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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

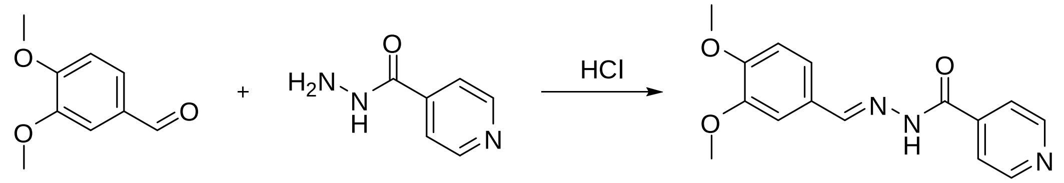
Organic compounds play an important role in the field of electrochemistry, nonlinear optics and photocurrent generation [1-3]. Especially, π-conjugated molecules bearing electron donating and accepting moieties are an important class of materials in optics and photoelectronics [4].

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.H_2O). 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.H_2O 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 50-4000cm^{-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'-dimethoxybendylidene) 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 1.224Å and 1.232Å respectively for (E)-N'((pyridine-2-yl)methylene) benzohydrazide (PMBH) [5]. The carbonyl ($C_{25}=O_{26}$) bond length is calculated 1.220Å. The bond N-N behaves as a part of the bridge between the benzene and pyridine rings and its bond length is calculated as 1.359Å while the literature value is: 1.375Å. Similarly, the $C_{20}=N_{22}/C_{25}-N_{23}$ bond length values are: 1.282/1.381Å and their corresponding literature values are 1.277/1.344Å [9]. The C_1-C_2/C_1-C_6 and C_3-C_4/C_2-C_3 bond lengths differ by 0.0178/0.0188Å 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.

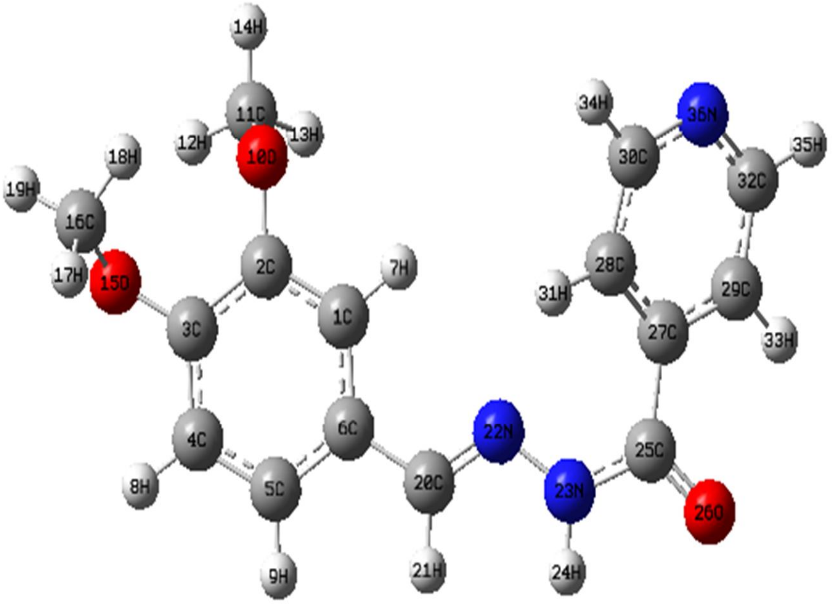


Fig.1. The optimized molecular structure of DMBINH

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

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

[b] Govindrarasu, 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: Γ_{Vib}= 69 A'+33A″; 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.

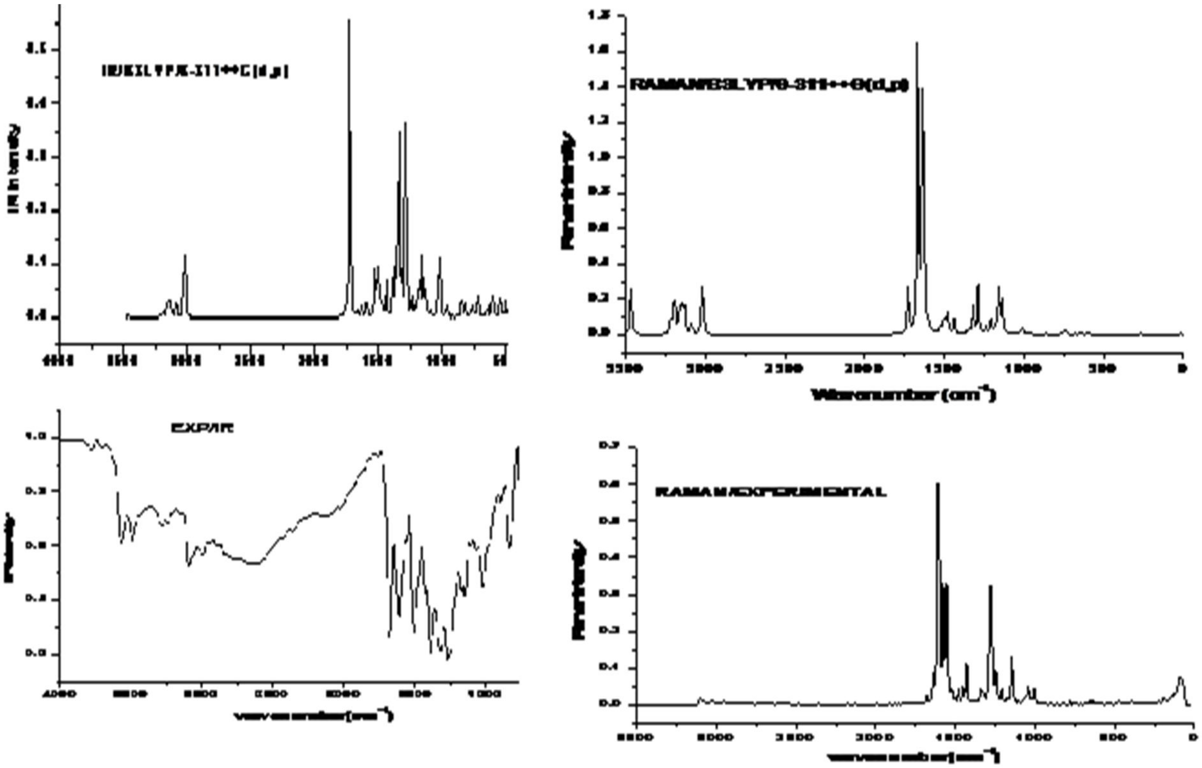


Fig. 2, 3. The combined theoretical and experimental IR, Raman spectra of DMBINH

1) *O-CH_3 vibrations:* In methoxy moiety, the important vibrational modes are νO-CH_3, νC-O-C, νphenyl-O and CH_3 deformations. The O-CH_3 stretching mode was assigned around ~1040cm^{-1} in the region of 1000-1100cm^{-1} for anisole and its derivatives [14-18]. The bands at 1026 and 1012cm^{-1} were assigned to νO-CH_3 modes [9]. The weak FTIR/FT-Raman bands at 1018/1004cm^{-1} are attributed to O_{10}-CH_3 stretching vibration while the corresponding harmonic wave number is 1036 cm^{-1} (mode no:51). Similarly the νO_{15}-CH_3 mode is assigned to mode no:50 (1020 980cm^{-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 δC-O-CH_3 mode was observed for anisole and its derivatives in the region 300-670cm^{-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-O10-CH3 and C-O15-CH3) and other planar modes is expected [22]. In DMBNH.H_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 (νO_{15}-C_3, νO_{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 502/136cm^{-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$^{\circ -1}$)]

Mode no	Calculated Frequencies (cm^{-1})		Observed Frequencies (cm^{-1})		IR Intensity		Raman Intensity		Reduced Masses	Force Constants	Vibrational Assignments≥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	$\tau C_5C_6C_{20}N_{22}(44)+\tau C_{20}N_{22}N_{23}C_{25}(20)$
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	$\beta C_6C_{20}N_{22}(10)+\tau C_6C_{20}N_{22}N_{23}(12)+\tau C_{27}C_{25}N_{23}N_{22}(25)+\tau C_4C_5C_6C_{20}(15)$
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	$\beta C_{25}C_{27}C_{29}(18)+\tau C_5C_6C_{20}N_{22}(15)+\tau C_{20}N_{22}N_{23}C_{25}(16)+\tau C_{27}C_{25}N_{23}N_{22}(17)$
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	$\beta C_{28}C_{27}C_{29}(10)+ \nu C_{25}C_{27}(13)+ \beta C_{27}C_{25}N_{23}(10)$
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	βC25C27C29 (25)+ τC3C2C4C5(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	$\nu C_3C_4(14)+ \beta C_2C_3O_{15}(14)+ \tau H_{24}N_{23}C_{25}C_{27}(10)$
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	$\beta C_{27}C_{28}C_{30}(14)+ \beta C_{29}C_{32}N_{36}(32)$
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	$\beta C_3C_4C_5(12)+ \nu C_2C_3(21)+ \beta C_2C_1C_6(10)$
36	754	724			2.16	0.36	113.54	11.29	5.47	1.83	$\nu C_{25}C_{27}(14)+ \beta C_{30}N_{36}C_{32}(23)$
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	$\nu O_{10}C_{11}(22)+ \beta C_4C_5C_6(12)$
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	$\nu N_{36}C_{32}(21)+ \nu C_{29}C_{32}(17)+ \beta C_{27}C_{28}C_{30}(17)$
50	1020	980			102.39	17.01	62.75	6.24	8.06	4.94	$\nu O_{15}C_{16}(70)$

51	1036	995	1018	1004	73.14	12.15	95.84	9.53	3.49	2.21	$ƲO_{10}C_{11}(46)+ \beta C_2C_1C_6(11)+ \beta C_4C_5C_6(11)$
52	1093	1050		1042	13.46	2.24	21.65	2.15	2.10	1.48	$ƲC_{29}C_{32}(12)+ \beta H_{33}C_{29}C_{27}(22)+ \beta C_{28}C_{30}N_{36}(16)+ \beta C_{30}N_{36}C_{32}(10)+ \beta C_{29}C_{32}N_{36}(15)$
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	$\beta C_{28}C_{27}C_{29}(10)+ ƲN_{23}N_{22}(15)$
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	$ƲN_{23}N_{22}(19)$
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	$ƲN_{23}N_{22}(18)+ \beta H_8C_4C_3(11)+ \Gamma C_{11}H_{13}O_{10}H_{12}(11)$
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	$ƲO_{15}C_3(14)+ \beta H_7C_1C_6(11)+\Gamma C_{16}H_{17}H_{18}O_{15}(17)$
63	1244	1195			5.46	0.91	17.80	1.77	1.28	1.17	$ƲN_{36}C_{30}(15)+ ƲN_{36}C_{32}(11)+ \beta H_{34}C_{30}N_{36}(19)+ \beta H_{35}C_{32}N_{36}(17)$
64	1274	1224		1210	6.61	1.10	17.38	1.73	6.69	6.40	$ƲN_{36}C_{30}(44)+ ƲC_{27}C_{29}(22)$
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	$ƲC_4C_3(13)+ ƲO_{15}C_3(22)+ ƲO_{10}C_2(10)$
67	1320	1268	1267	1279	55.53	9.22	499.88	49.72	7.82	8.03	$ƲC_6C_5(21)+ ƲC_2C_3(41)$
68	1342	1290			399.73	66.40	94.00	9.35	2.97	3.16	$ƲN_{23}C_{25}(26)+ ƲC_{27}C_{25}(15)+ \beta H_{31}C_{28}C_{30}(13)$
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	$ƲC_2C_1(10)+ \beta H_9C_5C_6(15)$
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	$ƲN_{36}C_{32}(33)+ ƲC_{27}C_{29}(32)$
83	1599	1536			9.62	1.60	74.05	7.36	6.63	9.98	$ƲC_4C_3(22)+ ƲC_2C_1(29)+ \beta C_2C_1C_6(13)$

84	1632	1568		1554	10.39	1.73	300.88	29.92	5.40	8.47	$\nu N_{36}C_{30}(11)+ \nu C_{29}C_{32}(29)+\beta C_{32}N_{36}C_{30}(13)$
85	1636	1572		1578	18.71	3.11	4639.62	461.43	6.08	9.59	$\nu C_2C_1(30)+ \nu C_4C_3(10)$
86	1669	1603	1609	1610	10.89	1.81	3626.75	360.70	7.61	12.49	$\nu N_{22}C_{20}(66)$
87	1729	1661	1677	1678	601.97	100.00	535.89	53.30	7.87	13.85	$\nu O_{26}C_{25}(78)$
88	3016	2898			59.65	9.91	50.09	4.98	1.03	5.54	$\nu C_{11}H_{12}(30)+ \nu C_{11}H_{13}(56)+ \nu C_{11}H_{14}(12)$
89	3019	2900			68.38	11.36	104.31	10.37	1.04	5.56	$\nu C_{16}H_{17}(64)+ \nu C_{16}H_{18}(22)+ \nu C_{16}H_{19}(12)$
90	3027	2909			48.15	8.00	53.27	5.30	1.09	5.87	$\nu C_{20}H_{21}(99)$
91	3084	2963			23.06	3.83	19.47	1.94	1.10	6.19	$\nu C_{16}H_{18}(58)+ \nu C_{16}H_{19}(39)$
92	3094	2973			21.87	3.63	24.51	2.44	1.10	6.21	$\nu C_{16}H_{17}(33)+ \nu C_{16}H_{18}(59)$
93	3132	3009	2994		19.96	3.32	51.70	5.14	1.10	6.37	$\nu C_{11}H_{12}(10)+ \nu C_{11}H_{14}(86)$
94	3135	3013			22.81	3.79	74.83	7.44	1.10	6.40	$\nu C_{16}H_{18}(17)+ \nu C_{16}H_{19}(80)$
95	3152	3029		3025	27.64	4.59	45.36	4.51	1.09	6.37	$\nu C_{30}H_{34}(70)+ \nu C_{32}H_{35}(28)$
96	3156	3032			9.11	1.51	77.18	7.68	1.09	6.41	$\nu C_{30}H_{34}(28)+ \nu C_{32}H_{35}(69)$
97	3167	3043			8.14	1.35	32.26	3.21	1.09	6.43	$\nu C_4H_8(10)+ \nu C_5H_9(90)$
98	3192	3067			7.08	1.18	81.87	8.14	1.09	6.57	$\nu C_4H_8(89)+ \nu C_5H_9(10)$
99	3201	3076			1.64	0.27	23.42	2.33	1.09	6.59	$\nu C_1H_7(99)$
100	3204	3078			3.22	0.54	52.72	5.24	1.09	6.61	$\nu C_{29}H_{33}(97)$
101	3222	3096	3094	3102	2.24	0.37	38.27	3.81	1.09	6.69	$\nu C_{28}H_{31}(98)$
102	3467	3331	3283		8.15	1.35	119.53	11.89	1.08	7.62	$\nu N_{23}H_{24}(100)$

ν: Stretching, β: in-plane-bending, Γ: out-of-plane bending, τ: Torsion, vw: very week, w: week, 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,   Ii =10-12 x (v0-vi)4 x$\frac{1}{vi}$ x RAi ---------(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 CH_3 group frequencies, one can expect nine fundamentals, that are associated with each CH_3 group, *viz.*, the symmetrical stretching in CH_3 (CH_3 sym. stretching) and asymmetrical stretching (CH_3 asym. stretching), in-plane stretching modes (in-plane hydrogen stretching mode), the symmetrical (CH_3 sym. deform) and asymmetrical (CH_3 asym. deform) deformation modes, the in-plane rocking (CH_3 in-plane rocking), the out-of-plane rocking (CH_3 out-of-plane rocking) and twisting (CH_3) 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-CH_3 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 O_{15}-C_{16}-H_{17}, H_{18}, H_{19} group (n-π*: $O_{15}\rightarrow C_{16}$-H_{17} /C_{16}-H_{18}:5.28/1.86 kJ/mol) with phenyl ring is not much different from that of O_{10}-C_{11}-H_{12}, H_{13}, H_{14} group (n-π*: $O_{10}\rightarrow C_{11}$-H_{13}/C_{11}-H_{12}: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, 2973cm^{-1}: mode nos: 94, 92/2900cm^{-1}: mode no:89) than the O_{10}-C_{11}-H_{12},H_{13},H_{14} group (3009, 2963cm^{-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 (2903-3032cm^{-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 1370-1390cm^{-1} [28]. According to the work by Govindarasu (2015) [9] on DMBNH. H_2O, the wavenumbers at 1470/1423cm^{-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 1451/1453cm^{-1}, (mode nos:79, 78) whereas in FT-Raman they occur at 1446cm^{-1}. The weak bands around 1426/1429cm^{-1} in the FTIR/FT-Raman spectra corresponding to β_{sym} HCH mode is in excellent agreement with the harmonic values 1429, 1423cm^{-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 cm^{-1} is close to the predicted region of 1070-1010cm^{-1} [29]. Based on this the calculated wavenumbers 1122, 1120 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 at1146 cm^{-1} and 1173 cm^{-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 400 cm^{-1}. In DMBINH, the CH_3 torsional mode is assigned to mode nos:11, 10 (150, 139cm^{-1}) which are in agreement with earlier assignments at 155 cm^{-1} and 132 cm^{-1} [9].

3) *C=O vibrations:* The carbon-oxygen double bond is formed by pπ-pπ 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 cm^{-1} [32, 33]. The very strong absorption frequency at 1653 cm^{-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 3100-3000cm^{-1}, characteristic of C-H stretching vibration [34] is due to $\nu_{C\text{-}H}$ of aromatic pyridine moiety. The characteristic C-H stretching modes calculated in the range 3073-3101cm^{-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/resonnce 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 3076-3043cm^{-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, $\beta_{C\text{-}H}/\Gamma_{C\text{-}H}$ vibrations would normally appear in the regions of 1000-1300/750-1000cm^{-1}, respectively [35,36]. The $\beta_{C\text{-}H}$ and $\Gamma_{C\text{-}H}$ modes in DMBNH.H_2O were identified in the regions 1215-1492cm^{-1} and 708 - 914cm^{-1} [9] respectively. In accordance with above conclusion, the calculated frequencies for DMBINH at 1227, 1383, 1472cm^{-1} (mode nos: 65, 72, 81) and at 883, 918, 931cm^{-1} (mode nos:43, 44, 46) are respectively designated as $\beta_{C\text{-}H}$ and $\Gamma_{C\text{-}H}$ 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 $\nu_{C\text{-}H}/\beta_{C\text{-}H}/\Gamma_{C\text{-}H}$ vibrations. In DMBNH.H_2O, the $\nu_{C\text{-}H}$, $\beta_{C\text{-}H}$ and $\Gamma_{C\text{-}H}$ modes belong to pyridine ring were assigned in the regions: 3042-3120, 1112-1457 and 803-964 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 3029-3096cm^{-1} (mode nos: 95-101) are designated as ν_{C-H} modes of pyridine ring on comparison with the reported values cited above for DMBNH.H$_2$O 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 835cm^{-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 Γ_{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 (ν_{CH}/2943; β_{CH}/1327; Γ_{CH}/940cm^{-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:1339cm^{-1} bands. According to the TED output (>21, 23%) the harmonic frequencies: 1462, 1381cm^{-1} are designated as $\beta H_{34}C_{30}N_{36}$, $\beta H_{35}C_{32}N_{36}$ modes, respectively.

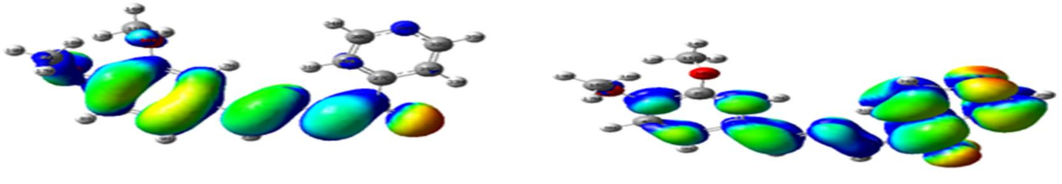
5) *C=N, C-N, N-N vibrations:* The identification of C=N, C-N (stretching, bending) vibrations are very difficult task [37], since the mixing of several bands are possible in the region. In DMBINH, the hydrozone linkage bridges the phenyl and pyridine rings, hence the C=N, C-N and N-N stretchings as well as bending modes are possible. The $\nu_{C=N}$ mode appears in the region of 1670-1600cm^{-1} [38]. The C-N stretching vibration is expected to occur in the region 1382-1266cm^{-1} for aromatic amines [38]. In our earlier study, the $\nu_{C=N}$/ν_{C-N} modes belong to hydrozone moiety were assigned respectively at 1611/1266cm^{-1} in FTIR spectrum [39]. For the same modes, Govindarasu (2015) [9] assigned at 1617/1355cm^{-1}. In our study, the C=N, C-N stretching modes are assigned at 1603/1290cm^{-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 1610cm^{-1}, while its FTIR counterpart at 1609cm^{-1} with weak intensity. In the substituted pyridine compounds, the vibrational bands (IR and Raman) observed between 1443 and 1227cm^{-1} were assigned to C-N stretching modes. In pyridine moiety, the $\nu_{C=N}$ and ν_{C-N} bands were recorded as mixed vibrations at 1424:FTIR/1431cm^{-1}:FT-Raman and at 1232cm^{-1}:FT-Raman, respectively [40]. In this study, the bands identified at 1522/1210cm^{-1} in FT-Raman spectra and harmonic bands at 1531/1224cm^{-1} (mode nos:82/64) are designated as $\nu C_{30}=N_{36}$/$\nu C_{32}-N_{36}$ 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 $C_{30}=N_{36}$ is positively (~91cm^{-1}) from the literature value (1431cm^{-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 $\beta C_{28}C_{30}N_{36}$, $\beta C_{29}C_{32}N_{36}$ and $\tau C_{27}C_{29}N_{36}C_{32}$, $\tau C_{27}C_{29}N_{36}C_{32}$ modes. These assignments are in line with the assignments made by Krishnakumar et al., (2006) [40] in the ranges of 1078-440cm^{-1} and 671-235cm^{-1}, respectively. According to the work by Ramesh Babu (2015) [5] on (E)-N'-((Pyridin-2yl)methylene)benzohydrazide (PMBH), the wavenumber 1127cm^{-1}/harmonic was assigned to ν_{N-N} mode of hydrozone moiety. According to TED result (19%), the observed 1105 cm^{-1}/FT-Raman/calculated frequency 1113cm^{-1}/mode no:56 is attributed to $\nu N_{22}-N_{23}$ mode, which was in agreement with the literature value:1095cm^{-1} [9]. The calculated wavenumbers 790, 790, 648 and 310, 243, 88cm^{-1} (mode nos:39, 39, 32 and 18, 16, 7) are attributed to $\beta C_6C_{20}N_{22}$, $\beta C_{20}N_{22}N_{23}$, $\beta C_{27}C_{25}N_{23}$ and $\tau C_6C_{20}N_{22}N_{23}$, $\tau C_{27}C_{25}N_{23}N_{22}$, $\tau C_{20}N_{22}N_{23}C_{25}$ 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 at780, 649 and 90cm^{-1}.

6) *N-H Vibrations:* In general, the N-H stretching frequencies occur in the region 3000-3500cm^{-1} [41]. Literature survey reveals that the observed/harmonic frequency (3224:FTIR/3153cm^{-1}) was assigned to ν_{NH} mode for hydrozone moiety [9]. In this study, the band observed at 3491cm^{-1} (very weak) in FTIR spectrum and its corresponding harmonic frequency 3331cm^{-1} (mode no: 102) is assigned to $\nu N_{23}H_{24}$ mode. This mode is very pure and its TED value is 100%. The observed frequency positively (~ 160cm^{-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 N_{23} transfer ($n-\pi^* \rightarrow C_{25}-O_{26}$) more energy (187.11KJ/mol) to the carbonyl bond ($C_{25}-O_{26}$). The N-H in-plane/out-of-plane bending modes were respectively assigned at 1504/838cm^{-1} [9]. In DMBINH, the calculated wavenumbers: 1445/585cm^{-1} (mode nos:77/29) with TED values: 27/73% are designated to β_{NH}/τ_{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 1380-1280cm^{-1} by Varsanyi (1974) [35]. Ramesh Babu et al., (2015) [5] predicted the ν_{C-C} vibrations in the region 1582-1300cm^{-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 ν_{C-C} mode. For the same mode, the corresponding harmonic DFT wavenumbers are in the range 1572-1239cm^{-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:1018/1004cm^{-1} and 748, 622, 481/471cm^{-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 1470-1510cm^{-1} [42]. In DMBINH, the harmonic bands at 1568, 1531, 1224, 1050cm^{-1} (mode nos:84, 82, 64, 52) are assigned to ν_{C-C} modes having considerable TED value (>12%). The observed FT-Raman bands around 1554, 1522, 1210 and 1042cm^{-1} support the present assignment. The theoretically computed harmonic frequencies 999, 609, 405 and 383cm^{-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, 377cm^{-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 372cm^{-1}) are respectively designated as $\beta C_{30}N_{36}C_{32}$ and $\tau C_{30}C_{28}N_{36}C_{32}$ 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 176cm^{-1} (mode nos: 68, 15, 25 and 13) are identified with νC_{25}-C_{27}, νC_{6}-C_{20}, $\beta C_{25}C_{27}C_{29}$ and $\Gamma C_{25}C_{27}C_{29}C_{28}$ 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.



HOMO= -6.547eV Energy gap= 4.403 eV LUMO= -2.144eV

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 $\nu C_{30}=N_{36}$ mode positively (91cm^{-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 O_{15}-C_{16}-H_{17}, H_{18}, H_{19} value 5.28/1.86KJ/mol is lesser on comparing with O_{10}-C_{11}-H_{12}, H_{13}, H_{14}. This is due to the influence of different spatial arrangement of the methyl groups.

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