>
<td>C-C</td>
<td>C1-C2,C2-C3, C3-C4, C4-C5,C5-C6, C6-C1, C20-C21,C21-C23, C23-C27,C27-C25, C25-C22, C22-C20.</td>
</tr>
<tr>
<td>13-14</td>
<td>pi</td>
<td>C-C(a)</td>
<td>C3-C12,C18-C20</td>
</tr>
<tr>
<td>25-26</td>
<td>qi</td>
<td>C-O</td>
<td>C12-O13, C18-O19.</td>
</tr>
<tr>
<td>29-30</td>
<td>ri</td>
<td>C-N</td>
<td>C12- N14,C18-N16.</td>
</tr>
<tr>
<td>31</td>
<td>ri</td>
<td>N-N</td>
<td>N14-N16.</td>
</tr>
<tr>
<td><strong>Bending</strong></td>
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<td></td>
<td></td>
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<tr>
<td><strong>In-plane bending</strong></td>
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<td></td>
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<tr>
<td>32-35</td>
<td>$\beta_i$</td>
<td>C-C-C</td>
<td>C2-C3-C12, C4-C3-C12, C21-C20-C18, C22-C20-C18.</td>
</tr>
<tr>
<td>56-57</td>
<td>$\alpha_i$</td>
<td>C-C-O</td>
<td>C3-C12- O13, C20-C18-O19.</td>
</tr>
<tr>
<td>60-61</td>
<td>$\theta_i$</td>
<td>C-C-N</td>
<td>C3-C12-N14,C20-C18-N16.</td>
</tr>
</tbody>
</table>
62-63 $\theta_i$ O-C-N O13-C12-N14, O19-C18-N16.
64-69 $\Phi_i$ C=C=C (ring1) C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2.

Out-of-plane bending
76-77 $\omega_i$ C-C C12-C3-C2-C4, C18-C20-C21-C22.
88-89 $\omega_i$ C-O O13-C12-C3-N14, O19-C18-C20-N16.

Torsion
92-93 $\tau_i$ C-O C4-C3-C12-O13, C21-C20-C18-O19.
96 $\tau_i$ C-N C12-N14-N16-C18
97-102 $\tau_i$ Tring 1 C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3.

For numbering of atoms refer Fig1.
Table 3: Definition of local symmetry coordinates of N,N'-DBH

<table>
<thead>
<tr>
<th>No.</th>
<th>Symbol a</th>
<th>Definition b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-12</td>
<td>CC</td>
<td>P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, P_9, P_{10}, P_{11}, P_{12}.</td>
</tr>
<tr>
<td>13-14</td>
<td>CC(a)</td>
<td>p_{13}, p_{14}.</td>
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<tr>
<td>15-24</td>
<td>CH</td>
<td>Q_{15}, Q_{16}, Q_{17}, Q_{18}, Q_{19}, Q_{20}, Q_{21}, Q_{22}, Q_{23}, Q_{24}.</td>
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<tr>
<td>25-26</td>
<td>CO</td>
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<td>27-28</td>
<td>NH</td>
<td>r_{27}, r_{28}.</td>
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<tr>
<td>29-30</td>
<td>CN</td>
<td>r_{29}, r_{30}.</td>
</tr>
<tr>
<td>31</td>
<td>NN</td>
<td>r_{31}.</td>
</tr>
<tr>
<td>32-33</td>
<td>bCC</td>
<td>(β_{12}− β_{33})/√2, (β_{14}− β_{33})/√2.</td>
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<tr>
<td>34-43</td>
<td>bCH</td>
<td>(β_{36}− β_{43})/√2, (β_{39}− β_{46})/√2, (β_{42}− β_{35})/√2, (β_{43}− β_{25})/√2, (β_{45}− β_{26})/√2, (β_{46}− β_{27})/√2, (β_{25}− β_{35})/√2, (β_{26}− β_{36})/√2.</td>
</tr>
<tr>
<td>44-45</td>
<td>bCO</td>
<td>α_{56}, α_{57}.</td>
</tr>
<tr>
<td>46-47</td>
<td>bNH</td>
<td>ρ_{58}, ρ_{59}.</td>
</tr>
<tr>
<td>48-49</td>
<td>bCN</td>
<td>θ_{60}, θ_{61}.</td>
</tr>
<tr>
<td>50-51</td>
<td>bOCN</td>
<td>θ_{62}, θ_{63}.</td>
</tr>
<tr>
<td>52</td>
<td>bring1</td>
<td>(Φ_{64}− Φ_{65} + Φ_{65}− Φ_{67} + Φ_{68}− Φ_{69})/√6.</td>
</tr>
<tr>
<td>53</td>
<td>bring1</td>
<td>(−Φ_{64}− Φ_{65} + 2Φ_{66}− Φ_{67} + Φ_{68}− 2Φ_{69})/√12.</td>
</tr>
<tr>
<td>54</td>
<td>bring1</td>
<td>(Φ_{64}− Φ_{65} + Φ_{66}− Φ_{67})/2.</td>
</tr>
<tr>
<td>55</td>
<td>bring2</td>
<td>(Φ_{70}− Φ_{71} + Φ_{72}− Φ_{73} + Φ_{74}− Φ_{75})/√6.</td>
</tr>
<tr>
<td>56</td>
<td>bring2</td>
<td>(−Φ_{70}− Φ_{71} + 2Φ_{72}− Φ_{73}− Φ_{74}+ 2Φ_{75})/√12.</td>
</tr>
<tr>
<td>57</td>
<td>bring2</td>
<td>(Φ_{70}− Φ_{71} + Φ_{72}− Φ_{75})/2.</td>
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<tr>
<td>58-59</td>
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<td>θ_{76}, θ_{77}.</td>
</tr>
<tr>
<td>60-69</td>
<td>αCH</td>
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</tr>
<tr>
<td>70-71</td>
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<td>72-73</td>
<td>αNH</td>
<td>θ_{90}, θ_{91}.</td>
</tr>
<tr>
<td>74-75</td>
<td>tCO</td>
<td>τ_{92}, τ_{93}.</td>
</tr>
<tr>
<td>76-77</td>
<td>tNH</td>
<td>τ_{94}, τ_{95}.</td>
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<tr>
<td>79</td>
<td>tring1</td>
<td>(τ_{97} + τ_{98} + τ_{99} + τ_{100} + τ_{101} + τ_{102})/√6.</td>
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<tr>
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<tr>
<td>81</td>
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<tr>
<td>82</td>
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<td>(τ_{103} + τ_{104} + τ_{105} + τ_{106} + 2τ_{107} + τ_{108})/√6.</td>
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<tr>
<td>83</td>
<td>tring2</td>
<td>(τ_{103} + τ_{104} + τ_{105} + 2τ_{106} + τ_{107}/2.</td>
</tr>
<tr>
<td>84</td>
<td>tring2</td>
<td>(−τ_{103} + 2τ_{104} + τ_{105} + 2τ_{106} + τ_{107} + τ_{108})/√12.</td>
</tr>
</tbody>
</table>

For visual comparison, the observed and calculated (simulated) FTIR and FT-Raman spectra are presented in Figs. 2 and 3.
Comparison between the calculated and observed vibrational spectra helps us to understand the observed spectral features. The results of our vibrational analysis, viz., calculated unscaled vibrational frequencies and IR intensities, SQM frequencies, potential energy distributions (PED) and assignment of the fundamentals, for the title compound are collected in Table 4.
2. **Carbon–hydrogen vibration**

The heteroaromatic structure showed the presence of C-H stretching vibrations in the region 3100–3000 cm$^{-1}$, which was the characteristic region for ready identification of C-H stretching vibrations [16]. Hence in the present investigation the calculated frequencies which lie in the region 3048–3012 cm$^{-1}$ were assigned to the C-H stretching vibrations of the title compound as shown in Table 4 and their experimental counterpart appear in the region 3088–2999 cm$^{-1}$ of the IR spectra and 3086-2918 cm$^{-1}$ of the Raman spectra. Thus there was a good agreement between experimental and calculated frequencies. The in-plane aromatic C–H deformation vibrations occur in the region 1300–1000 cm$^{-1}$ [17]. The C–H in-plane bending vibration computed at 1453-1042 cm$^{-1}$, while the experimental observation at 1443-1028 cm$^{-1}$ in FT-IR shows excellent agreement with theoretical values. C–H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900–667 cm$^{-1}$[18]. The calculated frequency at 893-596 cm$^{-1}$ is assigned for the C–H out-of-plane bending. In general the aromatic C–H vibrations (viz, stretching, in-plane and out of plane vibrations) calculated theoretically are in good agreement with experimentally accepted values.
<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Observed frequencies (cm⁻¹)</th>
<th>Calculated frequencies (cm⁻¹) with B3LYP/6–31G** force field</th>
<th>TED (%) among type of internal coordinates</th>
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<td>Raman</td>
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<tr>
<td>43</td>
<td>-</td>
<td>1005</td>
<td>1052</td>
</tr>
</tbody>
</table>
Abbreviations used: R: ring; b: bending; ω: wagging; t: torsion; Contributions larger than 10% are given.

*Relative absorption intensities normalized with highest peak absorption equal to 1.0.

*Relative Raman intensities calculated by E.2 and normalized to 100.
3. **Carbon–carbon vibrations**
The ring carbon–carbon stretching vibrations investigation occurs in the region in 1625–1430 cm\(^{-1}\) [19]. In the present, the bands of C–C stretching vibrations in benzene ring appear at 1672 - 1410 cm\(^{-1}\) in FT-IR are also consistent with the calculated one.

4. **Carbon–nitrogen vibrations**
The identification of C–N vibrations is a very difficult task, since the mixing of several bands is possible in the region. Nitro aromatic compounds show a C–N stretching vibrations near 870 cm\(^{-1}\) [20]. The observed frequency at 889 cm\(^{-1}\) in FT-IR and 809 cm\(^{-1}\) in Raman for N,N’-DBH are attributed to C–N aromatic stretching mode. For our title compound, it was good agreement with TED output. The C–N bending vibrations assigned to 721 and 610 cm\(^{-1}\) in FT-IR for title molecule. These assignments are good agreement with the literature values [21].

5. **Nitrogen–hydrogen vibrations**
In all the heterocyclic compounds, the N–H stretching vibrations [22] occur in the region 3500–3000 cm\(^{-1}\). The FT-IR band appears at 3260 and Raman appears at 3251 cm\(^{-1}\) for N,N’-DBH have been assigned to N–H stretching modes of vibrations.

6. **Ring vibrations**
Usually an in-plane deformation vibration is at higher frequencies than the out-of-plane vibration [23]. In the present study, the bands observed at 937-560 cm\(^{-1}\) in IR are attributed to ring in-plane bending modes. The ring out-of-plane bending mode frequencies are established at 496, 378, 137, 117, 94 and 75 cm\(^{-1}\) in Raman spectra as shown in Table 4.

### V. OTHER MOLECULAR PROPERTIES

(a) **Charge analysis**
Atomic charges of the title compound are calculated by DFT method at the B3LYP/6-31G** level of calculation, are shown in Table 5. The magnitude of the carbon atomic charges for the compound was found to be either positive or negative. These magnitude was obtained to change between -0.106051 and –0.070976 for N,N’-DBH. The magnitude of the hydrogen atomic charges was found to be positive and negative.

**Table 5: Atomic charges for optimized geometry of N,N’-DBH**

<table>
<thead>
<tr>
<th>Atoms (^a)</th>
<th>B3LYP/6-31G** Mulliken</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N’-DBH</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-0.106051</td>
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<tr>
<td>C2</td>
<td>-0.069049</td>
</tr>
<tr>
<td>C3</td>
<td>0.004669</td>
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<td>C4</td>
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<td>C6</td>
<td>-0.070976</td>
</tr>
<tr>
<td>H7</td>
<td>0.088546</td>
</tr>
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<td>H8</td>
<td>0.073514</td>
</tr>
<tr>
<td>H9</td>
<td>0.142094</td>
</tr>
<tr>
<td>H10</td>
<td>0.096536</td>
</tr>
<tr>
<td>H11</td>
<td>0.092964</td>
</tr>
<tr>
<td>C12</td>
<td>0.644517</td>
</tr>
<tr>
<td>O13</td>
<td>-0.531552</td>
</tr>
<tr>
<td>N14</td>
<td>-0.532976</td>
</tr>
<tr>
<td>H15</td>
<td>0.309413</td>
</tr>
</tbody>
</table>

\(^a\) All the atomic charges are reported in the table.
The atoms indicated in the parenthesis belongs to N,N’-DBH; for numbering of atoms refer Fig 1.

(b) Thermodynamic properties
Several calculated thermo dynamical parameters were presented in Table 6. Scale factors have been recommended [24] for an accurate prediction determining the zero-point vibrational energies for DFT calculation. The total energy of the molecule is the sum of the translational, rotational, vibrational and electronic energies.

Table 6: Theoretically computed energies (a.u), zero-point vibrational energies (kcal/mol), rotational constants (GHz), entropies (cal/mol-Kelvin) and dipole moment (Debye).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>B3LYP/6-31G** -N,N’-DBH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total energy</td>
<td>-800.6781</td>
</tr>
<tr>
<td>Zero-point energy</td>
<td>148.02294</td>
</tr>
<tr>
<td>Rotational constant</td>
<td>0.60165</td>
</tr>
<tr>
<td></td>
<td>0.32494</td>
</tr>
<tr>
<td></td>
<td>0.31235</td>
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<tr>
<td>**Entropy</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>127.321</td>
</tr>
<tr>
<td>Translational</td>
<td>42.329</td>
</tr>
<tr>
<td>Rotational</td>
<td>32.931</td>
</tr>
<tr>
<td>Vibrational</td>
<td>52.061</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>3.0224</td>
</tr>
</tbody>
</table>

(c) Dipole moment
Dipole moment reflects the molecular charge distribution and was given as a vector in three dimensions. Therefore, it can be used as descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of negative and positive charges. Dipole moments were strictly determined for neutral molecules. Dipole moment values of the title compounds are shown in Table 6.
VI. NLO PROPERTIES

The second-order polarizability or first order hyperpolarizability $\beta$, dipole moment $\mu$ and polarizability $\alpha$ was calculated using B3LYP/6-31G** basis set on the basis of the finite-field approach. The complete equations for calculating the magnitude of total static dipole moment $\mu$, the mean polarizability $\alpha_o$, the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability $\beta$, using the x, y, z components from Gaussian 03W output is as follow:

$$
\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}
$$

$$
\alpha_o = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})
$$

$$
\Delta\alpha = 1/2 \left\{ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 \right\}^{1/2}
$$

$$
\beta_{tot} = (\beta_{xxx}^2 + \beta_{xyy}^2 + \beta_{xzz}^2 + \beta_{yxy}^2 + \beta_{yzy}^2 + \beta_{yyz}^2 + \beta_{zxy}^2 + \beta_{zyy}^2 + \beta_{zzz}^2)^{1/2}
$$

Since the values of the polarizabilities ($\alpha$) and hyperpolarizability ($\beta$) of Gaussian 03 output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) ($\alpha$: 1 a.u. = 0.1482 × 10⁻¹² esu, $\beta$: 1 a.u. = 8.6393 × 10⁻³³ esu). Theoretically calculated values of polarizability and hyperpolarizability are as shown in Table 7. The large value of hyperpolarizability, $\beta$ which is a function of the non-linear optical activity of the molecular system was associated with the intramolecular charge transfer, resulting from the electron cloud movement through π conjugated framework from electron donor to electron acceptor groups. The physical properties of these conjugated molecules are governed by the high degree of electronic charge delocalization along the charge transfer axis and by the low band gaps.

Table 7: Calculated hyperpolarizability $\beta$, polarizability $\alpha$ of N,N'-DBH

<table>
<thead>
<tr>
<th>$\beta$</th>
<th>Values($10^{-36}$esu)</th>
<th>$\alpha$</th>
<th>Values($10^{-30}$esu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{xxx}$</td>
<td>8.617</td>
<td>$\alpha_{xx}$</td>
<td>51.091</td>
</tr>
<tr>
<td>$\beta_{xyy}$</td>
<td>16.176</td>
<td>$\alpha_{xy}$</td>
<td>2.503</td>
</tr>
<tr>
<td>$\beta_{yyz}$</td>
<td>9.994</td>
<td>$\alpha_{yz}$</td>
<td>121.669</td>
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<tr>
<td>$\beta_{zzz}$</td>
<td>23.007</td>
<td>$\alpha_{xz}$</td>
<td>43.387</td>
</tr>
<tr>
<td>$\beta_{yyz}$</td>
<td>12.438</td>
<td>$\alpha_{yz}$</td>
<td>4.842</td>
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<tr>
<td>$\beta_{yzz}$</td>
<td>22.814</td>
<td>$\alpha_{xz}$</td>
<td>11.9276</td>
</tr>
<tr>
<td>$\beta_{yzz}$</td>
<td>15.828</td>
<td>$\alpha_{zz}$</td>
<td>60.648</td>
</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td>-6.076</td>
<td>$\alpha_{zz}$</td>
<td>28.974</td>
</tr>
</tbody>
</table>

VII. FRONTIER MOLECULAR ORBITALS (FMOs)

Many organic molecules that contain conjugated π electrons are characterized hyperpolarizabilities and were analyzed by means of vibrational spectroscopy [25, 26]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. But the intermolecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for by ab initio calculations in π conjugated systems that predict exceptionally large Raman and infrared intensities for the same normal modes [25]. It is also observed in our title molecule the bands in FTIR spectrum have their counterparts in Raman shows that the relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through π conjugated framework work from electron donor to electron acceptor groups. The electron absorption corresponds to the
transition from the ground to the first excited state and is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The HOMO-LUMO energy gap of N,N'-DBH was calculated at the B3LYP/6-31** level and are shown in Table 8.

Table 8: HOMO – LUMO energy value calculated by B3LYP/6-31G**.

<table>
<thead>
<tr>
<th>Parameters (eV)</th>
<th>B3LYP/6-31G**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N,N'-DBH</td>
</tr>
<tr>
<td>HOMO</td>
<td>-0.253</td>
</tr>
<tr>
<td>LUMO</td>
<td>-0.050</td>
</tr>
<tr>
<td>HOMO-LUMO</td>
<td>-0.203</td>
</tr>
<tr>
<td>HOMO-1</td>
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</tr>
<tr>
<td>LUMO+1</td>
<td>-0.045</td>
</tr>
<tr>
<td>HOMO-1-LUMO+1</td>
<td>-0.211</td>
</tr>
<tr>
<td>HOMO-2</td>
<td>-0.259</td>
</tr>
<tr>
<td>LUMO+2</td>
<td>-0.012</td>
</tr>
<tr>
<td>HOMO-2-LUMO+2</td>
<td>-0.247</td>
</tr>
</tbody>
</table>

and the energy gap reflect the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron, HOMO represents the ability to donate an electron.

HOMO energy = -0.253eV  
LUMO energy = -0.050eV  
HOMO–LUMO energy gap = -0.203eV

The HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The atomic orbital compositions of the Frontier molecular orbital are shown in Fig. 4. The electronic properties of the molecule are calculated from the total energies and the Koopmans’ theorem. The ionization potential is determined from $IP = -E_{HOMO}$ while the electron affinity is computed from $EA = -E_{LUMO}$, respectively. The other important quantities such as electronegativity ($\chi$), hardness ($\eta$), softness ($\zeta$), and electrophilicity index ($\psi$) were deduced from ionization potential and electron affinity values.

Electro negativity ($\chi$) $\mu = -\kappa = \frac{IP+EA}{2}$
Chemical hardness ($\eta$) $\frac{1}{\eta} = \frac{IP-EA}{2}$
Softness ($\zeta$) $\frac{1}{2\eta}$
Electrophilicity index ($\psi$) $\frac{\mu^2}{2\eta}$
Fig 4. HOMO and LUMO plot of N,N'-DBH

\[ \Delta E_{\text{HOMO-LUMO}} = 0.203 \text{a.u} \]
The values of electro negativity, chemical hardness, softness, and electrophilicity index are 0.1515, 0.1015, 4.9261 and 0.1137 eV in DMSO, respectively, for the title molecule.

VIII. \( ^{13}C \) and \(^1H\) NMR SPECTRAL ANALYSIS

The molecular structure of the title compounds was optimized. Then, gauge – independent atomic orbital (GIAO) [27, 28]\(^{13}\)CNMR chemical shifts calculations of the title compounds had been carried out using B3LYP/functional with 6-31G** basis set. Experimental and theoretical chemical shifts of N,N’-DBH in \(^{13}\)C NMR and \(^1H\) NMR spectra were recorded and the obtained data are presented in Table 9. The coefficient of correlations between calculated and experimental data of \(^{13}\)C NMR and \(^1H\) NMR spectra were determined as 0.99994 and 0.99931 for N,N’-DBH. The correlations of \(^{13}\)C NMR spectra and \(^1H\) NMR spectra were presented in Fig.5 for N,N’-DBH. The agreement between the experimental and calculated data was satisfactory[29, 30]. In the present study, the \(^{13}\)C NMR chemical shifts in the ring for N,N’-DBH are >100 ppm, as they would be expected.

Table 9: Theoretical and experimental \(^1H\) NMR and \(^{13}\)C NMR spectra of N,N’-DBH (with respect to TMS, all values in ppm) for B3LYP/6-31G**

<table>
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<tr>
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<th>N,N’-DBH</th>
<th>EXP</th>
<th>CALC</th>
</tr>
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<td>C1</td>
<td>128.41</td>
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</tr>
<tr>
<td>C2</td>
<td>127.39</td>
<td>128.99</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>132.52</td>
<td>136.62</td>
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<td>C4</td>
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<td>C20</td>
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</tr>
<tr>
<td>H30</td>
<td>7.60</td>
<td>7.65</td>
<td></td>
</tr>
</tbody>
</table>

For numbering of atoms refer Fig 1.
Fig 5. The Linear regression between experimental and theoretical $^{13}\text{C}$ (a) $^1\text{H}$ (b) NMR Chemical Shift for N,N'-DBH
A complete vibrational analysis of N,N′-dibenzyloxydrazine (N,N′-DBH) is performed by DFT-B3LYP method with 6-31G** basis set. All the vibrational bands observed in the FT-IR and FT-Raman spectra of these compounds are assigned to the various modes of vibration. Most of the modes have wave numbers in the range suggested by previous assignments found in literature in the case of related molecules. The HOMO-LUMO energy gap calculated at the B3LYP/6-31** level reveals the chemical activity of the molecule. \(^1\)H and \(^13\)C NMR chemical shifts have been compared with experimental values. Finally, ab-initio calculations proved to be a useful tool to analyze the molecular structure and the optical properties of the new materials. The calculated first order hyperpolarizability of title molecule is about 4.7 times greater than that of urea. The above results show that N,N′-DBH is the best material for NLO applications.

REFERENCES