

Synthesis, spectroscopic (FT-IR, FT-Raman and UV) and computational studies on 2-Bromo-5-methoxybenzonitrile

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ABSTRACT

In this study, in which the group vibrations of 2-Bromo-5-methoxybenzonitrile (2B5MBN) were investigated by electronic structure calculations based on Density Functional Theory (DFT) carried out at B3LYP methods. The FTIR and FT-Raman (FTR) spectra of 2B5MBN had been traced in the solid phase. The equilibrium geometrical parameters and vibrational assignments of 2B5MBN for the ground state had been deliberated through the theoretical methods invoking a basis set. UV-vis absorbance of the title molecule was traced in the range between 200–800 nm and the electronic possessions for instance excitation energies, oscillator strength, wavelengths, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were estimated by time-dependent DFT (TD-DFT) approach. Moreover, thermodynamic properties of the title compound were predicted by B3LYP levels using above basis set.

KEY WORDS: 2B5MBN, DFT, TD-DFT.

1. INTRODUCTION

Benzonitrile and substituted benzonitrile is the hero compound in the production of large scale of agrochemicals, dyestuffs, pesticides, pharmaceuticals as well as factory and marketing purposes like beverages, Juices, Cigarettes, Hot drinks etc. (Sundaraganesan, 2005). Benzonitrile compounds had high toxic and irritating product. World Wide Organization set the range of benzonitrile while using the daily usage products. Toxicity effect used for evaluated in prokaryotic and eukaryotic systems. Which evaluation provided the sharp detail and carcinogenicity, chronic toxicity, and mutagenicity (Petra Lovecka, 2015). In analytical chemistry, the ortho-substituted derivatives of bromo are used as reagents also identified the anesthetic problems and brain diseases are cured through these drugs (Sundaraganesan, 2005). Chloroxynil is the one of the benzonitrile compound which had the important role of control the growth of weeds and their remainders in the agriculture fields. The cyano group is the main impact of interaction with the receptor and the companied group of benzonitrile is affects the structural, electronic, vibrational, optical and thermodynamical parameters (Vaschetto, 1999). Reactions between the aromatic ring and cyano group are the causes for the molecular equilibrium parameter changes. Organic NLO materials have been used as large number of applications of data transmission, information processing in optical, larger nonlinear optical coefficients, simpler preparation and reasonable cost while compare with inorganic and semiconductor materials (Femina Jasmine, 2016; Hochberg, 2006).

The benzene ring in 2-Bromo-5-methoxybenzonitrile (2B5MBN) has three substituents such that the bromo and methoxy groups are at ortho and meta position respectively with respect to the cyano group. The methoxy and cyano groups are generally referred to as electron donating substituents in aromatic ring systems. The joining of cyano group in benzonitrile and the aromatic ring creates the migration of the nitrogen atom.

Recently Sas (2015), reported 2-Bromo-1H-Benzimidazol: new preparation method, geometrical optimization, FTIR, FTR, dispersive Raman spectroscopic analysis, electronic structure and 1H and 13C nuclear magnetic resonance (NMR). Arjunan (2013), analyzed novel complexes 2-bromo-3-nitroacetophenone: molecular structures, spectral, vibrational analysis and electronic properties. Sundaraganesan (2005), investigated molecular structure, vibrational spectroscopic, Thermodynamical studies of 2-bromo-4-methyl-phenylamine. Danuta Michalska (2013), reported the experimental FTIR, FTR data and quantum studies and NBO, Thermo dynamical parameter, orbital analysis and NLO of 2-bromo-5-nitrothiazole. The conformer stability, equilibrium geometrical structural analysis, vibrational assignments, IR intensities and Raman activities, UV, NLO, Mulliken population analysis, electrostatic potential (ESP) and thermal analysis of 2-amino-5-bromo-6-methyl-4-pyrimidinol by computational calculations are investigated by Gladis Anitha (2015).

In my Literature survey make public that the computational (DFT) calculations of 2-Bromo-5-methoxybenzonitrile (2B5MOB) are not calculated is reported from the best of our knowledge. So In these research has been investigated the vibrational spectroscopic assignments and spectra. In addition, NLO, NBO analysis, UV spectral analysis, MEP, Mulliken & Natural population analysis and thermodynamical parameters have been predicted. The theoretical data of FTIR, FT-Raman match up to the observed data.

2. EXPERIMENTAL DETAILS

The compound 2B5MOB was provided a sturdy purity of larger than 99% and used as such as without any additional refinement by Sigma-Aldrich Chemical Company, the USA. The FTR spectrum of 2C3MOBN has been recorded using 1064nm line of Nd:YAG laser as excitation wavelength in the region 50-3500 cm^{-1} on a EZRaman, Enwaveoptronics, USA IFS 66 V spectrometer. The FTIR spectrum was recorded using 8400S Bruker, Alpha T, and Germany infrared spectrophotometer in the region 4000–400 cm^{-1} . At the normal temperature with scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ the spectra are traced. The association of both calculated and computed IR and Raman spectra of 2B5MOB showed. All spectra recorded out at our Nanotechnology Department.

The spectra are computerized using the B3LYP with some basic sets and the output spectra are monitored threw Gauss sum program, which gives the Raman intensities spectra directly. This program equating the intensity theory of Raman scattering derived relationship and produces the modified Raman intensities data.

The assignments give the same results while compared with the three basic sets. The Raman intensity data also merged with the dynamic basic sets which confirmed the formation of methyl benzonitrile. The calculated vibrational frequencies and assignments are tabulated.

Computational details: The GAUSSIAN 09W program is used for predicted the quantum computational calculations of 2B5MOB (Govidasamy, 2014; Frisch, 2009) with the original version with three parameter functional by way of applying ab-initio Becke-Lee-Yang-Parr hybrid method in correlations B3LYP (Murugan, 2012; Parr, 1989) level with different basis sets on Intel Core i3 1.9GHz processor personal computer to derive the complete geometry optimization (Sundaraganasan, 2009). Gaussian software is a super positioning tool for developing fields of computational physics like structural analysis, reaction mechanisms, potential energy values, charge distributions and excitation energies of the compound (Saravanan, 2015). The single point energy calculation is computing the energies of specific molecular structures and the allied molecular properties are predicted initially. Geometry optimizations calculating equilibrium structure of molecules, optimizing transition structures and energy minimizations at dynamic basic sets. From the second derivatives of the energy has calculated the FT-IR, Raman frequencies are computing and intensities plots are done by the Gauss sum program. The vibrational modes are assignments are calculated and explained using the Scaled quantum mechanical program using VEDA.4.0. Software (Rauhut, 1995; Saleem, 2015). An elevated degree of precision at the customarily considerations along with obtainable linked by the GAUSSVIEW program are made by the molecules vibrational frequency assignments.

The electronic oscillatory frequency and electronic properties such as HOMO and LUMO energy distribution Thermo dynamical parameters are resolute by the TD-DFT calculations (Anbarasan, 2011). The energy absorption spectra and energy gap plot drawn from Gauss view 5.0 programs (Lin-Vien, 1991).

3. RESULTS AND DISCUSSION

Optimized Geometry: 2-Bromo-5-methoxybenzonitrile compound optimized structure has been illustrated (Figure.1). The stable minimum energy calculated as -3012.65614652 and -3012.60068420 a.u, by B3LYP functional with the standard basis sets. The predicted atomic lengths, atomic angles and torsion angle or dihedral angles from the above method are tabulated in Table 1. There is no data on the optimized structure and equilibrium parameters of 2B5MBN do not exist in earlier reports through the literature survey. The microwave data are slightly small while compare with theoretical value of the optimized atomic lengths be in the right places to isolated title compound in gaseous phase. The predicted geometrical parameters of the two different basis sets are almost similar. The theoretical values had good agreement with the microwave data. Benzene ring had six carbon atoms and hydrogen atoms which carbons atoms had same lengths and angles and hydrogen atoms had some changes. The molecule have modify in the different chemical and physical assets because of the hydrogen in benzene ring which acts as the trepidation of the valence electron distribution. The recent molecule interactions to the substituents are indicating the benzene ring angular changes (Socrates, 1981).

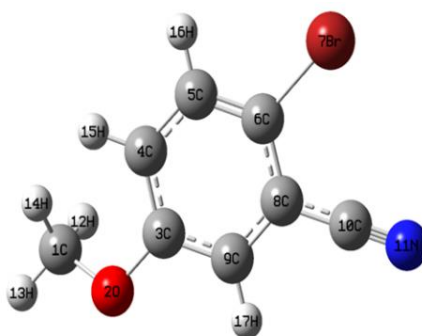


Figure.1. Optimized structure of 2B5MBN

Table.1. Equilibrium parameters of 2B5MBN

BondLength(Å)	Aug	B3LYP	Exp.	Bond Length(Å)	Aug	B3LYP	Exp.
C1-O2	1.430	1.430		C5-C6	1.358	1.358	1.379
C1-H12	1.070	1.070		C5-H16	1.070	1.070	0.930
C1-H13	1.070	1.070		C6-Br7	1.910	1.910	
C1-H14	1.070	1.070		C6-C8	1.403	1.403	1.375
O2-C3	1.430	1.430		C8-C9	1.400	1.400	
C3-C4	1.400	1.400	1.391	C8-C10	1.401	1.401	
C3-C9	1.398	1.398		C9-H17	1.070	1.070	0.930
C4-C5	1.403	1.403	1.391	C10-N11	1.147	1.147	1.135
C4-H15	1.070	1.070	0.930				
Bond Angle	Aug	B3LYP	Exp.	Bond Angle	Aug	B3LYP	Exp.
O2-C1-H12	109.5	109.5		C4-C5-H16	119.8	119.8	
O2-C1-H13	109.5	109.5		C6-C5-H16	119.8	119.8	
H12-C1-H14	109.5	109.5		C5-C6-Br7	119.8	119.8	
H12-C1-H13	109.5	109.5		C5-C6-C8	120.4	120.4	119.90
H12-C1-H14	109.5	109.5		Br7-C6-C8	119.8	119.8	
H13-C1-H14	109.5	109.5		C6-C8-C9	120.0	120.0	119.50
C1-O2-C3	109.5	109.5		C6-C8-C10	120.0	120.0	120.50
O2-C3-C4	120.2	120.2		C9-C8-C10	120.0	120.0	
O2-C3-C9	120.2	120.2		C3-C9-C8	119.6	119.6	120.50
C4-C3-C9	119.6	119.6		C3-C9-H17	120.2	120.2	
C3-C4-C5	120.0	120.0	122.80	C8-C9-H17	120.2	120.2	
C3-C4-H15	120.0	120.0		C8-C10-N11-Br7-1	180.0	180.0	
C5-C4-H15	120.0	120.0		C8-C10-N11-Br7-2	180.0	180.0	
C4-C5-C6	120.4	120.4	118.40				
Dihedral Angle	Aug	B3LYP		Dihedral Angle	Aug	B3LYP	
H12-C1-O2-C3	60	60		C3-C4-C5-H16	180	180	
H13-C1-O2-C3	180	180		H15-C4-C5-H16	0	0	
H14-C1-O2-C3	-60	-60		C4-C5-C6-Br7	180	180	
C1-O2-C3-C4	30	30		C4-C5-C6-C8	0	0	
C1-O2-C3-C9	-150	-150		H16-C5-C6-Br7	0	0	
O2-C3-C4-C5	180	180		H16-C5-C6-C8	-180	-180	
O2-C3-C4-H15	0	0		C5-C6-C8-C9	0	0	
C9-C3-C4-C5	0	0		C5-C6-C8-C10	180	180	
C9-C3-C4-H15	-180	-180		Br7-C8-C8-C9	180	180	
O2-C3-C9-C8	180	180		Br7-C8-C8-C10	0	0	
O2-C3-C9-H17	0	0		C6-C8-C9-C3	0	0	
C4-C3-C9-C8	0	0		C6-C8-C9-H17	-180	-180	
C4-C3-C9-H17	180	180		C10-C8-C9-C3	-180	-180	
C3-C4-C5-C6	0	0		C10-C8-C9-H17	0	0	

The benzene ring appears a small hazy with carbon to carbon atom bond length next to the substitutions place ($\approx 1.40\text{\AA}$) longer than the carbon bond (C5-6) in the middle of the ring substituted in the bromo ($\approx 1.35\text{\AA}$). The distorted elucidates that the substituted on the ring can affect the hybridization and bond lengths of the carbon atoms. The bond length of C-C increase while compare with benzene ring this shows the angle between substituted atoms has little modified hexagonal structure of the angles. The C5-Br7, C8-C10 and C3-O2 bonds in the ring can modify the angles of the C6-C8-C9, C5-C6-C8 and C4-C3-C9 respectively. The C \equiv N bond length is predicted DFT/B3LYP method in 1.1\AA both basis sets and compared with experimental value as 1.13\AA . And other atoms distance, angles are predicted and that result gives good correlation with microwave data.

Vibrational spectra: The recent compound predicted for structural analysis to C1 point group symmetry and turn on the frequency into same symmetry species (A). The molecule 2B5MBN consists of 17 atoms and 45 internal modes of vibrations are tabulated and compared the both frequencies of 2B5MBN and the details vibrational assignments with TED along with IR and Raman intensities, force constant and normal mode descriptions are also reported in Table.2. For visual comparison, the observed and calculated FTIR and FTR spectra of 2B5MBN at above basis set are shown in Figure.2 & Figure.3.

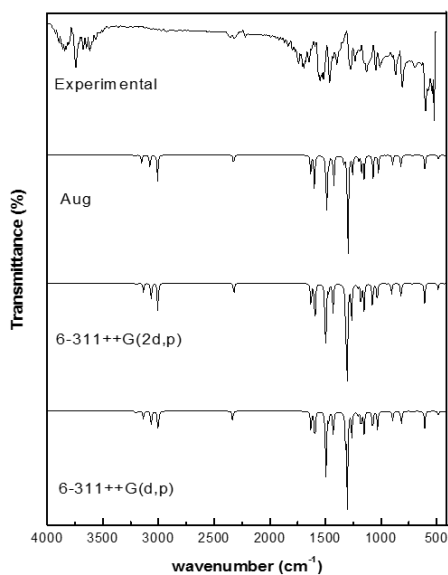


Figure.2. Experimental and theoretical DFT/B3LYP FT-IR of 2B5MBN

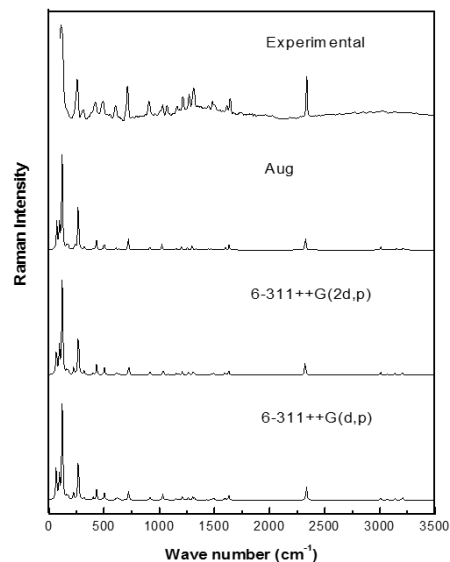


Figure.3. Experimental and theoretical DFT/B3LYP FTR of 2B5MBN

Table.2. The observed (FT-IR, FT-Raman) and calculated frequencies (cm⁻¹), IR intensity (km mol⁻¹), Raman intensity (Å⁴ amu⁻¹), force constant (m dyne Å⁻¹) and probable assignments of 2B5MBN

Mode	IR	Raman	Un scaled	Scaled	Reduced mass
1A			3214	3108	1.0938
2A			3209	3103	1.0921
3A			3199	3094	1.0887
4A			3144	3040	1.0995
5A			3072	2971	1.1067
6A			3010	2911	1.0345
7A	2356	2339	2339	2262	12.6782
8A	1647	1643	1634	1580	6.2118
9A	1596	1615	1599	1546	5.9737
10A	1562		1503	1453	1.0565
11A	1547		1498	1449	2.3715
12A	1517	1493	1494	1445	1.0454
13A	1463	1479	1474	1425	1.2939
14A	1430		1433	1385	3.6045
15A	1397	1312	1323	1279	7.265
16A			1306	1263	2.9331
17A	1272	1272	1265	1224	1.7768
18A	1234	1214	1211	1171	1.4788
19A			1182	1143	1.6828
20A		1160	1166	1128	1.2722
21A	1131		1156	1117	1.7487
22A		1074	1078	1043	4.2336
23A	1048	1033	1034	1000	5.8376
24A	1010		950	919	1.3223
25A		908	919	889	5.1469
26A	897		898	869	1.5281
27A	870		820	793	1.4259
28A	809		724	700	6.9436
29A	696	714	713	689	3.8615
30A	635		634	613	4.764
31A			620	600	6.7636
32A	600	604	609	589	5.6564
33A	522		504	487	7.4706

34A		490	486	470	3.7042
35A		422	434	419	6.4929
36A		378	402	388	4.7634
37A		314	320	309	4.9749
38A			302	293	5.1112
39A		258	267	259	8.6818
40A			223	216	1.1414
41A			173	167	5.208
42A			160	154	6.4155
43A		126	122	118	15.7759
44A			95	92	4.8682
45A			67	65	3.5373

Force constant	IR _{int}	Raman _{int}	Vibrational Assignments with TED%
6.6558	2.354	221.820	vCH (99)
6.6241	0.5917	168.077	vCH (99)
6.5648	1.788	59.868	vCH (99)
6.4016	16.022	252.265	vCH (92)
6.1549	32.031	119.758	vCH (98)
5.5243	49.72	393.474	vCH (92)
40.8627	20.785	1826.334	vNC (89) + vCC (11)
9.7677	39.776	643.224	vCC (67) + βHCC (10)
9.0002	68.393	382.144	vCC (64) + βHCC (12)
1.4058	16.647	87.452	βHCH (76) + βHCO (11)
3.1367	114.54	86.788	βHCC (35)
1.3746	10.457	226.824	βHCH (82) + δCHOH (15)
1.656	18.347	146.011	βHCO (29) + δCHOH (27) + βHCH (17)
4.3591	52.666	78.032	vCC (30) + βHCC (20)
7.4881	58.973	295.223	vCC (65) + vOC (10)
2.9465	192.82	385.774	vOC (20) + vCC (14) + βHCC (12)
1.6762	52.033	349.665	vCC (14) + vCC (11)
1.2769	8.329	460.353	βHCO (28) + δCHOH (26)
1.3859	36.607	78.531	βHCC (24) + βHCO (18) + δCHOH (12)
1.0199	0.739	77.863	δCHOH (83) + βHCH (16)
1.376	47.314	208.422	vCC (35) + βHCC (33)
2.9	44.149	72.521	vOC (44) + βCCC (15)
3.6804	36.278	777.411	vCC (20) + βCCC (14) + vOC (13)
0.7031	1.742	9.319	δCCCH (62) + δHCCC (28)
2.5609	0.853	506.047	vOC (34) + vCC (16) + βCCC (14)
0.7263	18.944	10.373	δHCCC (84)
0.5647	29.581	7.5585	τHCCC (51) + δCCCH (31)
2.1425	1.38	1320.035	βCCC (38) + vCC (20)
1.1551	1.943	13.856	τCCCC (69)
1.1293	0.984	181.189	τCCCC (50) + τCCCN (18) + τCCCO (14)
1.5324	0.359	306.684	βCCC (36) + βCCN (27)
1.2366	34.3255	149.472	βCCC (42) + vBrC (16) + vOC (12) + βCOC (11)
1.1171	0.657	912.682	βCCC (36) + vCC (19) + βCOC (13)
0.5153	9.975	134.689	τCCCC (59) + τCCCN (26)
0.7199	1.356	1344.171	βCCO (20) + βCCN (19) + βCOC (17)
0.4525	1.048	379.763	τCCCC (48) + τCCCN (32)
0.2994	2.270	328.913	τCCCO (41) + τCCCB (20) + τCCCC (13) + τHCOC (12)
0.2756	1.566	113.864	βCOC (22) + βCCO (21) + βCCBr (19) + vBrC (15)
0.3659	3.918	6239.369	vBrC (33) + βCCC (18) + βCOC (13) + βCCN (11)

0.0336	0.031	917.256	τ HCOC (82)
0.0918	0.1925	603.0181	β CCBr (40) + β CCO (26) + β COC (13)
0.0965	4.8601	394.3824	τ CCCC (54) + τ COCC (17) + τ CCCN (11)
0.1385	2.8166	13668.00	β CCC (42) + β CCN (33) + β CCBr (16)
0.026	0.3586	2959.966	τ CCCB (44) + τ CCCC (23) + τ COCC (13)
0.0093	0.8519	4993.736	τ COCC (59) + τ CCCO (20) + τ CCCC (10)
v- stretching; β -in plane bending; δ -Out-of-plane bending; τ -torsion; TED-Total Energy Distribution; int- Intensity.			

Table.3. Energy Excitations, Wavelength and Oscillator Strength of the 2B5MBN

Excitation energies (cm ⁻¹)	Wavelength (nm)	Oscillatory strength	Symmetry
35155.53072	284.4502642	0.0556	A-Signlet
41891.91984	238.7095182	0.0009	A-Signlet
42708.15856	234.1472997	0.0003	A-Signlet

Table.4. Energy calculations of 2B5MBN

Basic set	6-311++G(2d,p)
SCF energy(a.u)	-3012.63
Dipole moment(Debye)	6.29
LUMO(eV)	-2.16
HOMO(eV)	-7.04
ENERGY GAP(eV)	-4.88
Electro negativity (χ)	-4.6
Chemical Potential (μ)	4.6
Global Hardness (η)	2.44
Global softness (s)	0.41
Electrophilicity Index (ω)	5.61
EHOMO-1(eV)	-7.91
ELUMO+1(eV)	-1.24
EHOMO-1 - ELUMO+1(eV)	-6.67

CH vibrations: Optimized title compound 2B5MBN has the repeated weak bands in the region of above 3000 cm⁻¹ because of this stretching vibration. The 18 carbon hydrogen stretching vibrations are assigned in the molecule. The experimental spectra do not found in the region but the computed frequencies of vibrational assignments are assigned as 3225-3010 cm⁻¹ (mode no.1-6).

The interactions take place between C-C stretching vibrations. The six in-plane bending (β) are observed in the region 1300–1000 cm⁻¹ as intensive bands (Alcolea Palafox, 2013) and strongly disappear in the region as 1000-750 cm⁻¹ in the out-of-plane bending (δ) of carbon hydrogen vibrations. The six β vibrations and six torsion (τ) vibrations are found for the title compound. The β vibrations assigned in FT-IR and FTR as 1048,1131,1272 cm⁻¹ and 1033, 1074, 1160, 1214 cm⁻¹ respectively. The τ vibrations assigned in FT-IR and FTR as 600, 522 cm⁻¹ and 604, 490, 422, 378, 314 cm⁻¹ respectively. The calculated frequency values at 950-1265 cm⁻¹ and 750-300 cm⁻¹ are assigned in carbon hydrogen β vibration (mode no.18-23) and τ vibration (mode no.32-37), respectively.

C \equiv N vibrations: In the benzonitrile molecule, the cyano group (C \equiv N) vibrational wave number is almost unchanged because of it joined together the phenyl ring as a new substituent. For the aromatic compound which bears a C \equiv N group attached to the ring, a band of good intensity has been absorbed in the region 2240–2221 cm⁻¹ (Senthil Kumar, 2015) and it is being attributes to C \equiv N stretching. Br and OH are the electron – acceptor groups, it is decrease the IR band intensity and increase the wave number value to the higher limit of the characteristic spectral region. CH₃ is the electrons donating groups, it increase IR intensity and decrease wave number value (Colthup, 1991). These electron acceptor groups are the main impact for the shifting for C \equiv N vibrational wave number. In this compound, the FTIR and FTR spectra frequencies at 2356 and 2339 cm⁻¹ for C \equiv N (ν) vibrations for 2B5MBN respectively. The calculated fundamental frequencies are at 2339cm⁻¹ by B3LYP method with basis sets, has been assigned to C \equiv N stretching. The in-plane and out-of-plane bending C \equiv N have also been identified and presented in Table.2.

C-Br vibrations: This partial vibration is getting from the ring to Bromine atom. This vibration main significant is the mixing of vibrations is possible due to the presence of heavy atoms (Chiu, 1979). Carbon-bromine absorbed strongly in the lower frequency at 650–485 cm⁻¹ due to the vibration of stretching mode. In the present study, these stretching vibrations are observed at 600 cm⁻¹ and 604, 258 cm⁻¹ at FT-IR and FTR for 2B5MBN, respectively. The C-Br (β) vibrations are observed at 126cm⁻¹ and the torsion vibration of carbon-bromine bond are observed at 314cm⁻¹ at FT-Raman. The both stretching, bending, torsion vibrations are well agreement with B3LYP calculation method. The vibration modes are compared and harmony with literature.

Methoxy group vibrations: CH₃ is the electrons donating groups, it increase IR intensity and decrease wave number value. OH are the electron – acceptor groups, it is decrease the IR band intensity and increase the wave number value to the higher limit of the characteristic spectral region. These electron acceptor groups are the main impact for the shifting for methoxy vibrational wave number. The in-plane stretching frequencies of –CH₃ are assigned at 522 cm⁻¹ and 490 cm⁻¹ in both spectra. For the above, the calculated wavenumbers are at 504 and 486 cm⁻¹. Low intense bands at 3144, 3072 and 2890 cm⁻¹ are assigned to –CH₃ symmetric stretching.

HOMO–LUMO analysis: The two parental orbitals reacts each other which produces the two child orbitals of the antibonding and bonding orbitals. The energy is higher in the antibonding orbital when compared with the bonding orbital. Lewis base orbitals are filled with a pair of electrons and the other one is the Lewis acid, this is empty. The “filled-empty” interaction is stabilizing. Generally, two kinds of interactions like HOMO and LUMO of the molecule. These interactions allow the strong interact between the pair of orbitals (frontier orbitals) in the molecules and they lie at the outermost boundaries of the electrons of molecule (Arivazhagan, 2013). The HOMO-LUMO analysis for the 2B5MBN molecule plots and the excitation energies have been predicted and the result filled in Table.4.

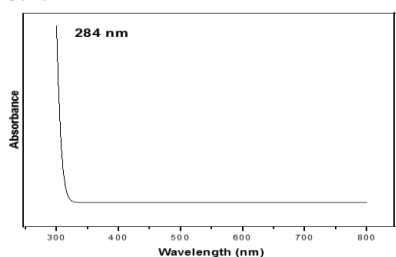


Figure.4. UV–vis spectra of the title compound

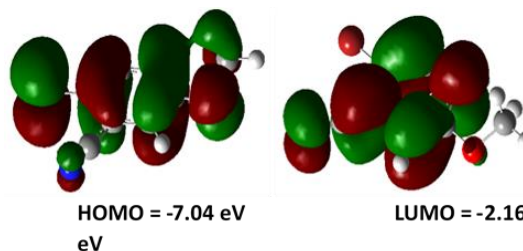


Figure.5. Molecular orbital surfaces and energies for the HOMO and LUMO of the title compound

Table.5. Thermodynamical parameters of 2B5MBN

Thermal Parameters		6-311g++(2d,p)
SCF(a.u)		-3012.629799
Zero point	vaibrational	75.80099
Energy(Kcal/Mol)		
Rotational Constant(GHz)		1.58973
		0.44184
		0.34651
Rotational Tempeartues(kelvin)		0.07629
		0.02121
		0.01663
Thermal(KCal/Mol)		
Total		82.2
Transitional		0.889
Rotational		0.889
Vibrational		80.423
Specific heat capacity at constant volume (cal/mol K)		
Total		36.791
Transitional		2.981
Rotational		2.981
Vibrational		30.829
Dipole moment (Debye)		6.8108
Lumo(eV)		
Homo(eV)		
Energy gap(eV)		
Entropy(S)(cal/mol K)		
Total		101.487
Transitional		41.943
Rotational		31.558
Vibrational		27.986
Gibbs Free Energy		0.083719
Enthalphy		0.131939

An electronic system with a larger HOMO–LUMO gap should be less reactive than one having a smaller gap (Kurtarany, 2007). The energy gap value of the molecule is 4.88eV obtained from the HOMO-LUMO analysis. The high energy band, with a peak at 284.45 nm in the UV-Vis spectra can be qualified to high delocalization of π -electrons in the title molecule, which is shown in Figure.4. & Figure.5. The highest occupied molecular orbitals are localized mainly on ring and nitrile group. The lowest unoccupied molecular orbitals are also localized on carbon atoms and nitrile group. This electronic absorption or transmittance are corresponds to the transition from the molecular orbital first excited state to ground state (HOMO-1 to LUMO+1), with transfer of an electron density to all compounds (Bromine, nitrile and methoxy groups) from benzene ring, and this is a π to π^* transition (Vikas Shukla, 2016). The computed excitation energies, Oscillator strength and electronic transition configuration are shown in Table.3.

Thermodynamic Parameters: Several calculated thermodynamic parameters are given in Table.5. Scale factors have been recommended for an accurate prediction of the zero-point vibration energies (ZPVE), and the entropy (S), vibration (T), Gibbs free energy, heat energy and minimum energy have been calculated. The margin values of 2B5MBN give the changes in the total entropy at room temperature. The energies of whole molecules, the change in the Self consistent field energy of 2B5MBN are tabulated.

4. CONCLUSION

The research the experimental FT-IR, FTR spectroscopic studies are investigated first time. The theoretical spectra are predicted using computational methods and well agreement with experimental results. The structure of the compound confirmed using geometrical parameters. This study is helpful for the further studies of thermodynamical studies. The vibrational assignments of the 2B5MBN are assigned with TED value. The title molecule qualified to high delocalization of π -electrons, high energy band gap 4.88eV and with a peak at 284.45 nm in the UV-Vis spectra. The μ and β values of the compound were 1.76 and 4.14 times greater than that of urea, respectively. Thermodynamic parameters also tabulated and thermal applications that is confirmed by the recent research.

REFERENCES

- Alcolea Palafox M, Bena Jothy V, Surabhi Singhal, Hubert Joe I, Satendra Kumar, Rastogi VK, FT-IR, FT-Raman spectra and other molecular properties of 3, 5-dichlorobenzonitrile: A DFT study, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 116, 2013, 509-517.
- Anbarasan P M, Subramanian M K, Manimegala S, Suguna K, Ilangovan V, Sundaraganesan N, 4-Chlorotoluene: Spectral studies and quantum chemical calculations, *Journal of Chemical and Pharmaceutical Research*, 3 (3), 2011, 123-136.
- Arivazhagan M, Meenakshi R, Prabhakaran S, Vibrational spectroscopic investigations, first hyperpolarizability, HOMO–LUMO and NMR analyzes of p-fluorobenzonitrile *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 102, 2013, 59–65.
- Arjunan V, Thillai Govindaraja S, Subramanian S, Mohan S, Conformational analysis, spectroscopic and quantum chemical investigations of 2-bromo-3-nitroacetophenone, *Journal of Molecular Structure*, 1037, 2013, 73–84.
- Chiu NS, Ewbank JD, Askari M, Schafer L, 2423 C 7 H 5 ClO 3-Chlorobenzaldehyde C s (anti), *Journal of Molecular Structure*, 1979, 54, 1979, 185–190.
- Colthup NB, Daly IH, Wiverly SE, *Introductions Infrared and Raman Spectroscopy*, third ed., Academic Press, Newyork, 1990.
- Danuta Michalska, Gobinath E, John Xavier R, Quantum chemical calculations, vibrational studies, HOMO–LUMO and NBO/NLMO analysis of 2-bromo-5-nitrothiazole, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 104, 2013, 394–402.
- Femina Jasmine G, Amalanathan M, Dawn Dharma Roy S, Molecular structure and charge transfer contributions to nonlinear optical property of 2-Methyl-4-nitroaniline: A DFT study, *Journal of Molecular Structure*, 1112, 2016, 63-70.
- Frisch M J, Trucks G W, Schlegel H. B, Scuseria G. E, Gaussian 09, Expanding the limits of Computational Chemistry, Revision A 02 (Inc, Wallingford CT), 2009.
- Gladis Anitha E, Joseph Vedhagiri S, Parimala K, Conformational stability, vibrational spectra, NLO properties, NBO and thermodynamic analysis of 2-amino-5-bromo-6-methyl-4-pyrimidinol for dye sensitized solar cells by DFT methods, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 140, 2015, 544–562.

Govidasamy P, Gunasekaran S, Srinivasan S, Molecular structure, vibrational, photophysical and nonlinear optical properties of L-threoninium picrate, A first-principles study Spectrochim, Acta Part A Mol. Biomol. Spectrosc, 130, 2014, 329-336.

Hochberg M, Baehr-Jones T, Wang G, Shearn M, Harvard K, Luo J, Chen B, Shi Z, Lawson R, Sullivan P, Jen A K, Terahertz all-optical modulation in a silicon-polymer hybrid system, Nature materials, 5 (9), 2006, 703-709.

John Xavier R, Gobinath E, Experimental and theoretical spectroscopic studies, HOMO-LUMO, NBO and NLMO analysis of 3,5-dibromo-2,6-dimethoxy pyridine, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 97, 2012, 215-222.

Kurtaran R, Odabasoglu S, Azizoglu A, Kara H, Atakol O, Experimental and computational study on [2, 6-bis (3, 5-dimethyl-N-pyrazolyl) pyridine]-(dithiocyanato) mercury (II), Polyhedron, 26 (17), 2007, 5069-5074.

Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG, The Handbook of Infrared and Raman Characteristics, Academic Press, New York, 1991.

Murugan M, Balachandran V, Karnan M, Vibrational spectra and electrostatic potential surface of 2-fluoro-6-methoxybenzotrile based on quantum chemical calculations, Journal of Chemical and Pharmaceutical Research, 4 (7), 2012, 3400-3413.

Parr RR, Yang RG, Density Functional Theory of Atoms and Molecules. Oxford University Press; New York, USA, and references therein, 1989.

Petra Lovecka, MarketaThimova, Petra Grznarova, Jan Lipov, ZdenekKnejzlik, Hana Stiborova, TjokordaGdeTirtaNindhia, Katerina Demnerova, Tomas Ruml, Corporation Bio medical research, 2015.

Rauhut G, Pulay P, Transferable Scaling Factors for Density Functional Derived Vibrational Force Fields, The Journal of Physical Chemistry, 1995, 99, 3093-3100.

Saleem H, Subashchandrabose S, Ramesh Babu N, Syed Ali Padusha M, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. (15)00168-7, 2015, 1386-1425.

Saravanan R R, Seshadri S, Gunasekaran S, Mendoza-Merono R, Garcia-Granda S, Conformational analysis, X-ray crystallographic, FT-IR, FT-Raman, DFT, MEP and molecular docking studies on 1-(1-(3-methoxyphenyl)ethylidene) thiosemicarbazide, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, 139, 321-328.

Sas EB, Kurt M, Karabacak M, Poiyamozi A, Sundaraganesan N, FT-IR, FT-Raman, dispersive Raman, NMR spectroscopic studies and NBO analysis of 2-bromo-1H-benzimidazol by density functional method, Journal of Molecular Structure, 1081, 2015, 506-518.

Senthil kumar J, Jeyavijayan S, Arivazhagan M, Vibrational spectral investigation, NBO, first hyperpolarizability and UV-Vis spectral analysis of 3,5-dichlorobenzotrile and m-bromobenzotrile by ab initio and density functional theory methods, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2015, 136, 234-246.

Socrates G, Infrared Characteristic Group Frequencies, John Wiley, New York, 1981.

Sundaraganesan N, Elango G, Sebastian S, Subramani P, Molecular structure, vibrational spectroscopic studies and analysis of 2-fluoro-5-methylbenzotrile, Indian Journal of Pure and Applied Physics, 47, 2009, 481-490.

Sundaraganesan N, Ilakiamani S, Saleem H, Wojciechowski P M, Michalska D, FT-Raman and FT-IR spectra, vibrational assignments and density functional studies of 5-bromo-2-nitropyridine, Spectrochimica Acta, 61A, 2005, 2995-3001.

Sundaraganesan N, Saleem H, Mohan S, Ramalingam M, Sethuraman V, FTIR, FT-Raman spectra and ab initio DFT vibrational analysis of 2-bromo-4-methyl-phenylamine, Spectrochimica Acta Part A, 62, 2005, 740-751.

Vaschetto ME, Retamal BA, Monkman AP, Density functional studies of aniline and substituted anilines, Journal of Molecular Structure: THEOCHEM, 468 (3), 1999, 209-221.

Vikas Shukla K, Alok Sachan K, Shilendra Pathak K, Ruchi Srivastava, Onkar Prasad, LeenaSinha, Prediction of molecular properties and spectroscopic profile of Riluzole with different functionals (B3LYP, M06-2X, MPWLYP): A combined theoretical and experimental study, Journal of Molecular Structure, 1106, 2016, 265-276.