



iJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 5 Issue: IX Month of publication: September 2017

DOI: <http://doi.org/10.22214/ijraset.2017.9014>

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Synthesis and Structural Analysis of (E)-N'-(3, 4-Dimethoxybenzylidene) Isonicotinohydrazide –A Combined Experimental and Theoretical Study

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Abstract: The structural and the harmonic vibrational frequency analyses of (E)-N'-(3, 4 dimethoxybenzylidene) isonicotinohydrazide (DMBINH) were carried out at the hybrid density-functional method (B3LYP/6-311++G(d,p)). The recorded FT-IR and FT-Raman spectra of (DMBINH) in the mid-IR region in the solid phase have been weighed against those of the theoretically computed frequencies. The electronic properties such as HOMO-LUMO.

Keywords: FT-IR, FT-Raman, TED, DMBINH, HOMO-LUMO.

I. INTRODUCTION

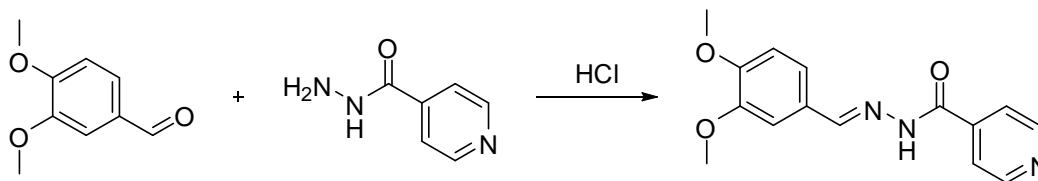
Organic compounds play an important role in the field of electrochemistry, nonlinear optics and photocurrent generation [1-3]. Especially, π -conjugated molecules bearing electron donating and accepting moieties are an important class of materials in optics and photoelectronics [4].

The experimental (XRD, FT-IR and FT-Raman) and theoretical (B3LYP/6-311++G(d,p)) structural and spectral parameters of several hydrazone derivatives have been reported by several investigators [5-7]. Recently Josephine Novina et al., (2014) [8] have reported the X-ray crystal structure of (E)-N'-(3, 4-Dimethoxybenzylidene)nicotinohydrazide 7 (DMBNH.H₂O). Govindarasu et al., (2015) [9] have made theoretical studies at DFT level invoking the exchange-correlation functional B3LYP and M06-2X using triple zeta split valence basis set on the synthesized DMBNH.H₂O to analyze experimental spectral data in addition to potential energy distribution value. The (E)-N'-(Pyridi-2yl)methylene benzohydrazide molecule was synthesized and its structural characterization was made by X-ray diffraction (XRD) method [5]. Based on the above literature survey, it is clear that there is no quantum mechanical study on the title molecule (DMBINH) so far. Therefore, the present study was undertaken to do the vibrational spectral, HOMO-LUMO. The NLO properties, the various thermodynamic properties were also carried out using 6-311++G(d,p) basis set at DFT level following B3LYP exchange-correlation functional.

II. EXPERIMENTAL DETAILS

A. Synthesis

Isonicotinic acid hydrazide (1.37g, 0.01mol) was dissolved in 10 ml of water and stirred for 10 minutes at room temperature followed by an addition of one drop of hydrochloric acid. Then 10 ml ethanolic solution of 3, 4-dimethoxybenzaldehyde (1.66g, 0.01mol) was added dropwise to the solution with efficient stirring for 45 minutes. The colorless product obtained was filtered, dried and washed with petroleum ether (40-60%). It is then recrystallized from ethanol.



B. FTIR, FT-Raman, NMR and UV-Vis spectra details

The FTIR spectrum in the mid-IR spectral range 4000-400 cm⁻¹ was recorded using KBr pellet technique with a FT-IR-Shimadzu spectrometer at room temperature with a scanning speed of 10 cm⁻¹ per minute at the spectral resolution of 2.0 cm⁻¹ in the Instrumentation laboratory, Jamal Mohamed College, Tiruchirappalli, Tamilnadu. FT-Raman spectrum was taken using laser source

Nd: YAG 1064 nm as excitation wavelength in the region $50\text{-}4000\text{cm}^{-1}$ on Bruker IFS 66v spectrophotometer equipped with a FRA 106 FT-Raman module accessory and at spectral resolution of 4 cm^{-1} . The FT-Raman spectrum was recorded at SAIF Laboratory, IIT Madras.

C. Computational details

Gaussian 03W quantum chemical software was used in all calculations [10]. The optimized structural parameters and vibrational wavenumbers for the DMBINH molecule were calculated using B3LYP functional with 6-311++G (d, p) basis set. The vibrational modes were assigned on the basis of TED analysis using VEDA program [11]. With respect to geometry and vibrations, only small differences are observed for the different functional and so we limited the study to the best-known B3LYP hybrid functional. All the computations have been done with (6-311++G(d, p) 0 triplet split valence basis set, augmented with diffuse sp- on heavy atoms and diffuse s- on hydrogen atoms and Polarization functions p on s of hydrogen atoms and d on p of heavy atoms for better treatment of electronegative atoms and polarizability evaluation.

III. RESULTS AND DISCUSSION

A. Geometrical parameters

The optimized structural parameters (bond lengths and bond angles) for the (E)-N'-dimethoxybenzylidene) isonicotinohydrazide were calculated and are shown in Table 1. The atomic numbering scheme is shown in Fig. 1 and the calculated bond parameters are compared with reported XRD data [12]. The theoretical values are in good agreement with the experimental values. The title molecule consists of benzene and pyridine rings fused by hydrozone linkage. In hydrozone linkage, the C=O bond length was observed as 1.224\AA and 1.232\AA respectively for (E)-N'((pyridine-2-yl)methylene) benzohydrazide (PMBH) [5]. The carbonyl ($\text{C}_{25}=\text{O}_{26}$) bond length is calculated 1.220\AA . The bond N-N behaves as a part of the bridge between the benzene and pyridine rings and its bond length is calculated as 1.359\AA while the literature value is: 1.375\AA . Similarly, the $\text{C}_{20}=\text{N}_{22}/\text{C}_{25}-\text{N}_{23}$ bond length values are: $1.282/1.381\text{\AA}$ and their corresponding literature values are $1.277/1.344\text{\AA}$ [9]. The $\text{C}_1-\text{C}_2/\text{C}_1-\text{C}_6$ and $\text{C}_3-\text{C}_4/\text{C}_2-\text{C}_3$ bond lengths differ by $0.0178/0.0188\text{\AA}$ respectively which may be due to the attachment of methoxy group at C_2 and C_3 atoms. The rest of the calculated bond lengths for phenyl, pyridine and methoxy groups are agreeable with literature [9] values with few exceptions.

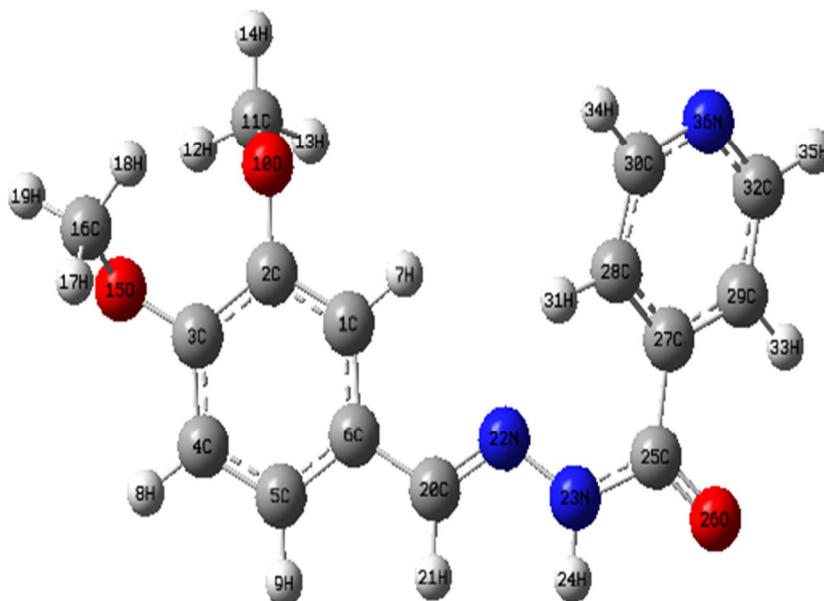


Fig.1. The optimized molecular structure of DMBINH

Table. 1. The optimized bond parameters of DMBINH using B3LYP/6-311++G(d, p) basis set

Bond Parameter	B3lyp/6-311++g(d, p)	X-ray data ^a	Literature ^b
Bond lengths(Å)			
C1-C2	1.386	1.393	1.366
C1-C6	1.404	1.374	1.398
C1-H7	1.083	0.96	0.930
C2-C3	1.411	1.402	1.412
C2-O10	1.375	1.366	1.365
C3-C4	1.392	1.377	1.373
C20-N22	1.282	1.267	1.277
N22-N23	1.359	1.382	1.375
N23-H24	1.019	0.901	0.860
N23-C25	1.381	1.399	1.344
C25-O26	1.220	1.254	1.232

^aQ.L. Zhang, L.Z. Yin, X.M. Deng, S.C. Liu, D.G. Song, Acta Cryst. 3E 65 (2009) 02392.

^bGovindarasu, Ph.D Thesis 2015 , Annamalai University.\

B. Vibrational assignments

The title compound belongs to C_s point group symmetry. It consists of 36 atoms which undergoes 102 normal modes of vibration. The normal modes of vibrations are possible and distributed as: $\Gamma_{\text{vib}} = 69 A' + 33 A''$; where A' and A'' represent in-plane and out-of-plane modes, respectively. The vibrational frequencies of the title molecule were calculated using DFT/6-311++G(d, p) basis set. The computed wavenumbers when linearly scaled down [13], were found to be in good agreement with the experimental observations.

The vibrational modes were assigned on the basis of TED analysis using VADA4 program [13]. The reduced mass and force constants are included in Table 2. The observed are theoretical IR and Raman spectra are constructed and are shown in Figs. 2 and 3 respectively.

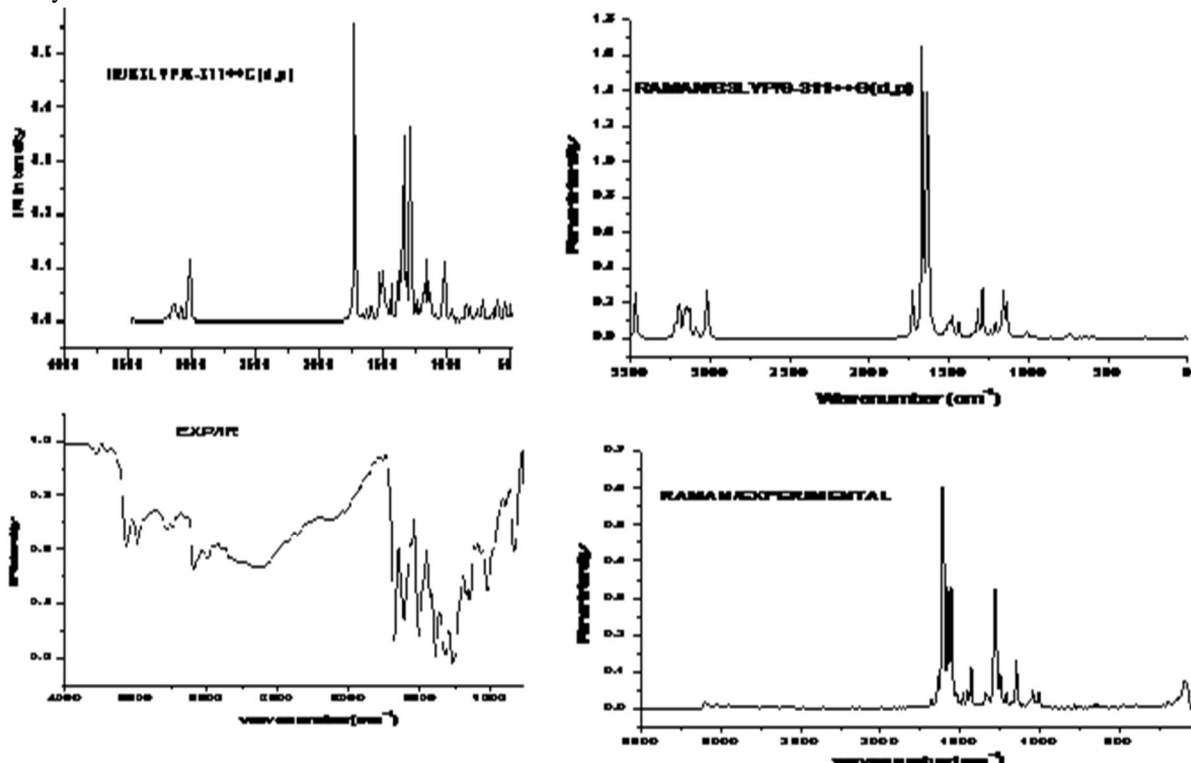


Fig. 2, 3. The combined theoretical and experimental IR, Raman spectra of DMBINH

1) *O-CH₃ vibrations*: In methoxy moiety, the important vibrational modes are ν_{O-CH_3} , ν_{C-O-C} , $\nu_{phenyl-O}$ and CH_3 deformations. The $O-CH_3$ stretching mode was assigned around $\sim 1040\text{cm}^{-1}$ in the region of $1000-1100\text{cm}^{-1}$ for anisole and its derivatives [14-18]. The bands at 1026 and 1012cm^{-1} were assigned to ν_{O-CH_3} modes [9]. The weak FTIR/FT-Raman bands at $1018/1004\text{cm}^{-1}$ are attributed to $O_{10}-CH_3$ stretching vibration while the corresponding harmonic wave number is 1036cm^{-1} (mode no:51). Similarly the $\nu_{O_{15}-CH_3}$ mode is assigned to mode no:50 ($1020\text{ }980\text{cm}^{-1}$). This assignment is in the expected region and is also supported by the literature values [9, 19, 20] in addition to TED value being $>46\%$. The δ_{C-O-CH_3} mode was observed for anisole and its derivatives in the region $300-670\text{cm}^{-1}$ by some workers [21]. As this mode lies in the region of the ring planar C-C-C angle bending modes, a strong mixing among these two modes ($C-O_{10}-CH_3$ and $C-O_{15}-CH_3$) and other planar modes is expected [22]. In $DMBNH_2O$, the β_{COC} and τ_{CCOC} modes were respectively assigned to wavenumbers: 497 and 334 & 84 and 72cm^{-1} [9]. Based on the above conclusions, the harmonic wavenumbers at 425 and 342 & 70 and 42cm^{-1} (mode nos: 23, 20 and 6, 4) are assigned to $\beta_{C_3O_{15}C_{16}}$ and $\beta_{C_2O_{10}C_{11}}$ & $\tau_{C_4C_3O_{15}C_{16}}$ and $\tau_{C_1C_2O_{10}C_{11}}$ modes, respectively. These assignments are having considerable TED values. In this study, Phenyl-O stretching ($\nu_{O_{15}-C_3}$, $\nu_{O_{10}-C_2}$) vibrations are assigned to wavenumbers 1239 , 1193cm^{-1} (mode nos: 66, 62), in which mode no:66 is in moderate agreement with the observed FT-Raman band : 1246cm^{-1} . These assignments are also having considerable TED value ($>14\%$) and also find support from our earlier study [5]. The $\beta_{C_2C_3O_{15}/\beta_{C_3C_2O_{10}}$ and $\tau_{C_1C_2C_3O_{15}/\tau_{C_4C_3C_2O_{10}}$ modes are attributed to the harmonic frequencies: $567/502$ and $502/136\text{cm}^{-1}$ (mode nos:28/26 and 26/9), respectively. It should be mentioned here that the C_3-O_{15} stretching, in-plane and out-of-plane bending modes are appearing at higher frequencies than the C_2-O_{10} stretching, bending modes.

Table. 2. The experimental and calculated frequencies of DMBINH using B3LYP/6-311++G(d, p) level of basis set [harmonic frequencies (cm^{-1}), IR, Raman intensity (Km/mol), reduced masses (amu) and force constants (mdynA^{-1})]

Mode no	Calculated Frequencies (cm^{-1})		Observed Intensity Frequencies (cm^{-1})				Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments $\geq 10\%$ (TED) ^d
	Unscaled	Scaled ^a	IR	Raman	Abs.	Rel. ^b	Abs.	Rel. ^c			
1	10	10			0.01	0.00	1005.48	100.00	4.58	0.00	$\tau_{C_3C_6C_{20}N_{22}(44)+\tau_{C_{20}N_{22}N_{23}C_{25}(20)}$
2	21	20			0.48	0.08	2095.93	208.45	4.59	0.00	$\beta_{C_{25}N_{23}N_{22}(17)+\beta_{C_{27}C_{25}N_{23}(11)+\tau_{C_{29}C_{27}C_{25}N_{23}(18)}$
3	32	31			0.14	0.02	322.85	32.11	5.79	0.00	$\beta_{C_6C_{20}N_{22}(10)+\tau_{C_6C_{20}N_{23}N_{23}(12)+\tau_{C_{27}C_{25}N_{23}N_{22}(25)+\tau_{C_4C_3C_6C_{20}(15)}$
4	44	42			1.66	0.28	809.76	80.53	3.41	0.00	$\tau_{C_{29}C_{27}C_{25}N_{23}(28)+\tau_{C_1C_2O_{10}C_{11}(40)}$
5	66	63			2.24	0.37	129.82	12.91	4.06	0.01	$\tau_{C_{29}C_{27}C_{25}N_{23}(22)+\tau_{C_1C_2O_{10}C_{11}(39)}$
6	73	70			5.25	0.87	300.33	29.87	2.62	0.01	$\tau_{C_4C_3O_{15}C_{16}(73)}$
7	91	88	90		1.35	0.22	301.09	29.95	6.06	0.03	$\tau_{C_{20}N_{22}N_{23}C_{25}(27)+\tau_{C_{27}C_{25}N_{23}N_{22}(11)+\tau_{C_1C_2C_3O_{15}(17)}$
8	113	109			0.69	0.11	101.15	10.06	4.79	0.04	$\beta_{C_1C_6C_{20}(11)+\beta_{C_{27}C_{25}N_{23}(10)+\Gamma_{C_{25}C_{27}C_{29}C_{28}(23)}$
9	142	136			1.97	0.33	121.14	12.05	2.48	0.03	$\beta_{C_2O_{10}C_{11}(15)+\tau_{H_{17}C_{16}O_{15}C_3(14)+\tau_{C_4C_3C_2O_{10}(46)}$
10	145	139			1.12	0.19	35.08	3.49	1.40	0.02	$\tau_{H_{12}C_{11}O_{10}C_2(11)+\tau_{H_{17}C_{16}O_{15}C_3(53)}$
11	156	150			0.22	0.04	8.60	0.85	1.42	0.02	$\tau_{H_{12}C_{11}O_{10}C_2(58)}$
12	175	168			3.07	0.51	57.06	5.68	2.22	0.04	$\beta_{C_{25}C_{27}C_{29}(10)+\tau_{H_{12}C_{11}O_{10}C_2(17)+\tau_{H_{17}C_{16}O_{15}C_3(14)}$
13	183	176	193		4.59	0.76	32.24	3.21	5.19	0.10	$\Gamma_{C_{25}C_{27}C_{29}C_{28}(10)}$
14	219	211			4.57	0.76	75.84	7.54	4.45	0.13	$\beta_{C_{25}C_{27}C_{29}(28)}$
15	246	236			1.21	0.20	66.65	6.63	7.34	0.26	$\beta_{C_1C_6C_5(10)+\nu_{C_6C_{20}(13)+\beta_{C_{20}N_{22}N_{23}(17)}$
16	253	243			10.72	1.78	69.72	6.93	3.76	0.14	$\beta_{C_{25}C_{27}C_{29}(18)+\tau_{C_3C_6C_{20}N_{22}(15)+\tau_{C_{20}N_{22}N_{23}C_{25}(16)+\tau_{C_{27}C_{25}N_{23}N_{22}(17)}$
17	271	260			13.63	2.26	121.56	12.09	6.11	0.26	$\beta_{C_2C_3O_{15}(17)+\beta_{C_3C_2O_{10}(17)}$

18	323	310			3.83	0.64	77.04	7.66	5.38	0.33	$\tau C_1C_6C_2C_3(14)+\tau C_6C_{20}N_{22}N_{23}(29)$
19	342	329			9.61	1.60	60.94	6.06	7.69	0.53	$\beta C_{28}C_{27}C_{29}(10)+VC_{25}C_{27}(13)+\beta C_{27}C_{25}N_{23}(10)$
20	356	342			2.02	0.34	10.12	1.01	4.87	0.36	$\beta C_2C_3O_{15}(16)+\beta C_2O_{10}C_{11}(21)+\tau C_1C_6C_2C_3(14)$
21	387	372			0.13	0.02	9.76	0.97	2.81	0.25	$\tau C_{30}C_{28}N_{36}C_{32}(28)+\tau C_{27}C_{29}N_{36}C_{32}(26)$
22	392	377			4.57	0.76	42.72	4.25	6.05	0.55	$\beta C_{28}C_{27}C_{29}(10)+\beta C_{27}C_{25}O_{26}(12)+\tau C_{29}C_{30}C_{32}N_{36}(17)+\tau C_{27}C_{29}N_{36}C_{32}(11)$
23	442	425			1.18	0.20	30.21	3.00	4.35	0.50	$\beta C_3O_{15}C_{16}(12)+\tau C_3C_2C_4C_5(13)+\tau C_6C_{20}N_{22}N_{23}(12)+\tau C_4C_5C_6C_{20}(27)$
24	457	439			12.82	2.13	27.01	2.69	5.02	0.62	$\beta C_2C_3C_4(14)+\tau C_{29}C_{30}C_{32}N_{36}(13)$
25	499	480	481	471	28.46	4.73	30.24	3.01	4.91	0.72	$\beta C_{25}C_{27}C_{29}(25)+\tau C_3C_{2C}4C_5(12)$
26	523	502			7.73	1.28	22.44	2.23	4.00	0.64	$\beta C_3C_2O_{10}(11)+\tau C_1C_2C_3O_{15}(10)$
27	546	525	527		54.85	9.11	7.59	0.76	5.79	1.02	$\beta C_1C_6C_5(10)+\beta C_{27}C_{25}O_{26}(12)$
28	590	567	566		4.31	0.72	68.60	6.82	3.87	0.79	$VC_3C_4(14)+\beta C_2C_3O_{15}(14)+\tau H_{24}N_{23}C_{25}C_{27}(10)$
29	608	585			44.44	7.38	142.81	14.20	1.39	0.30	$\tau H_{24}N_{23}C_{25}C_{27}(73)$
30	643	618			23.62	3.92	97.74	9.72	4.95	1.21	$\beta C_{27}C_{25}O_{26}(23)+\beta C_{30}N_{36}C_{32}(10)+\beta C_{20}N_{22}N_{23}(10)$
31	652	626	622		8.93	1.48	32.78	3.26	4.26	1.07	$\tau C_1C_6C_4C_5(59)$
32	674	648		649	3.49	0.58	31.70	3.15	5.36	1.43	$\beta C_{25}N_{23}N_{22}(11)+\beta C_{27}C_{25}N_{23}(16)$
33	683	656			1.86	0.31	41.82	4.16	6.48	1.78	$\beta C_{27}C_{28}C_{30}(14)+\beta C_{25}C_{32}N_{36}(32)$
34	722	693	681		43.93	7.30	38.14	3.79	4.60	1.41	$\tau C_{30}C_{28}N_{36}C_{32}(11)+\tau C_{27}C_{29}N_{36}C_{32}(12)+\Gamma O_{26}C_{27}N_{23}C_{25}(45)$
35	742	713			8.10	1.34	220.93	21.97	5.90	1.91	$\beta C_3C_4C_5(12)+VC_2C_3(21)+\beta C_2C_1C_6(10)$
36	754	724			2.16	0.36	113.54	11.29	5.47	1.83	$VC_{25}C_{27}(14)+\beta C_{30}N_{36}C_{32}(23)$
37	766	736			22.03	3.66	21.38	2.13	2.57	0.89	$\tau C_{30}C_{28}N_{36}C_{32}(22)+\tau C_{29}C_{30}C_{32}N_{36}(18)+\tau C_{27}C_{29}N_{36}C_{32}(31)+\Gamma O_{26}C_{27}N_{23}C_{25}(12)$
38	777	746	748		11.79	1.96	24.31	2.42	2.96	1.05	$\tau C_1C_6C_2C_3(28)+\tau C_3C_2C_4C_5(17)$
39	822	790		780	27.01	4.49	26.23	2.61	4.28	1.71	$\beta C_6C_{20}N_{22}(11)+\beta C_{20}N_{22}N_{23}(15)$
40	847	814			30.23	5.02	3.01	0.30	1.67	0.70	$\tau H_8C_4C_3O_{15}(36)+\Gamma C_5C_4C_6C_9(41)$
41	858	824	834		16.89	2.81	40.14	3.99	1.90	0.83	$\Gamma C_{28}C_{27}C_{30}H_{31}(35)+\Gamma C_{29}C_{27}C_{32}H_{33}(17)+\Gamma O_{26}C_{27}N_{23}C_{25}(12)+\Gamma C_{25}C_{27}C_{29}C_{28}(16)$
42	890	855			2.13	0.35	5.40	0.54	1.26	0.59	$\Gamma C_{28}C_{27}C_{30}H_{31}(32)+\Gamma C_{29}C_{27}C_{32}H_{33}(54)$
43	919	883	893		2.10	0.35	1.07	0.11	1.47	0.73	$\Gamma C_1C_2C_6H_7(74)$
44	956	918			3.70	0.61	20.29	2.02	1.52	0.82	$\Gamma C_1C_2C_6H_7(10)+\tau H_8C_4C_3O_{15}(27)+\Gamma C_5C_4C_6H_9(15)+\Gamma C_{20}C_6N_{22}H_{21}(31)$
45	965	928			28.87	4.80	11.91	1.18	3.29	1.81	$VO_{10}C_{11}(22)+\beta C_4C_5C_6(12)$
46	969	931			5.15	0.86	28.07	2.79	1.48	0.82	$\tau H_8C_4C_3O_{15}(18)+\Gamma C_5C_4C_6H_9(27)+\Gamma C_{20}C_6N_{22}H_{21}(47)$
47	984	945			1.44	0.24	1.87	0.19	1.34	0.77	$\tau H_{31}C_{28}C_{30}H_{34}(58)+\tau H_{33}C_{29}C_{32}H_{35}(27)$
48	1002	962			1.50	0.25	5.39	0.54	1.51	0.89	$\Gamma C_{29}C_{27}C_{32}H_{33}(10)+\tau H_{31}C_{28}C_{30}H_{34}(26)+\tau H_{33}C_{29}C_{32}H_{35}(51)$
49	1012	972			3.68	0.61	195.61	19.45	6.33	3.82	$VN_{36}C_{32}(21)+VC_{29}C_{32}(17)+\beta C_{27}C_{28}C_{30}(17)$
50	1020	980			102.39	17.01	62.75	6.24	8.06	4.94	$VO_{15}C_{16}(70)$

51	1036	995	1018	1004	73.14	12.15	95.84	9.53	3.49	2.21	$VO_{10}C_{11}(46)+\beta C_2C_1C_6(11)+\beta C_4C_5C_6(11)$
52	1093	1050		1042	13.46	2.24	21.65	2.15	2.10	1.48	$VC_{29}C_{32}(12)+\beta H_{33}C_{29}C_{27}(22)+\beta C_{28}C_{30}N_{36}(16)+\beta C_{30}N_{36}C_{32}(10)+\beta C_{29}C_{32}N_{36}(15)$
53	1111	1067			0.89	0.15	3.94	0.39	1.56	1.14	$\beta H_{31}C_{28}C_{30}(25)+\beta H_{33}C_{29}C_{27}(12)+\beta C_{28}C_{30}N_{36}(20)$
54	1128	1084			45.19	7.51	117.28	11.66	2.89	2.17	$\beta C_{28}C_{27}C_{29}(10)+VN_{23}N_{22}(15)$
55	1139	1094			23.65	3.93	793.43	78.91	2.24	1.71	$\beta C_3C_4C_5(13)+\beta H_9C_5C_6(16)$
56	1158	1113		1105	123.44	20.51	1051.54	104.58	2.64	2.09	$VN_{23}N_{22}(19)$
57	1166	1120			3.11	0.52	215.71	21.45	1.30	1.04	$\beta H_{12}C_{11}H_{14}(12)+\Gamma C_{11}H_{13}O_{10}H_{14}(59)+\Gamma C_{16}H_{18}O_{15}H_{19}(13)$
58	1168	1122			2.94	0.49	10.96	1.09	1.25	1.01	$\beta H_{17}C_{16}H_{19}(10)+\Gamma C_{11}H_{13}O_{10}H_{14}(13)+\Gamma C_{16}H_{18}O_{15}H_{19}(66)$
59	1184	1137	1144		87.40	14.52	173.77	17.28	2.02	1.67	$VN_{23}N_{22}(18)+\beta H_8C_4C_3(11)+\Gamma C_{11}H_{13}O_{10}H_{12}(11)$
60	1200	1153		1146	3.62	0.60	61.11	6.08	1.43	1.21	$\Gamma C_{16}H_{17}H_{18}O_{15}(53)$
61	1212	1165	1172		19.44	3.23	350.72	34.88	1.62	1.40	$\Gamma C_{11}H_{13}O_{10}H_{12}(49)$
62	1242	1193			34.64	5.75	129.22	12.85	2.10	1.90	$VO_{15}C_3(14)+\beta H_7C_1C_6(11)+\Gamma C_{16}H_{17}H_{18}O_{15}(17)$
63	1244	1195			5.46	0.91	17.80	1.77	1.28	1.17	$VN_{36}C_{30}(15)+VN_{36}C_{32}(11)+\beta H_{34}C_{30}N_{36}(19)+\beta H_{35}C_{32}N_{36}(17)$
64	1274	1224		1210	6.61	1.10	17.38	1.73	6.69	6.40	$VN_{36}C_{30}(44)+VC_{27}C_{29}(22)$
65	1277	1227			7.66	1.27	14.20	1.41	1.67	1.61	$\beta H_7C_1C_6(20)+\beta H_8C_4C_3(15)+\beta H_9C_5C_6(18)$
66	1290	1239		1246	357.59	59.40	957.25	95.20	3.80	3.73	$VC_4C_3(13)+VO_{15}C_3(22)+VO_{10}C_2(10)$
67	1320	1268	1267	1279	55.53	9.22	499.88	49.72	7.82	8.03	$VC_6C_5(21)+VC_2C_3(41)$
68	1342	1290			399.73	66.40	94.00	9.35	2.97	3.16	$VN_{23}C_{25}(26)+VC_{27}C_{25}(15)+\beta H_{31}C_{28}C_{30}(13)$
69	1356	1303			99.34	16.50	76.69	7.63	1.55	1.68	$\beta H_{31}C_{28}C_{30}(14)+\beta H_{33}C_{29}C_{27}(22)+\beta H_{34}C_{30}N_{36}(1)+\beta H_{35}C_{32}N_{36}(18)$
70	1384	1329	1318	1339	125.97	20.93	56.05	5.57	1.53	1.72	$\beta H_{24}N_{23}N_{22}(23)+\beta H_{21}C_{20}N_{22}(39)$
71	1438	1381			24.99	4.15	87.51	8.70	1.98	2.41	$\beta H_{34}C_{30}N_{36}(29)+\beta H_{35}C_{32}N_{36}(24)$
72	1439	1383	1386		43.40	7.21	193.45	19.24	2.36	2.88	$VC_2C_1(10)+\beta H_9C_5C_6(15)$
73	1463	1405			8.54	1.42	13.61	1.35	1.21	1.52	$\beta H_{17}C_{16}H_{19}(11)+\beta H_{17}C_{16}H_{18}(21)+\beta H_{18}C_{16}H_{19}(36)$
74	1481	1423			18.00	2.99	276.24	27.47	1.38	1.79	$\beta H_{12}C_{11}H_{14}(21)+\beta H_{12}C_{11}H_{13}(18)+\beta H_{13}C_{11}H_{14}(12)+\beta H_{17}C_{16}H_{19}(18)$
75	1487	1429	1425	1429	12.25	2.03	61.29	6.10	1.05	1.37	$\beta H_{12}C_{11}H_{14}(16)+\beta H_{13}C_{11}H_{14}(13)+\beta H_{17}C_{16}H_{19}(31)+\beta H_{18}C_{16}H_{19}(18)$
76	1488	1430			3.89	0.65	80.98	8.05	1.08	1.42	$\beta H_{13}C_{11}H_{14}(48)+\beta H_{17}C_{16}H_{19}(14)$
77	1504	1445			88.09	14.63	144.46	14.37	1.42	1.90	$\beta H_{24}N_{23}N_{22}(27)+\beta H_{12}C_{11}H_{13}(22)$
78	1505	1446			53.19	8.84	134.31	13.36	1.26	1.68	$\beta H_{24}N_{23}N_{22}(16)+\beta H_{12}C_{11}H_{14}(11)+\beta H_{12}C_{11}H_{13}(28)+\beta H_{17}C_{16}H_{19}(11)$
79	1510	1451		1453	19.34	3.21	40.25	4.00	1.05	1.42	$\beta H_{17}C_{16}H_{18}(53)+\beta H_{18}C_{16}H_{19}(23)$
80	1521	1462			20.79	3.45	47.26	4.70	2.17	2.96	$\beta H_{31}C_{28}C_{30}(14)+\beta H_{33}C_{29}C_{27}(11)+\beta H_{34}C_{30}N_{36}(21)+\beta H_{35}C_{32}N_{36}(23)$
81	1532	1472		1480	83.33	13.84	69.58	6.92	3.05	4.21	$\beta H_8C_4C_3(15)$
82	1594	1531	1503	1522	32.92	5.47	17.54	1.74	7.57	11.33	$VN_{36}C_{32}(33)+VC_{27}C_{29}(32)$
83	1599	1536			9.62	1.60	74.05	7.36	6.63	9.98	$VC_4C_3(22)+VC_2C_1(29)+\beta C_2C_1C_6(13)$

84	1632	1568		1554	10.39	1.73	300.88	29.92	5.40	8.47	VN ₃₆ C ₃₀ (11)+ VC ₂₉ C ₃₂ (29)+βC ₃₂ N ₃₆ C ₃₀ (13)
85	1636	1572		1578	18.71	3.11	4639.62	461.43	6.08	9.59	VC ₂ C ₁ (30)+ VC ₄ C ₃ (10)
86	1669	1603	1609	1610	10.89	1.81	3626.75	360.70	7.61	12.49	VN ₂₂ C ₂₀ (66)
87	1729	1661	1677	1678	601.97	100.00	535.89	53.30	7.87	13.85	VO ₂₆ C ₂₅ (78)
88	3016	2898			59.65	9.91	50.09	4.98	1.03	5.54	VC ₁₁ H ₁₂ (30)+ VC ₁₁ H ₁₃ (56)+ VC ₁₁ H ₁₄ (12)
89	3019	2900			68.38	11.36	104.31	10.37	1.04	5.56	VC ₁₆ H ₁₇ (64)+ VC ₁₆ H ₁₈ (22)+ VC ₁₆ H ₁₉ (12)
90	3027	2909			48.15	8.00	53.27	5.30	1.09	5.87	VC ₂₀ H ₂₁ (99)
91	3084	2963			23.06	3.83	19.47	1.94	1.10	6.19	VC ₁₆ H ₁₈ (58)+ VC ₁₆ H ₁₉ (39)
92	3094	2973			21.87	3.63	24.51	2.44	1.10	6.21	VC ₁₆ H ₁₇ (33)+ VC ₁₆ H ₁₈ (59)
93	3132	3009	2994		19.96	3.32	51.70	5.14	1.10	6.37	VC ₁₁ H ₁₂ (10)+ VC ₁₁ H ₁₄ (86)
94	3135	3013			22.81	3.79	74.83	7.44	1.10	6.40	VC ₁₆ H ₁₈ (17)+ VC ₁₆ H ₁₉ (80)
95	3152	3029		3025	27.64	4.59	45.36	4.51	1.09	6.37	VC ₃₀ H ₃₄ (70)+ VC ₃₂ H ₃₅ (28)
96	3156	3032			9.11	1.51	77.18	7.68	1.09	6.41	VC ₃₀ H ₃₄ (28)+ VC ₃₂ H ₃₅ (69)
97	3167	3043			8.14	1.35	32.26	3.21	1.09	6.43	VC ₄ H ₈ (10)+ VC ₅ H ₉ (90)
98	3192	3067			7.08	1.18	81.87	8.14	1.09	6.57	VC ₄ H ₈ (89)+ VC ₅ H ₉ (10)
99	3201	3076			1.64	0.27	23.42	2.33	1.09	6.59	VC ₁ H ₇ (99)
100	3204	3078			3.22	0.54	52.72	5.24	1.09	6.61	VC ₂₉ H ₃₃ (97)
101	3222	3096	3094	3102	2.24	0.37	38.27	3.81	1.09	6.69	VC ₂₈ H ₃₁ (98)
102	3467	3331	3283		8.15	1.35	119.53	11.89	1.08	7.62	VN ₂₃ H ₂₄ (100)

v: Stretching, β: in-plane-bending, Γ: out-of-plane bending, τ: Torsion, vw: very weak, w: weak, m: medium, s: strong, vs: very strong,

a Scaling factor: 0.9608 (Radom et al., 1970 and Pople et al., 1993),

b Relative IR absorption intensities normalized with highest peak absorption equal to 100,

c Relative Raman intensities calculated by Equation (1) and normalized to 100, $I_i = 10 - 12 \times \frac{(v_0 - v_i)^4}{v_i} \times R A_i$ -----(1)

d Total energy distribution calculated at B3LYP/6-311++G(d,p) level.

2) *Methyl group vibrations*: Methyl group has generally electron-donating/electron repelling nature in the aromatic ring system. For the assignments of CH₃ group frequencies, one can expect nine fundamentals, that are associated with each CH₃ group, viz., the symmetrical stretching in CH₃ (CH₃ sym. stretching) and asymmetrical stretching (CH₃ asym. stretching), in-plane stretching modes (in-plane hydrogen stretching mode), the symmetrical (CH₃ sym. deform) and asymmetrical (CH₃ asym. deform) deformation modes, the in-plane rocking (CH₃ in-plane rocking), the out-of-plane rocking (CH₃ out-of-plane rocking) and twisting (CH₃) bending modes. The ν_{C-H} and β_{C-H} bands of methyl in methoxy may be shifted to new positions due to electronic effects. The methoxy stretching modes are expected to appear in a wider range due to their difference in orientation with the major lobe of oxygen lone pairs [23]. The conjugation of phenyl ring π-orbital with oxygen lone pair orbital will be strong when both orbitals lie in the same plane. Further, the hydrogen atoms O-CH₃ group are subjected simultaneously to induction [24] and back donation [25] due to neighboring oxygen atom. The ν_{asy} CH and ν_{sym} CH absorption bands of methoxy have been observed at 3016/2937cm⁻¹ and 2917/2834cm⁻¹ (FTIR) respectively by James et al., (2008) [26] and Sumathi et al., (2015) [6]. The nπ conjugation of O₁₅-C₁₆-H₁₇, H₁₈, H₁₉ group (n-π*: O₁₅→C₁₆-H₁₇/C₁₆-H₁₈:5.28/1.86 kJ/mol) with phenyl ring is not much different from that of O₁₀-C₁₁-H₁₂, H₁₃, H₁₄ group (n-π*: O₁₀→C₁₁-H₁₃/C₁₁-H₁₂:5.37/2.04KJ/Mol). This is due to

similar spatial arrangement of the methyl groups on the opposite directions. The other $O_{10}-C_{11}-H_{12}, H_{13}, H_{14}$ group vibrations observed as intense bands in both Raman and IR with decrease in wavenumber from its expected values [27], due to back-donation of charge from nO_{10} to the σ^* (C-H) bonds. Based on the above facts, the ν_{asy}/ν_{sym} vibrations of $O_{15}-C_{16}-H_{17}, H_{18}, H_{19}$ group assigned at little higher frequencies ($3013, 2973\text{cm}^{-1}$: mode nos: 94, 92/ 2900cm^{-1} : mode no:89) than the $O_{10}-C_{11}-H_{12}, H_{13}, H_{14}$ group ($3009, 2963\text{cm}^{-1}$: mode nos: 93, 91/ 2898cm^{-1} : mode no:88). Similarly trend was observed by James, C. et al., (2008) [26] in the case of combretastatin A-4-Prodrug. Further, the present assignment is in line with the assignment ($2903-3032\text{cm}^{-1}$) made by Govindarasu [9] for structurally similar molecule (DMBNH. H_2O). These assignments having considerable TED value and also find support from observed weak FT-Raman band: 2994cm^{-1} . Usually the asymmetric (β_{asy} HCH) and symmetric (β_{sym} HCH) bending vibration of CH_3 group appear in the respective regions of $1440-1465$ and $1370-1390\text{cm}^{-1}$ [28]. According to the work by Govindarasu (2015) [9] on DMBNH. H_2O , the wavenumbers at $1470/1423\text{cm}^{-1}$ (1425cm^{-1} : FT-Raman) in the FTIR spectrum were designated as β_{asy}/β_{sym} modes, respectively. The β_{asy} HCH modes have been computed to be $1451/1453\text{cm}^{-1}$, (mode nos:79, 78) whereas in FT-Raman they occur at 1446cm^{-1} . The weak bands around $1426/1429\text{cm}^{-1}$ in the FTIR/FT-Raman spectra corresponding to β_{sym} HCH mode is in excellent agreement with the harmonic values $1429, 1423\text{cm}^{-1}$ (mode nos:75, 74). These assignments coincide with the reported values [9] and also find support from TED values (>39% & >60%). The calculated CH_3 rocking vibrations of DMBNH. H_2O [9] in the in the range $1131-1166\text{cm}^{-1}$ is close to the predicted region of $1070-1010\text{cm}^{-1}$ [29]. Based on this the calculated wavenumbers $1122, 1120\text{cm}^{-1}$ (mode nos:58, 57) for DMBINH have been attributed to CH_3 rocking mode. The mode nos:60, 61 having considerable TED value 53, 49% are designated as CH_3 twisting modes. These modes match with the observed frequencies at 1146cm^{-1} and 1173cm^{-1} FT-Raman and FTIR spectra respectively. These assignments also find support from literature [30]. As the torsional mode of CH_3 group is expected to occur below 400cm^{-1} . In DMBINH, the CH_3 torsional mode is assigned to mode nos:11, 10 ($150, 139\text{cm}^{-1}$) which are in agreement with earlier assignments at 155cm^{-1} and 132cm^{-1} [9].

- 3) *C=O vibrations*: The carbon-oxygen double bond is formed by $\pi\pi$ - $\pi\pi$ bonding between carbon and oxygen atoms. The lone pair of electrons on oxygen also determines the nature of the carbonyl group [31]. The carbonyl C=O stretching vibrations is would normally occur in the region $1680-1715\text{cm}^{-1}$ [32, 33]. The very strong absorption frequency at 1653cm^{-1} in FTIR for DMBNH. H_2O [9] is attributed to $\nu_{C=O}$. In the present investigation, a very strong band appears at 1677cm^{-1} in FT-IR and at 1678cm^{-1} as a weak band in FT-Raman spectra are assigned to $\nu_{C=O}$ mode. This assignment is supported by the calculated harmonic vibrational frequency of 1661cm^{-1} with 100% IR intensity (mode no:87; Table 2). This assignment agrees with the reported values [32, 33] in addition to TED value of 78%. The theoretically predicted value at 618cm^{-1} (mode no:30) is characteristic of $\beta_{C=O}$ in DMBINH. The out-plane bending vibration observed at 681cm^{-1} in FT-IR spectrum corresponds to the theoretical value of 693cm^{-1} (mode no:34). This assignment is in moderate agreement with literature value [9] in addition to TED (45%) output.
- 4) *C-H vibrations*: The vibration absorption noticed in the region $3100-3000\text{cm}^{-1}$, characteristic of C-H stretching vibration [34] is due to ν_{C-H} of aromatic pyridine moiety. The characteristic C-H stretching modes calculated in the range $3073-3101\text{cm}^{-1}$ at B3LYP/6-311++G(d,p) level fall in the experimentally observed region around 3060cm^{-1} in FT-Raman spectrum [9]. However, as with any complex molecules, vibrational interactions occur and these levels only indicate the predominant vibration. Substituted benzenes have large number of sensitive bands, significantly affected by the mass and electronic properties, mesomeric/resonance or inductive effects of the substituents. The triply substituted benzene ring of DMBINH is associated with three free C-H units *viz.*, at 2, 5 and 6 – positions. Hence, one can expect three C-H stretching modes of $C_1-H_7, C_4-H_8, C_5-H_9$ units and these are predicted in the range $3076-3043\text{cm}^{-1}$ (mode nos: 99, 97) after scaling down. These three modes are purely stretching in nature as evident from TED column with TED contribution of 99%. For this mode the corresponding experimental vibrational bands are missing. In aromatic compounds, β_{C-H}/Γ_{C-H} vibrations would normally appear in the regions of $1000-1300/750-1000\text{cm}^{-1}$, respectively [35,36]. The β_{C-H} and Γ_{C-H} modes in DMBNH. H_2O were identified in the regions $1215-1492\text{cm}^{-1}$ and $708 - 914\text{cm}^{-1}$ [9] respectively. In accordance with above conclusion, the calculated frequencies for DMBINH at $1227, 1383, 1472\text{cm}^{-1}$ (mode nos: 65, 72, 81) and at $883, 918, 931\text{cm}^{-1}$ (mode nos:43, 44, 46) are respectively designated as β_{C-H} and Γ_{C-H} modes. These theoretical assignments within the characteristic region having appreciable TED values (>15% and >25%) find support from the observed FTIR bands at 1386 and 893cm^{-1} . In DMBINH, the pyridine ring has two pairs of C-H units separated by the plane passing through N_{35} and C_{27} atoms resulting in four $\nu_{C-H}/\beta_{C-H}/\Gamma_{C-H}$ vibrations. In DMBNH. H_2O , the ν_{C-H}, β_{C-H} and Γ_{C-H} modes belong to pyridine ring were assigned in the regions: $3042-3120, 1112-1457$ and $803-964\text{cm}^{-1}$,

respectively [9]. The bands observed at 3094/ FT-IR and 3102 & 3025 cm^{-1} / FT-Raman and their corresponding computed harmonic frequencies in the range 3029-3096 cm^{-1} (mode nos: 95-101) are designated as $\nu_{\text{C-H}}$ modes of pyridine ring on comparison with the reported values cited above for DMBNH.H₂O and further our inference draws support from the TED value (>97%). The bands for C-H in-plane bending vibrations are recognized at 1042 cm^{-1} as a weak band in FT-Raman spectrum and the corresponding DFT value is distributed over 1462, 1303, 1290 ad1050 cm^{-1} . Similarly the band observed at 835 cm^{-1} as a weak band in FTIR spectrum and the calculated values at 962, 855, 824 cm^{-1} (mode nos:48, 42, 41) are attributed to $\Gamma_{\text{C-H}}$ modes. These assignments are having considerable TED values (>22%, 10%). Further, the mode nos: 90, 70 and 46 (2909, 1329 and 931 cm^{-1}) are assigned respectively to ν_{CH} , β_{CH} and Γ_{CH} modes of hydrozone linkage. These assignments are made in accordance with assignments ($\nu_{\text{CH}}/2943$; $\beta_{\text{CH}}/1327$; $\Gamma_{\text{CH}}/940\text{cm}^{-1}$) proposed by Govindarasu (2015) [9] and also find support from their respective TED values (100%, 33% and 78%). In addition, the mode no: 70 is in agreement with the observed FTIR: 1318/FT-Raman:1339 cm^{-1} bands. According to the TED output (>21, 23%) the harmonic frequencies: 1462, 1381 cm^{-1} are designated as $\beta_{\text{H}_{34}\text{C}_{30}\text{N}_{36}}$, $\beta_{\text{H}_{35}\text{C}_{32}\text{N}_{36}}$ modes, respectively.

- 5) *C=N, C-N, N-N vibrations:* The identification of C=N, C-N (stretching, bending) vibrations are very difficult task [37], since the mixing of several bands are possible in the region. In DMBINH, the hydrozone linkage bridges the phenyl and pyridine rings, hence the C=N, C-N and N-N stretchings as well as bending modes are possible. The $\nu_{\text{C=N}}$ mode appears in the region of 1670-1600 cm^{-1} [38]. The C-N stretching vibration is expected to occur in the region 1382-1266 cm^{-1} for aromatic amines [38]. In our earlier study, the $\nu_{\text{C=N}}/\nu_{\text{C-N}}$ modes belong to hydrozone moiety were assigned respectively at 1611/1266 cm^{-1} in FTIR spectrum [39]. For the same modes, Govindarasu (2015) [9] assigned at 1617/1355 cm^{-1} . In our study, the C=N, C-N stretching modes are assigned at 1603/1290 cm^{-1} (mode nos:86/68). These modes are having considerable TED values (66/26%). The mode no:86 is further supported by the observed strong FT-Raman band at 1610 cm^{-1} , while its FTIR counterpart at 1609 cm^{-1} with weak intensity. In the substituted pyridine compounds, the vibrational bands (IR and Raman) observed between 1443 and 1227 cm^{-1} were assigned to C-N stretching modes. In pyridine moiety, the $\nu_{\text{C=N}}$ and $\nu_{\text{C-N}}$ bands were recorded as mixed vibrations at 1424:FTIR/1431 cm^{-1} :FT-Raman and at 1232 cm^{-1} :FT-Raman, respectively [40]. In this study, the bands identified at 1522/1210 cm^{-1} in FT-Raman spectra and harmonic bands at 1531/1224 cm^{-1} (mode nos:82/64) are designated as $\nu_{\text{C}_{30}=\text{N}_{36}}/\nu_{\text{C}_{32}-\text{N}_{36}}$ modes, respectively. These observed and calculated values are in moderate agreement with the above literature values and also find support from TED values (33/44%). The observed stretching frequencies of $\text{C}_{30}=\text{N}_{36}$ is positively ($\sim 91\text{cm}^{-1}$) from the literature value (1431 cm^{-1}) which may be due to the carbonyl group attached at para position in pyridine ring. The calculated harmonic frequencies 1050, 656 and 377, 372 cm^{-1} (mode nos:52, 33 and 22, 21) having moderate TED values (16, 32 and 11, 26%) are respectively assigned to $\beta_{\text{C}_{28}\text{C}_{30}\text{N}_{36}}$, $\beta_{\text{C}_{29}\text{C}_{32}\text{N}_{36}}$ and $\tau_{\text{C}_{27}\text{C}_{29}\text{N}_{36}\text{C}_{32}}$, $\tau_{\text{C}_{27}\text{C}_{29}\text{N}_{36}\text{C}_{32}}$ modes. These assignments are in line with the assignments made by Krishnakumar et al., (2006) [40] in the ranges of 1078-440 cm^{-1} and 671-235 cm^{-1} , respectively. According to the work by Ramesh Babu (2015) [5] on (E)-N'-(Pyridin-2yl)methylene)benzohydrazide (PMBH), the wavenumber 1127 cm^{-1} /harmonic was assigned to $\nu_{\text{N-N}}$ mode of hydrozone moiety. According to TED result (19%), the observed 1105 cm^{-1} /FT-Raman/calculated frequency 1113 cm^{-1} /mode no:56 is attributed to $\nu_{\text{N}_{22}-\text{N}_{23}}$ mode, which was in agreement with the literature value:1095 cm^{-1} [9]. The calculated wavenumbers 790, 790, 648 and 310, 243, 88 cm^{-1} (mode nos:39, 39, 32 and 18, 16, 7) are attributed to $\beta_{\text{C}_6\text{C}_{20}\text{N}_{22}}$, $\beta_{\text{C}_{20}\text{N}_{22}\text{N}_{23}}$, $\beta_{\text{C}_{27}\text{C}_{25}\text{N}_{23}}$ and $\tau_{\text{C}_6\text{C}_{20}\text{N}_{22}\text{N}_{23}}$, $\tau_{\text{C}_{27}\text{C}_{25}\text{N}_{23}\text{N}_{22}}$, $\tau_{\text{C}_{20}\text{N}_{22}\text{N}_{23}\text{C}_{25}}$ modes, respectively. These assignments also have substantial TED (>11%) values. The mode nos:39, 32 and 7 find support from the observed FT-Raman bands at 780, 649 and 90 cm^{-1} .
- 6) *N-H Vibrations:* In general, the N-H stretching frequencies occur in the region 3000-3500 cm^{-1} [41]. Literature survey reveals that the observed/harmonic frequency (3224:FTIR/3153 cm^{-1}) was assigned to ν_{NH} mode for hydrozone moiety [9]. In this study, the band observed at 3491 cm^{-1} (very weak) in FTIR spectrum and its corresponding harmonic frequency 3331 cm^{-1} (mode no: 102) is assigned to $\nu_{\text{N}_{23}\text{H}_{24}}$ mode. This mode is very pure and its TED value is 100%. The observed frequency positively ($\sim 160\text{cm}^{-1}$) deviates from its harmonic value, which is due to the intra-molecular charge transfer between amino and carbonyl groups in the hydrozone linkage. As it is evident from the Table 5, the lone pair on N₂₃ transfer ($n-\pi^* \rightarrow \text{C}_{25}-\text{O}_{26}$) more energy (187.11KJ/mol) to the carbonyl bond ($\text{C}_{25}-\text{O}_{26}$). The N-H in-plane/out-of-plane bending modes were respectively assigned at 1504/838 cm^{-1} [9]. In DMBINH, the calculated wavenumbers: 1445/585 cm^{-1} (mode nos:77/29) with TED values: 27/73% are designated to $\beta_{\text{NH}}/\tau_{\text{NH}}$ modes, respectively. These assignments also find support from our earlier study in the case of (E)-N'-(Pyridi-2yl) methylene)benzohydrazide (PMBH) [5].

- 7) *C-C vibrations*: The benzene ring carbon-carbon stretching vibrations were reported in the regions of 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1280 cm^{-1} by Varsanyi (1974) [35]. Ramesh Babu et al., (2015) [5] predicted the $\nu_{\text{C-C}}$ vibrations in the region 1582-1300 cm^{-1} for PMBH. The medium to weak bands observed at 1386(w), 1268(w) in FTIR and at 1279 (m), 1246(vw) cm^{-1} in FT-Raman spectra are assigned to $\nu_{\text{C-C}}$ mode. For the same mode, the corresponding harmonic DFT wavenumbers are in the range 1572-1239 cm^{-1} (mode nos:85, 83, 72, 67, 66) and their TED contribution is >10%. The β_{CCC} and Γ_{CCC} modes are associated with smaller force constant than the stretching one and hence attributed to lower frequencies. The theoretically calculated β_{CCC} (995, 928, 713/mode nos:51, 45, 35) and τ_{CCC} bending (746, 626, 480/mode nos:38, 31, 25) modes have been found to be consistent with the observed FTIR/FT-Raman bands:1018/1004 cm^{-1} and 748, 622, 481/471 cm^{-1} and the TED contributions are >12%. In the pyridine moiety of 3- or 5-methoxy substituted 2-N-ethylamino-4-nitropyridine N-oxides, the carbon-carbon stretching vibrations were usually observed at 1590-1640, 1560-1580 and 1470-1510 cm^{-1} [42]. In DMBINH, the harmonic bands at 1568, 1531, 1224, 1050 cm^{-1} (mode nos:84, 82, 64, 52) are assigned to $\nu_{\text{C-C}}$ modes having considerable TED value (>12%). The observed FT-Raman bands around 1554, 1522, 1210 and 1042 cm^{-1} support the present assignment. The theoretically computed harmonic frequencies 999, 609, 405 and 383 cm^{-1} were assigned to CCC in-plane and out-of-plane bending modes of pyridine ring [5]. In this study, the calculated frequencies 972, 656 and 439, 377 cm^{-1} (mode nos:49, 33 and 24, 22) are assigned to β_{CCC} and τ_{CCC} modes of pyridine ring. The mode nos: 36 and 21 (724 and 372 cm^{-1}) are respectively designated as $\beta_{\text{C}_{30}\text{N}_{36}\text{C}_{32}}$ and $\tau_{\text{C}_{30}\text{C}_{28}\text{N}_{36}\text{C}_{32}}$ modes with considerable TED values (23 and 28%). These assignments find support from the reported values [9]. Based on the TED contributions (15, 13, 25 and 10%), the calculated harmonic frequencies 1290, 236, 480 and 176 cm^{-1} (mode nos: 68, 15, 25 and 13) are identified with $\nu_{\text{C}_{25}\text{-C}_{27}}$, $\nu_{\text{C}_6\text{-C}_{20}}$, $\beta_{\text{C}_{25}\text{C}_{27}\text{C}_{29}}$ and $\Gamma_{\text{C}_{25}\text{C}_{27}\text{C}_{29}\text{C}_{28}}$ modes, respectively. The observed FTIR: 481/FT-Raman: 471 bands support the mode no: 25.

C. HOMO-LUMO analysis

The HOMO and the LUMO are very important parameters for chemical reaction. The HOMO is the orbital that primarily acts as an electron donor and the LUMO is the orbital that largely acts as the electron acceptor, and the gap between HOMO and LUMO characterizes the molecular chemical stability. The HLEG (HOMO – LUMO Energy Gap) is a critical parameter in determining the molecular electrical transport property, since it is a measure of electron conductivity. The HOMO & LUMO energies and HLEG value evaluated at DFT level using B3LYP hybrid functional invoking 6-311++G (d, p) basis set are listed in Table 6 and also illustrated in Fig. 3. HOMO is located over benzene, hydrozone moieties and some parts of the methoxy groups. Similarly, the LUMO encompasses almost the entire molecule except for some parts of methoxy groups. The calculated HOMO, HLEG are -6.547, -2.144 and 4.403 eV, respectively. The eigen values of HOMO-LUMO and energy gap reflect the biological activities of the molecule.

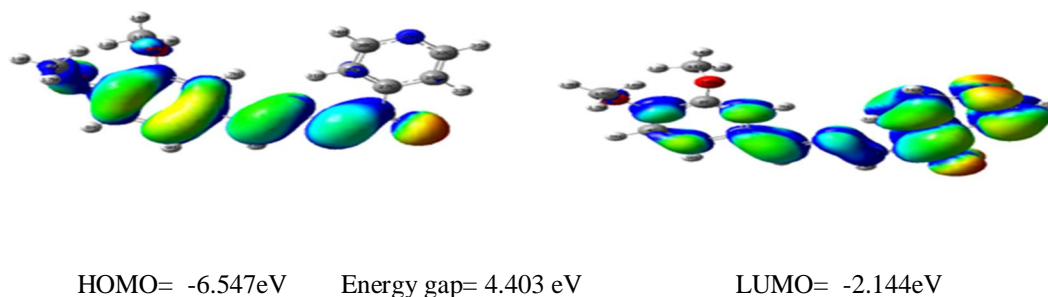


Fig. 3. The frontier molecular orbitals of DMBINH

IV. CONCLUSION

The title molecule was synthesized and characterized by spectral analysis such as FTIR and FT-Raman, spectral studies. A complete vibrational analysis was carried out for the first time on the molecule DMBINH. The bond parameters were calculated and compared with the related XRD data. The conjugation of phenyl ring π -orbital with oxygen lone pair orbital was found to be strong when both orbitals lie in the same plane. The conjugation would be weak when they are in perpendicular. The $\nu_{\text{C}_{30}=\text{N}_{36}}$ mode positively (91 cm^{-1}) deviates from the literature value, which may be due to the carbonyl group attached at para position of the pyridine. The $n\pi$ conjugation of $\text{O}_{15}\text{-C}_{16}\text{-H}_{17}$, H_{18} , H_{19} value 5.28/1.86KJ/mol is lesser on comparing with $\text{O}_{10}\text{-C}_{11}\text{-H}_{12}$, H_{13} , H_{14} . This is due to the influence of different spatial arrangement of the methyl groups.



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