

Experimental and theoretical spectroscopic investigations of 4-Bromo-3-methylbenzonitrile

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ABSTRACT

The experimental and theoretical studies of 4-Bromo-3-methylbenzonitrile (4B3MBN) were inspected for electronic structure, vibrational and other properties by Density Functional Theory (DFT). The FTIR (4000–400 cm^{-1}) and FT-Raman (FTR) (3500–50 cm^{-1}) spectra of 4B3MBN were recorded in the liquid phase (acetone). The molecular geometry and vibrational frequencies of 4B3MBN in the ground state have been calculated by using the theoretical methods (B3LYP) invoking a basis set. In addition, Molecular electrostatic potential (MEP) and atomic charges of carbon, nitrogen and oxygen were calculated. Moreover, thermodynamic properties of the title compound were predicted by computational methods.

KEY WORDS: 4B3MBN, MEP, B3LYP.

1. INTRODUCTION

The many organic molecules investigated for future applications through the experimental as well as the theoretical methods in the various twigs of the science and engineering (Arockiasamy Ajaypraveenkumar, 2017). The theoretical methods have the fast and furious results for the larger molecules to evaluate the applications in addition to their physicochemical properties. The computational techniques powerful tool for the pin pointed answers for the molecules, So as to corroborate and yet expand the experimental results. It is a vast and versatile component in the chemicals, which is called cyanobenzene or phenyl cyanide. The special benzonitrile derivatives like organic acids (benzoic acid, mandelic acid), amines (benzyl amine, pyridine), neutrals (benzonitrile, toluene) and benzonitrile herbicides. Benzonitrile is an applicable as solvent and precursor to number of derivatives. One of the benzonitrile derivatives is used in Pharmaceutical and Agrochemical Intermediates, Epoxy curing agent. Moreover Benzonitrile is mainly used for the agriculture fields, which households to control the growth of weeds and their residues persist in the environment (Arockiasamy Ajaypraveenkumar, 2017).

Benzonitrile compound is the best solvent in the chemical and physical laboratories. Because of benzene has an aprotic polar molecule with a dipole moment of 4.18Debye. The properties enhanced while added the substituted roles to the benzene. The substitution benzonitrile compounds had weak effect and strong inhibitory effect as a consequence of its position. The catalytic rate of the nitrilase enzyme is the vast cause for the weak effect in the meta or para position of benzonitrile. In the ortho position of the benzonitrile has strong effect due to steric hindrance (Murugan, 2012). Benzonitrile is used as antiseptic, anti-urinary, pharmaceutical, agrochemical intermediates, epoxy curing agent and dye sensitizers etc.

The title compound 4B3MBN is almost planar and the derivatives are used like midways in the production of phthalocyanine dyes. The surrogated phthalocyanine dyes are used for DSSC, photo redox responses and photodynamic cancer therapy (Arockiasamy Ajaypraveenkumar, 2017). To the best of our knowledge, the vibrational assignments and other properties never determined for this compound still now. So this article going to serve about complete vibrational assignments of different modes of molecules. And electronic and thermo studies are simultaneously take over to the molecule.

2. METHODOLOGY

General: The molecule 4-Bromo-3-methylbenzonitrile (4B3MBN) of spectral grade was purchased from sigma Aldrich Chemical Co. U.S.A, in powder form and was used as such without further purification.

Spectral measurements: The spectroscopic analytical purpose, The Fourier-transform infrared (FTIR) and The Fourier-transform Raman (FT Raman) spectra have been recorded at normal temperature in the region 400-4000 cm^{-1} and 50-3500 cm^{-1} respectively. Infrared spectrum recorded using 8400S Bruker, Alpha T, and Germany infrared spectrophotometer with scanning speed of 30 $\text{cm}^{-1} \text{min}^{-1}$ the spectra are traced. FT Raman spectrum has been recorded using 1064nm line of Nd: YAG laser as excitation wavelength on an EZRaman, Enwaveoptronics, and USA IFS 66 V spectrometer. All spectra recorded out at our campus of the Nanotechnology Department. The spectra are exposed in figures.3 & 4.

Computational Details: The Gaussian 09W software package has been used for predicting the whole vibrational assignments and optimized geometrical parameters of 4B3MBN with the original version (Alen, 2015). The complete geometry parameter has been derived from B3LYP is the three parameter functional by way of applying ab-initio Becke-Lee-Yang-Parr hybrid method (Govidasamy, 2014) on Intel Core i3 3.3GHz processor personal computer (Frisch, 2009). The total energy distribution (TED) was calculated and explained using the Scaled quantum

mechanical program using VEDA.4.0. Software (Diwaker, 2015) and vibrational modes also calculated through their TED. 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 MEP map had been drawn and Mulliken atomic charge distribution (MA) & Thermo dynamical parameters are resolute by Gaussian 09W software package.

3. RESULTS AND DISCUSSIONS

Optimized geometry: The B3LYP/6311++G (d, p) energy values are most probable global minimum energy and good agreement with experiment data (Muhammad Shahid, 2009). Table.1, shows the equilibrium geometry parameters of the 4B3MBN molecule for two dissimilar basis sets. Figure.1, shows the computerized structure of the 4B3MBN molecule with same basis set. The length should be increased between every atom in the calculated values while compared with experimental values because of substituent of the title molecule. The length and angle of the Br substituent are longer value 1.91Å in all other compound bonding. Carbon interactions are short value in the whole molecule. These effects are qualified for the intra charge transformations (ICT) for stability of the molecule.

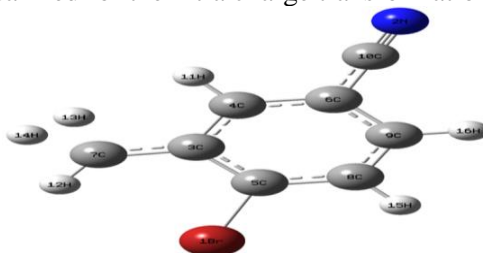


Figure.1. Optimized structure of 4B3MBN

Table.1. Optimized parameters compared with Experimental data

Bond Length	B3LYP	Exp.	Bond Angle	B3LYP	Exp.	Dihedral Angle	B3LYP
Br1-C5	1.91	1.882 (a)	C4-C3-C5	120	121.0 (3)	C5-C3-C4-C6	0
N2-C10	1.1466	1.133 (b)	C4-C3-C7	120	120.8 (3)	C5-C3-C4-H11	180
C3-C4	1.54	1.503 (b)	C4-C3-H13	76.55		C7-C3-C4-C6	180
C3-C5	1.3552	1.371 (b)	C5-C3-C7	120		C7-C3-C4-H11	0
C3-C7	1.54	1.503 (b)	C5-C3-H13	163.45		H13-C3-C4-C6	180
C3-H13	1.2703		C3-C4-C6	120	120.8 (3)	H13-C3-C4-H11	0
C4-C6	1.3552	1.371 (b)	C3-C4-H11	120	119.9	C4-C3-C5-Br1	180
C4-H11	1.07	0.96	C6-C4-H11	120	119.9	C4-C3-C5-C8	0
C5-C8	1.54	1.503 (b)	Br1-C5-C3	120	119.6 (c)	C7-C3-C5-Br1	0
C6-C9	1.54	1.503 (b)	Br1-C5-C8	120	119.6 (c)	C7-C3-C5-C8	180
C6-C10	1.54	1.503 (b)	C3-C5-C8	120	118.6 (3)	H13-C3-C5-Br1	0
C7-H12	1.07	0.96	C4-C6-C9	120	121.8 (3)	H13-C3-C5-C8	180
C7-H13	1.07	0.96	C4-C6-C10	120	119.6 (3)	C4-C3-C7-H12	180
C7-H14	1.07	0.96	C9-C6-C10	120	120.3 (3)	C4-C3-C7-H14	0
C8-C9	1.3552	1.371 (b)	C3-C7-H12	90	109.5	C5-C3-C7-H12	0
C8-H15	1.07	0.93	C3-C7-H14	144.74		C5-C3-C7-H14	180
C9-H16	1.07	0.93	H12-C7-H13	144.74		C3-C4-C6-C9	0
			H12-C7-H14	125.26		C3-C4-C6-C10	180
			H13-C7-H14	90	109.5	H11-C4-C6-C9	180
			C5-C8-C9	120	119.9	H11-C4-C6-C10	0
			C5-C8-H15	120	119.9	Br1-C5-C8-C9	180
			C9-C8-H15	120	119.9	Br1-C5-C8-H15	0
			C6-C9-C8	120		C3-C5-C8-C9	0
			C6-C9-H16	120	119.9	C3-C5-C8-H15	180
			C8-C9-H16	120	119.9	C4-C6-C9-C8	0
						C4-C6-C9-H16	180
						C10-C6-C9-C8	180
						C10-C6-C9-H16	0
						C5-C8-C9-C6	0
						C5-C8-C9-H16	180
						H15-C8-C9-C6	180
						H15-C8-C9-H16	0

a - Farrugia (1997), b - Farrugia (1999), c - Johnson (1941)

Charge analysis: The charges are computed by MA with same basic sets tabulated in table.3. MA graph of 4B3MBN molecule has been drawn in the figure.2. MA charges are the main impact for the functions like as quantum

mechanical calculations, electronic effects, polarizability changes, Dipole moments and other properties of the molecules. The polarization changes decided the charges by the different basis sets. In this research molecule, Carbon atom has both sign values in two methods. The positive charge distribution of Hydrogen atoms are acts as an acceptors, and the opposite trends of the atoms Nitrogen, Bromine are acts as a donor. Conclude from the overall comparison, (2d, p) basis sets atoms charge distribution values are higher than (d, p).

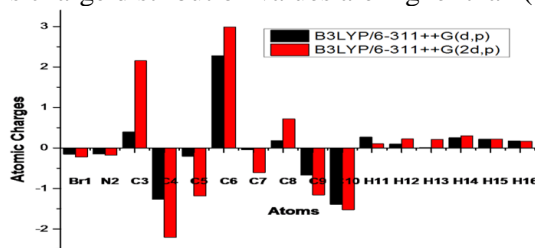


Figure.2. Mulliken charges comparison of two basis sets for 4B3MBN

Table.2. Vibrational assignments with TED% of 4B3MBN molecule

Normal Modes		Experimental (cm ⁻¹)		Scaled Wavenumbers (cm ⁻¹)			Vibrational assignments
Mode	Label	FT-IR	FT-Raman	B3LYP	IR Intensity (Km/mol)	Raman Intensity	
1	A''			-2252	0.246	303.223	δ CHCH(99)
2	A''			-613	257.277	473.250	δ CHCH(84)+ τ HCCC(13)
3	A''			73	4.238	9407.325	τ CCCC(41)+ τ CCC β r(35)
4	A'		134	135	6.947	9062.251	β CCC(46)+ β CCN(38)+ β CC β r(11)
5	A'			144	4.597	818.871	τ CCCC(60)+ τ HCCC(17)
6	A''			208	10.281	414.616	τ CCC β r(28)+ τ HCCC(26)+ τ CCCC(19)
7	A'			219	7.462	3594.329	β CC β r(62)+ β CCC(23)
8	A'		254	266	0.919	3760.133	ν β rC(46)+ β CCC(28)
9	A''			277	3.120	93.043	τ HCCC(40)+ τ CCC β r(22)+ τ CCCC(13)
10	A'		380	361	16.581	1306.858	β CCC(44)+ β CCN(12)+ β HCC(12)+ β CC β r(10)
11	A''			402	10.840	59.070	τ CCCC(72)+ τ CCCN(10)
12	A''		496	472	9.471	506.472	τ CCCC(54)+ τ CCCN(31)+ τ CCC β r(11)
13	A'		522	525	2.798	240.879	β CCC(35)+ ν CC(22)+ ν β rC(18)
14	A'		548	553	3.841	1931.634	β CCC(43)+ β CCN(12)
15	A''	578	572	580	1.482	19.100	τ CCCC(77)+ τ CCCN(15)
16	A'			587	8.496	302.955	β CCC(31)+ β CCN(28)
17	A''	627		648	4.103	239.624	τ CCCC(67)+ τ CCCN(14)
18	A'	697		686	17.909	694.714	β HCC(42)+ β CCC(38)
19	A'		712	735	13.119	1733.726	β CCC(31)+ ν CC(13)
20	A''			794	10.720	16.150	τ HCCC(55)+ δ CCCH(20)+ τ HCCH(17)
21	A''	811		815	37.046	80.179	δ CCCH(70)+ τ HCCC(12)
22	A''	888		941	0.242	19.861	τ HCCH(72)+ τ HCCC(19)
23	A'			965	8.577	280.184	ν CC(57)
24	A'	1023	1040	1022	86.113	1197.028	β CCC(47)+ ν CC(26)+ ν β rC(10)
25	A'			1141	6.624	10.146	β HCC(39)+ ν CC(16)
26	A'			1170	0.274	191.564	β HCC(56)+ ν CC(16)
27	A'		1250	1209	9.482	1596.052	β HCC(32)+ ν CC(22)
28	A'	1266		1283	15.357	281.706	β HCC(51)+ ν CC(21)
29	A'			1315	39.844	201.944	ν CC(73)
30	A'	1375	1374	1343	126.961	499.217	β HCC(45)+ ν CC(24)
31	A'	1428	1416	1411	75.293	152.166	ν CC(53)+ β HCC(16)

32	A'	1459		1492	95.942	199.388	$\nu_{CC}(46)+\beta_{HCC}(36)$
33	A'	1541		1569	41.204	789.702	$\nu_{CC}(53)+\beta_{HCC}(16)$
34	A'	1648	1612	1612	131.186	1422.424	$\nu_{CC}(52)+\beta_{HCC}(12)$
35	A'	1698		1701	32.549	172.222	$\nu_{CH}(55)+\beta_{HCH}(32)$
36	A'	2217	2338	2331	62.212	3298.040	$\nu_{NC}(89)+\nu_{CC}(11)$
37	A'	2319		2431	108.420	137.357	$\nu_{CH}(95)$
38	A'			3135	21.637	533.274	$\nu_{CH}(68)+\beta_{HCH}(19)$
39	A'			3145	72.690	215.473	$\nu_{CH}(24)+\beta_{HCH}(24)$
40	A'			3195	0.526	98.421	$\nu_{CH}(99)$
41	A'			3215	0.121	244.687	$\nu_{CH}(99)$
42	A'			3301	29.107	23.606	$\nu_{CH}(80)+\beta_{HCH}(11)$

ν -stretching; β -in plane bending; δ -Out-Of-plane bending; τ -torsion; TED-Total Energy Distribution

Vibrational assignments: There are 41 vibrational assignments are assigns for the 4B3MBN molecule. In the 42 assignments C1 point group symmetry includes the 30 in-plane (β) and 12 out-of-plane (γ) bending vibrations. The experimental and calculated graphical representations of both spectra (FTIR & FTR) are illustrated in the Figure.3 and Figure.4. The molecule vibrational modes have been separated by 16 stretching (ν), 13 bending, 13 torsion (τ) and 18 CH modes are tabulates in Table.2.

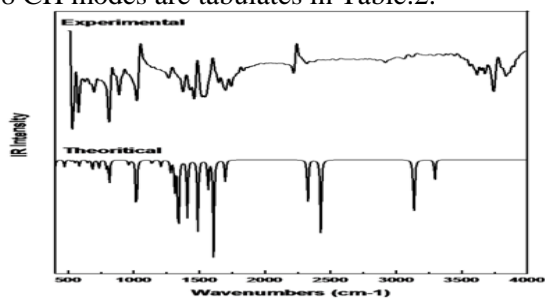


Figure.3. FTIR spectra of 4B3MBN

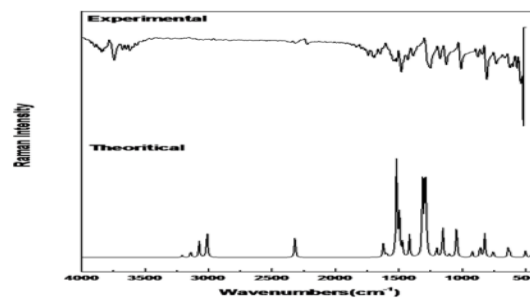


Figure. 4. FTIR spectra of 4B3MBN

Table.3. Mulliken charges comparison of two basis sets

Atoms	B3LYP/6-311++G (d, p)	B3LYP/6-311++G (2d, p)
Br1	-0.15408	-0.222339
N2	-0.150128	-0.179589
C3	0.396872	2.155135
C4	-1.267684	-2.206806
C5	-0.205711	-1.186348
C6	2.279358	2.985091
C7	-0.042021	-0.606776
C8	0.181521	0.720511
C9	-0.669698	-1.159324
C10	-1.391472	-1.527169
H11	0.269781	0.102939
H12	0.098612	0.224981
H13	0.008825	0.212824
H14	0.25304	0.299695
H15	0.218397	0.21994
H16	0.17439	0.167236

CH vibrations: Four kinds of CH moieties are calculated in the title compound 4B3MBN. In this CH moieties have been listed, six ν_{CH} and β_{CH} as well as three torsion and δ bending vibrations. The scenery of the substituent does not align because of these stretching vibrations. The stretching has most feasible frequency between the region at $3100-3000\text{cm}^{-1}$ (Parr, 1983; Premkumar, 2014). The calculated stretching vibrations of the title compound region, in between $3301-2431\text{cm}^{-1}$. The experimental frequencies have been observed at the regions $1698, 2319\text{cm}^{-1}$. The CH stretching and β bending vibrations are incorporate with each other. The calculated CH β bending vibrations of 4B3MBN occurs in the region of $1233-1017\text{cm}^{-1}$ and observed FTIR and FTR spectra at 1023cm^{-1} and 1040cm^{-1} , respectively. The CH δ bending transpires at the region $950-800\text{cm}^{-1}$ generally. The analyzed δ bending vibrations of 4B3MBN are found at $815, 941, 965\text{cm}^{-1}$ and observed in FTIR arises in the region $811, 888\text{cm}^{-1}$. In this case,

the δ bending has been merged with the torsion vibrations. Calculate and observed values good agreement with each other.

CBr vibrations: CBr moieties tabulated on the root of calculated energy distribution and separated three kinds of styles. Two stretching and three in-plane bending vibrations are packed in the CBr atom. In the literature survey, the authors assigned vibrations frequency range of $1129\text{--}480\text{ cm}^{-1}$ while the Carbon interactions with others heavy atoms like Cl, Br, I (Mooney, 1964). The 4B3MBN compound has the strong stretching vibrations in the region of $254, 522$ and 1040 cm^{-1} found from Raman spectrum. Bending vibrations in the FTIR spectra occurs in the range of $134, 380\text{ cm}^{-1}$ and the calculated frequency of the title molecule transpire in the range at $135, 219, 361\text{ cm}^{-1}$. These vibrations are very well agreed with literature survey (Sundaraganesan, 2005).

CN vibrations: In the CN moieties, stretching frequency is the intensively localized one due to the TED for this frequency contains good contribution from that constant value of stretching force. The benzonitrile compound wavenumbers of stretching vibrations fall in the range $2220\text{--}2240\text{ cm}^{-1}$ (Dollish, 1974). IR intensity modulated depends upon add the substituent to the benzonitrile. In this research compound has been identified at 2338 and 2217 cm^{-1} in Raman and FTIR spectra respectively. The calculated wavenumbers of stretching vibrations at 2331 cm^{-1} coincide with the Raman value. This is the ideal frequency of the whole molecule which confirmed the CN stretching with 89% assignment. The bending vibrations (β) of the title molecule spotted at $134, 380, 548\text{ cm}^{-1}$ in Raman spectra. These experiment values are well agreement with the calculated frequencies.

CC vibrations: There are six equivalents and two out of CC bonding in the 4B3MBN compound and totally eight CC stretching vibrations exist. Generally, the benzene ring ν_{CC} vibrational modes fall in the constituency $1650\text{--}1200\text{ cm}^{-1}$ (Varsanyi, 1974). The title compound ν_{CC} vibrations are found in the regions at $1203, 1375, 1428, 1459, 1541, 1648, 2217\text{ cm}^{-1}$ and $712, 1040, 1250, 1374, 1416, 1612\text{ cm}^{-1}$ ($735, 965, 1022, 1141, 1170, 1209, 1283, 1315, 1343, 1411, 1492, 1569, 1612, 2331\text{ cm}^{-1}$ by theoretically) through IR & Raman spectra, correspondingly. In addition, some other modes are couples with CC bending vibrations (β) are found in the regions at 1023 cm^{-1} and 2217 cm^{-1} ($1022, 2231\text{ cm}^{-1}$ by theoretically) through spectra respectively.

CCCC torsional vibrations: The ring torsions have been assigned in the region at below 800 cm^{-1} which is discussed in present paper referred by earlier reports (Rastogi, 2010). The IR and Raman spectra peak observe in the regions at $578, 627\text{ cm}^{-1}$ and $496, 572\text{ cm}^{-1}$, respectively. These peaks have been calculated at the region at $73, 144, 208, 277, 402, 472, 580, 648\text{ cm}^{-1}$ by B3LYP methods which are well merge with observed values. And these wavenumbers are mixed with CCCN torsions in the investigated molecules.

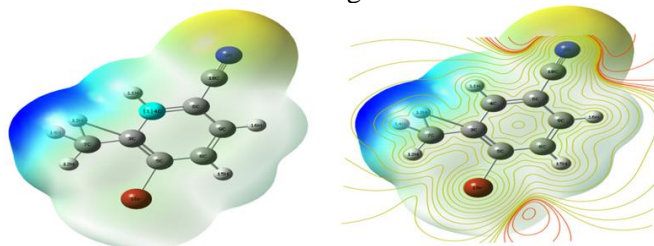


Figure.5. Electrostatic potential map & Counter map for 4B3MBN

Molecular electrostatic potential: The visual representations are the mostly welcomed one compared with other studies. Molecular electrostatic potential (MEP) is the versatile used visual illustration for find out the reactivity of the molecule which explains through its colors (Prasad, 2015), hydrogen bonding interactions and biological detection methods (Apoorva Dwivedi, 2014). The electrophilic and nucleophilic attacks are demonstrated by two different colors. The MEP's of 4B3MBN calculated and drawn by the computational method in Figure. 5. The colors are increased the order of red, yellow, green, blue. The red color starts from negative region for electrophilic reactivity and blue ends with positive region for nucleophilic reactivity regions. The values of the regions increased from red to blue (-9.944 to 9.944) for the title molecule. The carbon, nitrogen and Bromine groups are almost negative electrostatic potential for electrophilic attack. The hydrogen atoms are the positive one for nucleophilic attack. The Mulliken population analysis is showing the electronic charges distribution of the molecules which identified the support of MEP maps.

Table.4. Thermodynamical parameters of 4B3MBN

Thermodynamic parameters	B3LYP	Thermodynamic parameters	B3LYP
Self-consistent field energy (a.u)	-2937.178	Specific heat capacity at constant volume (cal/mol K)	
Zero point vibrational energy (kcal/mol)	67.773	Total	34.125
Rotational constant (GHz)	2.746	Translational	2.981
	0.462	Rotational	2.981
	0.395	Vibrational	28.163

Rotational temperature (K)	0.132	Dipole moment (Debye)	2.144
	0.022	Entropy(S)(cal/mol K)	
	0.019	Total	96.275
Thermal energy (kcal/mol)		Translational	41.708
Total	73.615	Rotational	30.840
Translational	0.889	Vibrational	23.726
Rotational	0.889	Gibbs Free Energy	0.073
Vibrational	71.838	Enthalpy	0.118

Thermodynamical parameter: Several calculated thermodynamic parameters of 4B3MBN are given in Table.4. Scale factors have been recommended for an accurate prediction of the zero-point vibration energies (ZPVE), and the entropy (S), vibration (T), Enthalpy, Gibbs free energy, heat energy and minimum energy have been calculated. The margin values of the molecule at room temperature at different methods give the changes in the total entropy. The energies of whole molecules, the change in the total entropy and Self consistent field energy of 4B3MBN at room temperature at different basic sets are also tabulated. These parameters are helpful for the future applications for the researchers and the scientists.

4. CONCLUSION

The 4B3MBN molecule has been observed FTIR and FTR spectra for experimental studies. The theoretical calculations are performed for the B3LYP/6-311++G (d, p) and (2d, p) method. These basis sets were the best and minimum energy values compared with others. The vibrational assignments with TED % has been predicted and analyzes the vibrational studies. Both experimental and theoretical studies were compared and tabulated. MEP map drawn and explained the different charges and interactions of the molecules. The optimized parameters are the great impact for the above all. At last the thermodynamical parameters were calculated using theoretically.

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