

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. The ¹H 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 X and absolute hardness η were performed by DFT approach. The first order hyperpolarizability (β^*) of these novel molecular system and related properties (β , α_0 and $\Delta\alpha$) 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 hydrazine are reported to act as inhibitors of 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–

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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 50–4000cm⁻¹ on a Bruker IFS66v spectrophotometer equipped with FRA 106 FT-Raman module accessory. The FTIR spectrum of this compound was recorded in the region 400–4000cm⁻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 2cm⁻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 (S_i) calculated by Gaussian 03 and adjusted during scaling procedure with MOLVIB were converted to relative Raman intensity (I_i) using the following relation from the basic theory of Raman scattering [14, 15]

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

Where ν_o is the exciting wavenumber (in cm⁻¹ units), ν_i the vibrational wavenumber of the ith 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.

IV.RESULTS AND DISCUSSION

1. Structural properties

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

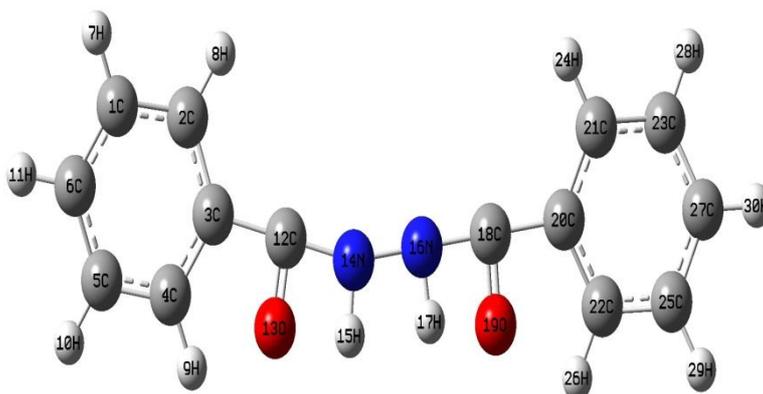


Fig.1: Molecular Structure of N,N'-dibenzoylhydrazine along with Numbering of atoms.

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 1: Optimized geometrical parameters of N,N'-DBH obtained by B3LYP 6/31G density functional calculations.**

Bond length	Value (\AA)	Bond Angle	Value ($^\circ$)
	N,N'-DBH		N,N'-DBH
C1-C2	1.394	C1-C2-C3	120.1818
C2-C3	1.402	C2-C3-C4	119.1160
C3-C4	1.404	C3-C4-C5	120.5539
C4-C5	1.391	C4-C5-C6	119.9742
C5-C6	1.396	C2-C1-H7	119.5980
C1-H7	1.085	C3-C2-H8	120.5481
C2-H8	1.082	C3-C4-H9	119.3517
C4-H9	1.084	C4-C5-H10	120.1678
C5-H10	1.085	C5-C6-H11	120.1156
C6-H11	1.086	C2-C3-C12	121.9179
C3-C12	1.499	C3-C12-O13	104.6717
C12-O13	1.224	O13-C12-N14	100.8960
C12-N14	1.386	C12-N14-H15	112.8833
N14-H15	1.015	H15-N14-N16	118.0780
N14-N16	1.388	N14-N16-H17	100.4327
N16-H17	1.016	H17-N16-C18	95.7104
N16-C18	1.402	N16-C18-O19	100.1180
C18-O19	1.222	O19-C18-C20	104.4002
C18-C20	1.494	C18-C20-C21	123.6537
C20-C21	1.401	C21-C20-C22	119.5046
C20-C22	1.402	C20-C21-C23	119.9938
C21-C23	1.394	C20-C21-H24	120.3318
C21-H24	1.083	C20-C22-H25	120.3033

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C22-C25	1.392	C25-C22-H26	121.0117
C22-H26	1.084	C21-C23-C27	120.2231
C25-C27	1.396	C27-C23-H28	120.1398
C23-H28	1.085	C27-H25-H29	120.1590
C25-H29	1.085	C25-C27-H30	120.0323
C27-H30	1.086		

The atom indicated in the parenthesis belongs to N,N'-DBH; for numbering of atoms refer Fig 1.

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 Raman spectrum the in-plane vibrations give rise to polarized bands while the out-of-plane ones 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

No	Symbol	Type	Definition
Stretching			
1-12	Pi	C-C	C1-C2,C2-C3, C3-C4, C4-C5,C5-C6, C6-C1, C20-C21,C21-C23, C23-C27,C27-C25, C25-C22, C22-C20.
13-14	pi	C-C(a)	C3-C12,C18-C20
15-24	Qi	C-H	C1-H7,C2-H8,C4-H9,C5-H10, C6-H11,C21-H24,C22-H26, C23-H28,C25-H29,C27-H30.
25-26	qi	C-O	C12-O13, C18-O19.
27-28	Ri	N-H	N14- H15,N16-H17.
29-30	ri	C-N	C12- N14,C18-N16.
31	ri	N-N	N14-N16.
Bending			
In- plane bending			
32-35	β_i	C-C-C	C2-C3-C12, C4-C3-C12, C21-C20-C18, C22-C20-C18.
36-55	β_i	C-C-H	C2-C1- H7,C6-C1-H7, C3-C2- H8, C1-C2- H8, C3-C4- H9, C5-C4- H9, C4-C5- H10, C6- C5-H10,C5-C6-H11,C1-C6- H11, C20-C21-H24,C23-C21-H24,C20-C22-H26,C25-C22-H26,C21-C23- H28,C27-C23-H28,C22-C25-H29,C27- C25-H29, C25-C27-H30,C23-C27-H30.
56-57	α_i	C-C-O	C3-C12- O13, C20-C18-O19.
58-59	ρ_i	C-N-H	C12-N14-H15,C18-N16-H17.
60-61	θ_i	C-C-N	C3-C12-N14,C20-C18-N16.

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62-63	θ_i	O-C-N	O13-C12-N14, O19-C18-N16.
64-69	Φ_i	C-C-C (ring1)	C1-C2-C3, C2-C3-C4, C3-C4-C5, C4-C5-C6, C5-C6-C1, C6-C1-C2.
70-75	Φ_i	C-C-C (ring2)	C20-C21-C23, C21-C23- C27, C23-C27- C25, C27-C25-C22,C25-C22-C20, C22-C20-C21.
Out-of-plane bending			
76-77	ω_i	C-C	C12-C3-C2-C4,C18-C20-C21-C22.
78-87	ω_i	C-H	H7-C1-C2-C6,H8-C2-C1-C3,H9-C4-C5-C3,H10-C5-C6-C4,H11-C6-C1-C5,H24-C21-C23-C20,H26-C22-C20-C25,H28-C23-C27-C21,H29-C25-C27-C22,H30-C27-C25-C23.
88-89	ω_i	C-O	O13-C12-C3-N14,O19-C18-C20-N16.
90-91	ω_i	N-H	H15-N14-N16-C12, H17-N16-N14-C18.
Torsion			
92-93	τ_i	C-O	C4-C3-C12-O13,C21-C20-C18-O19.
94-95	τ_i	N-H	H15-N14-C12-C3, H17-N16-C18-C20.
96	τ_i	C-N	C12-N14-N16-C18
97-102	τ_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.
103-108	τ_i	Tring 2	C20-C21-C23-C27,C21-C23-C27-C25,C23-C27- C25-C22,C27-C25-C22-C20, C25-C22-C20-C21,C22-C20-C21-C23.

For numbering of atoms refer Fig1.

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Table 3: Definition of local symmetry coordinates of N,N'-DBH

^aThese symbols are used for description of the normal modes by PED in Table 4.

^bThe internal coordinates used here are defined in Table 2.

No.	Symbol ^a	Definition ^b
1-12	CC	P ₁ , P ₂ , P ₃ , P ₄ , P ₅ , P ₆ , P ₇ , P ₈ , P ₉ , P ₁₀ , P ₁₁ , P ₁₂ .
13-14	CC(a)	P ₁₃ , P ₁₄ .
15-24	CH	Q ₁₅ , Q ₁₆ , Q ₁₇ , Q ₁₈ , Q ₁₉ , Q ₂₀ , Q ₂₁ , Q ₂₂ , Q ₂₃ , Q ₂₄ .
25-26	CO	q ₂₅ , q ₂₆ .
27-28	NH	R ₂₇ , R ₂₈ .
29-30	CN	r ₂₉ , r ₃₀ .
31	NN	r ₃₁ .
32-33	bCC	(β ₃₂ - β ₃₃)/√2, (β ₃₄ - β ₃₅)/√2.
34-43	bCH	(β ₃₆ - β ₃₇)/√2, (β ₃₈ - β ₃₉)/√2, (β ₄₀ - β ₄₁)/√2, (β ₄₂ - β ₄₃)/√2, (β ₄₄ - β ₄₅)/√2, (β ₄₆ - β ₄₇)/√2, (β ₄₈ - β ₄₉)/√2, (β ₅₀ - β ₅₁)/√2, (β ₅₂ - β ₅₃)/√2, (β ₅₄ - β ₅₅)/√2.
44-45	bCO	α ₅₆ , α ₅₇ .
46-47	bNH	ρ ₅₈ , ρ ₅₉ .
48-49	bCN	θ ₆₀ , θ ₆₁ .
50-51	boCN	θ ₆₂ , θ ₆₃ .
52	bring1	(Φ ₆₄ - Φ ₆₅ + Φ ₆₆ - Φ ₆₇ + Φ ₆₈ - Φ ₆₉)/√6
53	bring1	(-Φ ₆₄ - Φ ₆₅ + 2Φ ₆₆ - Φ ₆₇ - Φ ₆₈ + 2Φ ₆₉)/√12
54	bring1	(Φ ₆₄ - Φ ₆₅ + Φ ₆₆ - Φ ₆₇)/2
55	bring2	(Φ ₇₀ - Φ ₇₁ + Φ ₇₂ - Φ ₇₃ + Φ ₇₄ - Φ ₇₅)/√6
56	bring2	(-Φ ₇₀ - Φ ₇₁ + 2Φ ₇₂ - Φ ₇₃ - Φ ₇₄ + 2Φ ₇₅)/√12
57	bring2	(Φ ₇₀ - Φ ₇₁ + Φ ₇₂ - Φ ₇₃)/2
58-59	ωCC	ω ₇₆ , ω ₇₇ .
60-69	ωCH	ω ₇₈ , ω ₇₉ , ω ₈₀ , ω ₈₁ , ω ₈₂ , ω ₈₃ , ω ₈₄ , ω ₈₅ , ω ₈₆ , ω ₈₇ .
70-71	ωCO	ω ₈₈ , ω ₈₉ .
72-73	ωNH	ω ₉₀ , ω ₉₁ .
74-75	tCO	τ ₉₂ , τ ₉₃ .
76-77	tNH	τ ₉₄ , τ ₉₅ .
78	tCN	τ ₉₆ .
79	tring1	(τ ₉₇ + τ ₉₈ + τ ₉₉ + τ ₁₀₀ + τ ₁₀₁ + τ ₁₀₂)/√6
80	tring1	(τ ₉₇ + τ ₉₈ + τ ₉₉ + τ ₁₀₀)/2
81	tring1	(-τ ₉₇ + 2τ ₉₈ - τ ₉₉ - τ ₁₀₀ + 2τ ₁₀₁ - τ ₁₀₂)/√12
82	tring2	(τ ₁₀₃ + τ ₁₀₄ + τ ₁₀₅ + τ ₁₀₆ + τ ₁₀₇ + τ ₁₀₈)/√6
83	tring2	(τ ₁₀₃ + τ ₁₀₄ + τ ₁₀₅ + τ ₁₀₆)/2
84	tring2	(-τ ₁₀₃ + 2τ ₁₀₄ - τ ₁₀₅ - τ ₁₀₆ + 2τ ₁₀₇ - τ ₁₀₈)/√12

For visual comparison, the observed and calculated (simulated) FTIR and FT-Raman spectra are presented in Figs. 2 and 3.

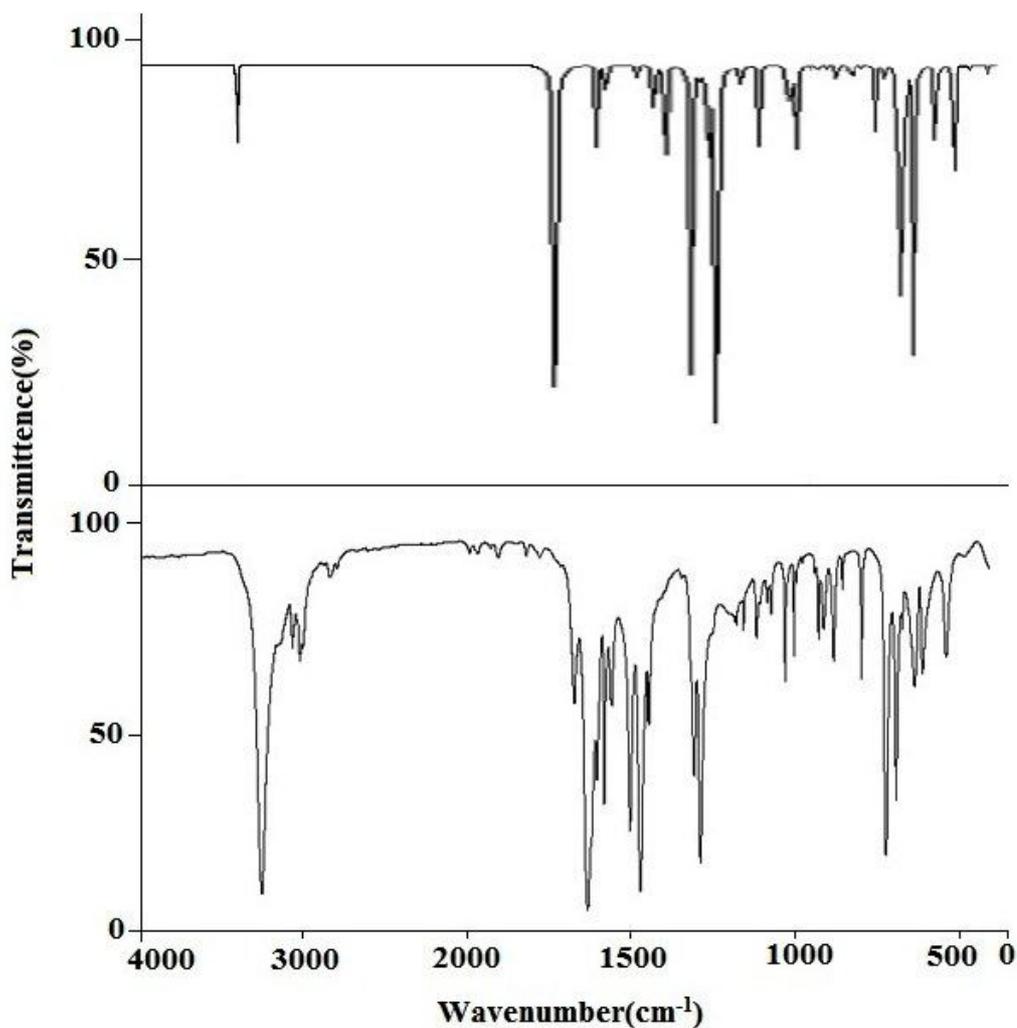


Fig.2: Comparison of observed and calculated FTIR Spectra of N,N'-DBH

- a) Calculated with B3 LYP/6-31G**
- b) Observed with KBr disc

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.

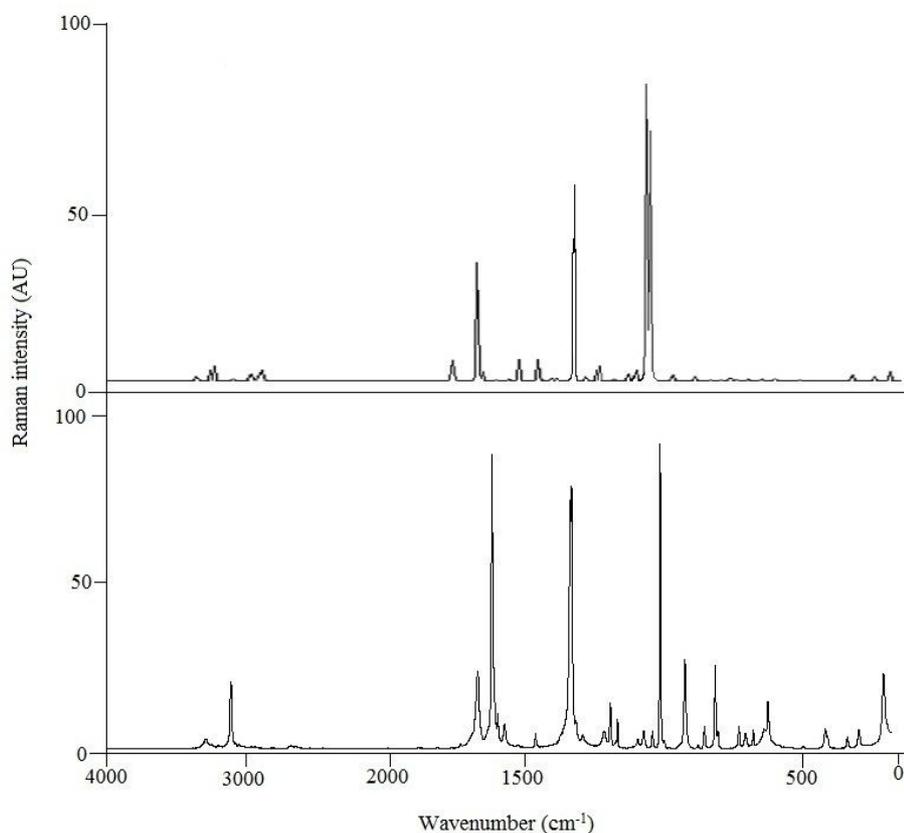


Fig.3: Comparison of observed and calculated FT-Raman Spectra of N,N'-DBH

- (a) Calculated with B3 LYP/6-31G**
(b) Observed with KBr disc

2. Carbon–hydrogen vibration

The heteroaromatic structure showed the presence of C-H stretching vibrations in the region $3100\text{--}3000\text{ cm}^{-1}$, 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 $3048\text{--}3012\text{ cm}^{-1}$ 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 $3088\text{--}2999\text{ cm}^{-1}$ of the IR spectra and $3086\text{--}2918\text{ cm}^{-1}$ 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 $1300\text{--}1000\text{ cm}^{-1}$ [17]. The C–H in-plane bending vibration computed at $1453\text{--}1042\text{ cm}^{-1}$, while the experimental observation at $1443\text{--}1028\text{ cm}^{-1}$ 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 $900\text{--}667\text{ cm}^{-1}$ [18]. The calculated frequency at $893\text{--}596\text{ cm}^{-1}$ 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.

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Table4: Observed and B3LYP/6–31G level Calculated vibrational frequency (cm⁻¹) of N,N'-DBH**

Sl. No	Observed frequencies (cm ⁻¹)		Calculated frequencies (cm ⁻¹) with B3LYP/6–31G** force field				TED (%)among type of internal coordinates
	Infrared	Raman	Un scaled	Scaled	IR ^a (A _i)	Raman ^b (I _i)	
1	3260	-	3575	3381	25.2905	78.5178	NH (99)
2	-	3251	3564	3371	16.8359	151.1675	NH (99)
3	3088	-	3222	3048	1.2627	74.8878	CH (100)
4	-	3086	3222	3048	2.7618	185.8541	CH (100)
5	3078	-	3206	3032	12.5157	87.6408	CH (100)
6	3061	-	3205	3031	12.8239	54.8417	CH (100)
7	3050	-	3196	3023	24.4954	176.7186	CH (99)
8	3016	-	3219	3045	21.1402	50.8717	CH (88)
9	-	3010	3218	3044	6.2406	179.5964	CH (84)
10	2999	-	3195	3022	10.6671	29.0714	CH (99)
11	-	2932	3185	3013	0.0023	11.6088	CH (99)
12	-	2918	3184	3012	0.7306	90.1752	CH (99)
13	1672	-	1775	1679	1.4564	41.6168	CC(89)
14	-	1655	1773	1677	426.5388	16.1235	CC(73),bCH(11)
15	1631	-	1740	1646	8.2707	40.0809	CC(73),bCH(11)
16	-	1605	1712	1619	13.7586	63.3957	CC(67), bCH(11),bring(11),
17	-	1584	1660	1570	0.4455	9.3912	bCH(44), bCC(13),bCO(11)
18	1580	-	1659	1569	7.6419	1.0155	CC(65),bCH(21)
19	1557	-	1637	1548	0.8157	1.4643	CC(73),bCH(11)
20	1501	-	1636	1547	4.1585	0.5143	CC(51),bCH(12) bring(11)
21	1470	-	1537	1454	8.1040	2.7535	CCa(54),bring(19),bCC (11)
22	1443	-	1536	1453	24.4083	2.9448	bCH(44), bCC(13),bCO(11)
23	-	1434	1490	1409	27.1850	6.3215	CC(51),bCH(12) bring(11)
24	1410	-	1489	1408	1.4952	9.8039	CC(51),bCH(12) bring(11)
25	-	1321	1460	1381	154.1500	35.3237	CC(73),bCH(11)
26	-	1318	1459	1380	6.2030	0.4112	CC(73),bCH (19), bCN (11)
27	1308	-	1389	1313	1.8394	1.0116	CO(48),bOCN(15),bring(13)
28	1287	-	1364	1290	37.9396	1.2049	bring(73)
29	-	1278	1363	1289	3.2037	2.7353	CC (63), bCH (21)
30	-	1234	1343	1270	393.8221	12.4709	CCa(45),bring(29),bCN (11)
31	-	1218	1340	1264	14.8852	14.2051	bOCN(57), bCO(16)
32	-	1203	1321	1249	1.2369	2.6230	CO(57), bCC(14)
33	1188	-	1255	1187	19.8596	6.1486	bCH(63),bCN(12),bring(11)
34	1182	-	1249	1181	0.1616	3.7223	bCH(78),bring(13)
35	-	1157	1207	1141	0.0796	8.5200	bCH(78),bring(13)
36	1156	-	1206	1140	39.6708	1.2332	NN(64),bCN(18)
37	1116	-	1190	1125	2.1306	3.1765	bCH(44), bCC(13),bCO(11)
38	1106	-	1189	1124	28.9089	0.0191	bCH(44), bCC(13),bCO(11)
39	1082	-	1127	1066	7.5211	4.0988	bCC(53),bCH(14),bring(11)
40	1071	-	1117	1056	12.0023	3.0281	bCO(61),bOCN(17)
41	-	1036	1108	1048	1.7840	26.0801	bCH(46),bCC(25)
42	1028	-	1102	1042	2.1440	4.0472	bCH(78),bring(13)
43	-	1005	1052	995	1.3644	37.5196	bring(72)
44	1002	-	1051	994	0.6061	0.5278	bring(49), CC(19),bCH(13)

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45	987	-	1019	963	0.0973	0.0200	bCH(78),bring(13)
46	965	-	1018	963	0.0711	0.1417	bNH(54),bCC(11),bCH(11)
47	937	-	1009	954	0.7042	0.2967	bring(69)
48	926	-	1006	951	4.7295	5.9415	bCC(48),bCH(17),bring(12)
49	-	917	984	930	3.3659	0.7311	ω CH(43), tring(20)
50	911	-	980	927	0.6258	7.0245	bCO(65),bOCN(14)
51	889	-	945	893	1.2529	2.2186	CN(69),bring(21)
52	881	-	944	893	13.9141	1.2352	ω CH(43), ω CC(13),tring(11)
53	843	-	862	815	7.4476	0.3674	ω CH(51), tring(16), ω CC(10)
54	-	809	860	813	6.4379	2.9736	CN(52),bCN(16),bNH(11)
55	796	-	815	770	6.5244	14.0710	ω CC(59), ω NH(18)
56	-	746	812	768	17.4405	0.1400	ω CH(41), ω CO(28)
57	721	-	782	739	91.4711	1.4363	bCN(58),bNH(18)
58	-	704	742	701	119.4373	2.6488	ω CH(53), tring(12)
59	690	-	736	696	6.8292	0.0865	ω CH(43), ω CC(13), tring(11)
60	671	-	725	685	0.6492	0.2647	bring(49), CC(19),bCH(13)
61	-	660	718	679	206.1663	6.0680	ω CH(38), ω CO(23)
62	624	-	703	665	0.1300	7.6804	bNH(51),bCC(13),bCH(11)
63	-	621	701	663	0.0316	1.1465	ω CH(38), ω CO(23)
64	610	-	676	639	27.3619	0.5654	bCN(52),bNH(11),bring(11)
65	598	-	632	597	3.2772	6.0918	ω CH(43), ω CC(13), tring(11)
66	-	580	631	596	40.8580	0.4004	ω CH(66), tring(20)
67	-	568	602	569	5.4518	3.5096	tNH(61), ω CO(24)
68	560	-	583	551	2.5737	1.3665	bring(49), CC(19),bCH(13)
69	538	-	538	508	3.7459	0.5786	ω CC(56), ω CO(15),tring(12)
70	-	496	524	495	0.0159	0.6446	tring(61), ω CH (14)
71	-	432	470	444	0.1461	0.1124	ω NH(42), ω CC (23)
72	-	412	442	418	1.0346	1.6962	ω NH(42), ω CC (23)
73	-	378	415	392	0.6057	2.3842	tring(61), ω CH (14)
74	-	371	415	392	2.4939	0.6753	ω CO(64), ω NH (13)
75	-	342	388	367	12.9266	3.9871	bOCN(57), bCO(16)
76	-	337	363	343	1.7082	0.2188	ω CO(55), ω CC (14),tring(12)
77	-	298	277	262	0.0725	5.4637	tCO(64), ω CH (13)
78	-	293	277	262	2.9407	0.9928	tCO(64), ω CH (13)
79	-	209	216	204	0.1439	8.8600	tNH(67), ω CO(19)
80	-	137	191	180	0.0680	0.9636	tring(61), ω CH (14)
81	-	117	140	132	2.5952	6.8516	tring(74)
82	-	110	135	127	0.6665	5.7932	tCN(53), ω CO (13), ω CH(11)
83	-	94	97	91	0.0282	6.2156	tring(49), ω CO(27)
84	-	75	62	58	0.2851	6.5312	tring(61), ω CH (14)

Abbreviations used: R: ring; b:bending; ω : ω agging; t:torsion; Contributions larger than 10% are given.

^aRelative absorption intensities normalized with highest peak absorption equal to 1.0.

^bRelative 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 1625–1430cm⁻¹ [19]. In the present, the bands of C–C stretching vibrations in benzene ring appear at 1672 -1410cm⁻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 870cm⁻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

Atoms ^a	B3LYP/6-31G**
	Mulliken
N,N'-DBH	
C1	-0.106051
C2	-0.069049
C3	0.004669
C4	-0.062197
C5	-0.096414
C6	-0.070976
H7	0.088546
H8	0.073514
H9	0.142094
H10	0.096536
H11	0.092964
C12	0.644517
O13	-0.531552
N14	-0.532976
H15	0.309413

N16	-0.463131
H17	0.282472
C18	0.605392
O19	-0.526867
C20	0.018529
C21	-0.062524
C22	-0.058350
C23	-0.103315
H24	0.074324
C25	-0.097258
H26	0.139696
C27	-0.070832
H28	0.090427
H29	0.095988
H30	0.092414

^aThe 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).

Parameters	B3LYP/6-31G**
	N,N'-DBH
Total energy	-800.6781
Zero-point energy	148.02294
Rotational constant	0.60165
	0.32494
	0.31235
Entropy	
Total	127.321
Translational	42.329
Rotational	32.931
Vibrational	52.061
Dipole moment	3.0224

(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 β , dipole moment μ and polarizability α 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 μ , the mean polarizability α_o , the anisotropy of the polarizability $\Delta\alpha$ and the mean first hyperpolarizability β , using the x, y, z components from Gaussian 03W output is as follow;

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

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

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

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

$$\beta_{tot} = \{ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \}^{1/2}$$

Since the values of the polarizabilities (α) and hyperpolarizability (β) of Gaussian 03 output are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) (α : 1 a.u. = 0.1482×10^{-12} esu, β : 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, β 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 frame work 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 β , polarizability α of N,N'-DBH

β	Values(10^{-30} esu)	α	Values(10^{-30} esu)
β_{xxx}	8.617	α_{xx}	51.091
β_{xxy}	16.176	α_{xy}	2.503
β_{xyy}	9.994	α_{yy}	121.669
β_{yyy}	23.007	α_{yz}	43.387
β_{xxz}	12.438	α_{zz}	4.842
β_{xyz}	22.814	α_{xz}	119.276
β_{yyz}	15.828		
β_{xzz}	-6.076		
β_{yzz}	28.974		
β_{zzz}	-64.448		

VII. FRONTIER MOLECULAR ORBITALS (FMOs)

Many organic molecules that containing 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 frame 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.**

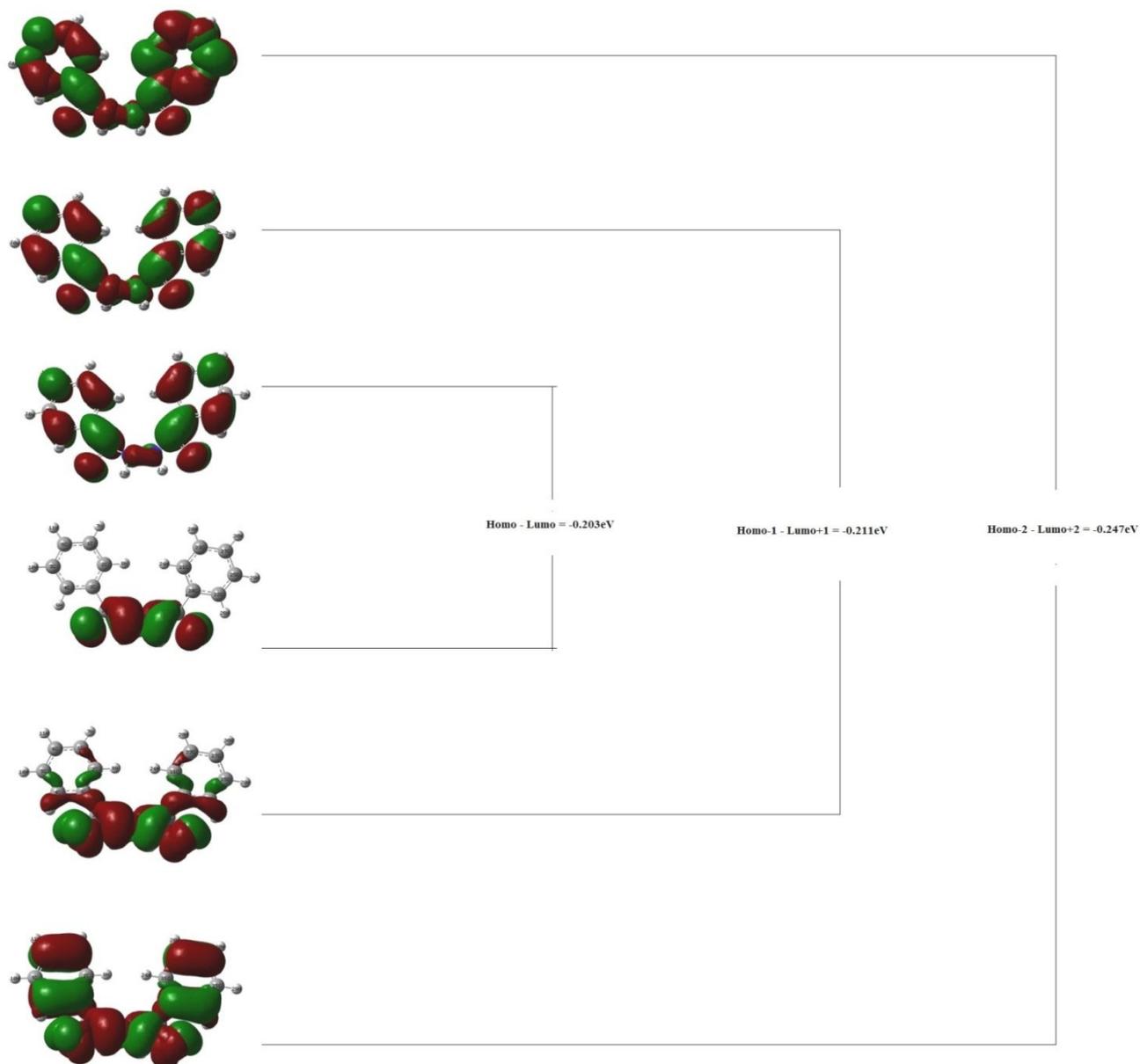
Parameters (eV)	B3LYP/6-31G**
	N,N'-DBH
HOMO	-0.253
LUMO	-0.050
HOMO-LUMO	-0.203
HOMO-1	-0.256
LUMO+1	-0.045
HOMO-1-LUMO+1	-0.211
HOMO-2	-0.259
LUMO+2	-0.012
HOMO-2-LUMO+2	-0.247

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.

$$\begin{aligned} \text{HOMO energy} &= -0.253\text{eV} \\ \text{LUMO energy} &= -0.050\text{eV} \\ \text{HOMO-LUMO energy gap} &= -0.203\text{eV} \end{aligned}$$

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 $IP = -E_{\text{HOMO}}$ while the electron affinity is computed from $EA = -E_{\text{LUMO}}$, respectively. The other important quantities such as electronegativity (χ), hardness (η), softness (ζ), and electrophilicity index (ψ) were deduced from ionization potential and electron affinity values.

$$\begin{aligned} \text{Electro negativity } (\chi) \mu &= -\chi = -\frac{IP+EA}{2} \\ \text{Chemical hardness } (\eta) &= \frac{IP-EA}{2} \\ \text{Softness } (\zeta) &= \frac{1}{2\eta} \\ \text{Electrophilicity index } (\psi) &= \frac{\mu^2}{2\eta} \end{aligned}$$



$$\Delta E_{\text{HOMO-LUMO}} = 0.203 \text{ a.u.}$$

Fig 4. HOMO and LUMO plot of N,N'-DBH

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. ¹³C and ¹H NMR SPECTRAL ANALYSIS

The molecular structure of the title compounds was optimized. Then, gauge – independent atomic orbital (GIAO) [27, 28]¹³CNMR 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 ¹³C 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 ¹³C NMR and ¹H NMR spectra were determined as 0.99994 and 0.99931 for N,N'-DBH. The correlations of ¹³C NMR spectra and ¹H NMR spectra are presented in Fig.5for N,N'-DBH. The agreement between the experimental and calculated data was satisfactory[29, 30]. In the present study, the ¹³C 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 ¹³C NMR spectra of N,N'-DBH (with respect to TMS, all values in ppm) for B3LYP/6-31G**

ATOM	N,N'-DBH	
	EXP	CALC
C1	128.41	128.89
C2	127.39	128.99
C3	132.52	136.62
C4	127.39	130.38
C5	128.39	128.89
C6	131.76	132.72
C12	165.80	165.85
C18	165.80	164.08
C20	132.52	133.95
C21	127.39	129.55
C22	127.39	129.97
C23	128.41	128.89
C25	127.39	128.75
C27	131.76	132.53
H7	7.53	7.55
H8	7.96	7.54
H9	7.96	8.44
H10	7.53	7.75
H11	7.60	7.66
H15	10.60	10.59
H17	10.60	10.96
H24	7.96	8.56
H26	7.96	7.44
H28	7.53	7.68
H29	7.53	7.53
H30	7.60	7.65

For numbering of atoms refer Fig 1.

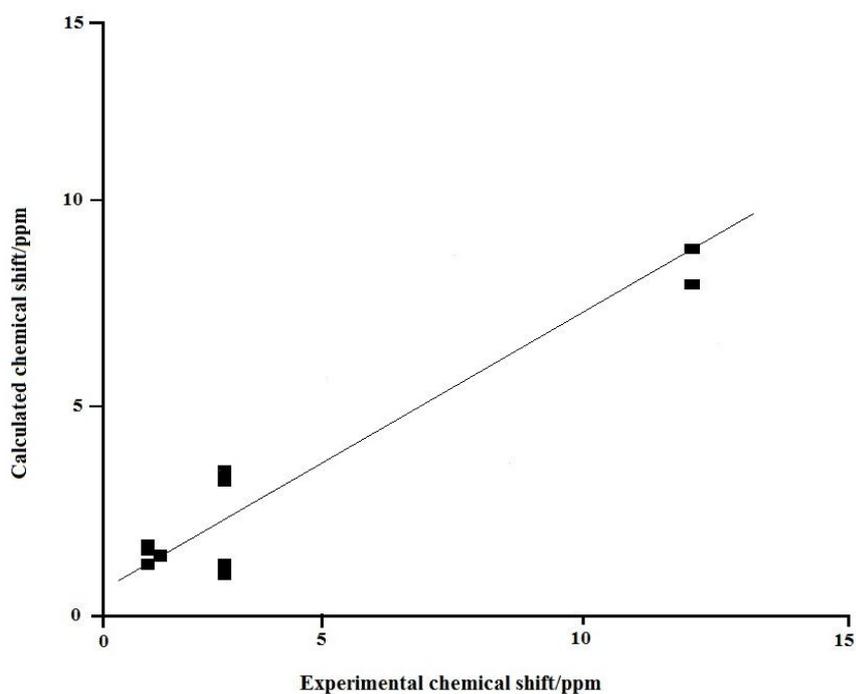
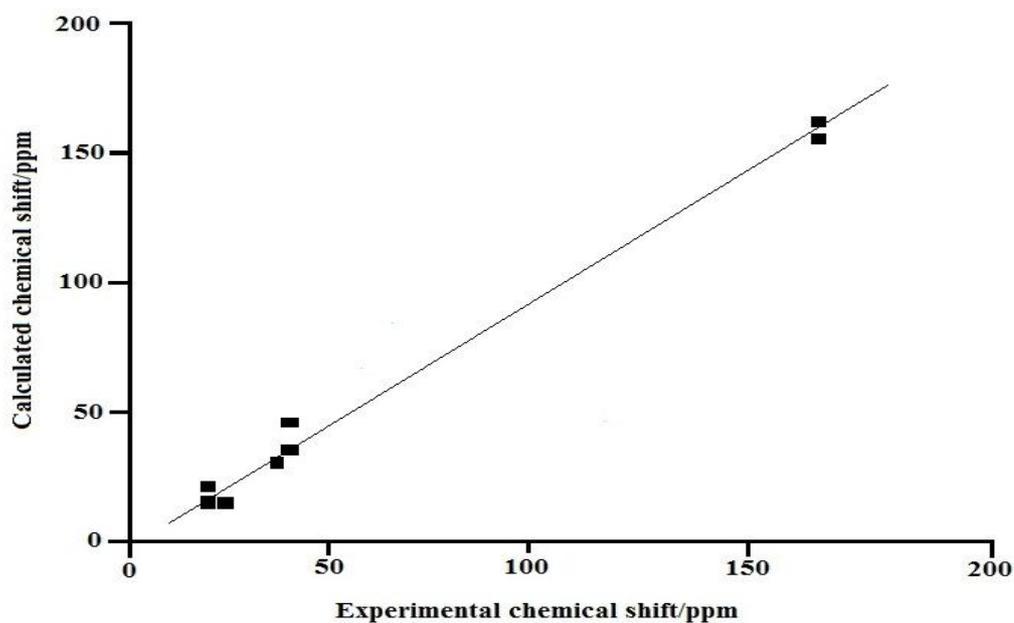


Fig 5. The Linear regression between experimental and theoretical ¹³C (a) ¹H (b) NMR Chemical Shift for N,N'-DBH

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IX. CONCLUSION

A complete vibrational analysis of N,N'-dibenzoylhydrazine (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. ¹H and ¹³C 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.

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