

## Experimental and theoretical spectroscopic investigations of 2-Bromo-4-methylbenzonitrile

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### ABSTRACT

The experimental and theoretical studies of 2-Bromo-4-methylbenzonitrile (2B4MBN) were inspected for electronic structure, vibrational and other properties by Density Functional Theory (DFT). The FTIR (4000–400 cm<sup>-1</sup>) and FT-Raman (FTR) (3500–50 cm<sup>-1</sup>) spectra of 2B4MBN were recorded in the liquid phase (acetone). The molecular geometry and vibrational frequencies of 2B4MBN 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:** 2B4MBN, hyper conjugative, TD-DFT.

### 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 (Lago, 2007). 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.

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 (Rastogi, 2010). Benzonitrile is used as antiseptic, anti-urinary, pharmaceutical, agrochemical intermediates, epoxy curing agent and dye sensitizers etc. Dye-sensitized solar cell (DSSC) system is very low cost solar electricity. In DSSC, dye sensitizers are most important part act as a bridge between the layers and surface of the semiconductors which is used for electrode transformations and photoelectric conversion (Prakasam, 2013).

The title compound 2B4MBN, C<sub>8</sub>H<sub>6</sub>BrN, is almost planar and the derivatives are used as intermediates in the synthesis of phthalocyanine dyes (Arjunan, 2016). The substituted phthalocyanine dyes are used for DSSC, photo redox reactions and photodynamic cancer therapy (Li, 2008; Simon, 1989). To the best of our knowledge, 2-Bromo-4-methylbenzonitrile compound crystalline structure determined and reported by Muhammad Shahid (Muhammad Shahid, 2011). The vibrational assignments and other properties never determined and no literature data for this compound still now. So this article going to serve about complete vibrational assignments of different modes of molecules. The stability of the molecule determined using NBO analysis. And electronic and thermo studies are simultaneously take over to the molecule.

### 2. METHODOLOGY

**General:** The molecule 2-Bromo-4-methylbenzonitrile (2B4MBN) of spectral grade was purchased from sigma Aldrich Chemical Co. U.S.A in powder form and was used as such without further purification.

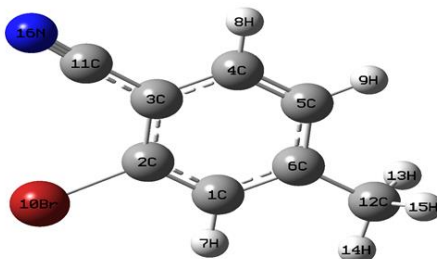
**Spectral measurements:** The spectroscopic analytical purpose, The Fourier-transform infrared (FTIR) and the Fourier-transform Raman (FT Raman) spectra have been recorded at normal temperature in the region 400-4000cm<sup>-1</sup> and 50-3500cm<sup>-1</sup> respectively. Infrared spectrum recorded using 8400S Bruker, Alpha T, and Germany infrared spectrophotometer with scanning speed of 30 cm<sup>-1</sup> min<sup>-1</sup> 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 Figure.2 & 3.

**Computational Details:** The Gaussian 09W software package has been used for predicting the whole vibrational assignments and optimized geometrical parameters of 2B4MBN with the original version (Govidasamy, 2014; Frisch, 2009). The complete geometry parameters have been derived from B3LYP which are three parameters functional by applying *ab-initio* Becke-Lee-Yang-Parr hybrid method (Chengteh Lee, 1988; Miehlich, 1989) on Intel Core i3 1.9GHz processor personal computer. The vibrational wavenumbers corrected by introducing the scaling factor. The Scaling factor values are 0.9556 and 0.9959 at 6-311++G (d, p) and 6-311++G (2d, p), respectively

(Karabacak, 2009; Sundaraganesan, 2005). The total energy distribution (TED) was calculated and explained using the Scaled quantum mechanical program using VEDA.4.0. Software (Rauhut, 1995; Saleem, 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 energy absorption spectra, energy gap plot and MEP map had been drawn and Thermo dynamical parameters are resolute by Gaussian09 DFT.

### 3. RESULTS AND DISCUSSIONS

**Optimized geometry:** The global minimum energy with various basis sets calculated. The structure has been confirmed for the best basis set and tabulated in Table.1. The B3LYP/6311++G(2d,p)/(d,p) energy values are most probable global minimum energy and good agreement with experiment data collected from crystal structure of 2-Bromo-4-methylbenzonitrile reported by Muhammad Shahid (2009). Table.2, shows the bond length, angle and dihedral angle of the 2B4MBN molecule for two different basis sets.



**Figure.1. Optimized structure of 2B4MBN**

Figure.1, shows the optimized structure of the 2B4MBN 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.

**Table.1. Global minimum Energy of various basis sets**

S.No	Basic sets	Minimum energy (a.u)
<b>HF</b>		
1	6-31+G(d,p)	-2930.8214
2	6-311+G(d,p)	-2933.3302
3	6-311++G(d,p)	-2933.3356
4	6-311++G(2d,p)	-2933.3382
<b>B3LYP</b>		
1	6-31+G(d,p)	-2934.9584
2	6-311+G(d,p)	-2937.4441
3	6-311++G(d,p)	-2937.4442
4	6-311++G(2d,p)	-2937.4462

**Table.2. Optimized parameters compared with Experimental data**

Bond Length	2dp	dp	Exp. (Ref.)	Bond Angle	2dp	dp	Exp. (Ref.)	Dihedral angle	dp	dp
C1-C2	1.39	1.39	1.36	C2-C1-C6	119.56	119.56	121.0	C3-C11-N16-Br10-1	180	180
C1-C6	1.39	1.39	1.38	C2-C1-H7	120.21	120.21	119.5	C3-C11-N16-Br10-2	180	180
C1-H7	1.07	1.07	0.93	C6-C1-H7	120.21	120.21	119.5	C6-C1-C2-C3	0	0
C2-C3	1.39	1.39	1.38	C1-C2-C3	119.56	119.56	120.8	C6-C1-C2-Br10	180	180
C2-Br10	1.91	1.91	1.88	C1-C2-Br10	120.21	120.21	119.6	H7-C1-C2-C3	180	180
C3-C4	1.403	1.40	1.38	C3-C2-Br10	120.21	120.21	119.6	H7-C1-C2-Br10	0	0
C3-C11	1.40	1.40	1.44	C2-C3-C4	120.00	120.00	118.6	C2-C1-C6-C5	0	0
C4-C5	1.35	1.35	1.37	C2-C3-C11	119.99	119.99	121.8	C2-C1-C6-C12	180	180
C4-H8	1.07	1.07	0.93	C4-C3-C11	119.99	119.99	119.6	H7-C1-C6-C5	180	180
C5-C6	1.403	1.40	1.38	C3-C4-C5	120.43	120.43	120.3	H7-C1-C6-C12	0	0
C5-H9	1.07	1.07	0.93	C3-C4-H8	119.78	119.78	119.9	C1-C2-C3-C4	0	0
C6-C12	1.54	1.54	1.50	C5-C4-H8	119.78	119.78	119.9	C1-C2-C3-C11	180	180
C11-N16	1.14	1.14	1.13	C4-C5-C6	120.43	120.43	121.2	Br10-C2-C3-C4	180	180
C12-H13	1.07	1.07	0.96	C4-C5-H9	119.78	119.78	119.4	Br10-C2-C3-C11	0	0

C12-H14	1.07	1.07	0.96	C6-C5-H9	119.78	119.78	119.4	C2-C3-C4-C5	0	0
C12-H15	1.07	1.07	0.96	C1-C6-C5	120.00	120.00	118.2	C2-C3-C4-H8	180	180
				C1-C6-C12	119.99	119.99	121.0	C11-C3-C4-C5	180	180
				C5-C6-C12	119.99	119.99	120.8	C11-C3-C4-H8	0	0
				C6-C12-H13	109.47	109.47	109.5	C3-C4-C5-C6	0	0
				C6-C12-H14	109.47	109.47	109.5	C3-C4-C5-H9	180	180
				C6-C12-H15	109.47	109.47	109.5	H8-C4-C5-C6	180	180
				H13-C12-H14	109.47	109.47	109.5	H8-C4-C5-H9	0	0
				H13-C12-H15	109.47	109.47	109.5	C4-C5-C6-C1	0	0
				H14-C12-H15	109.47	109.47	109.5	C4-C5-C6-C12	180	180
								H9-C5-C6-C1	180	180
								H9-C5-C6-C12	0	0
								C1-C6-C12-H13	150	150
								C1-C6-C12-H14	30	30
								C1-C6-C12-H15	-90	-90
								C5-C6-C12-H13	-30	-30
								C5-C6-C12-H14	-150	-150
								C5-C6-C12-H15	90	90

B3LYP/6-311++G (2dp) - 2dp; B3LYP/6-311++G (dp) - dp; Exp - Experimental. Ref. (Farrugia, 1997; Farrugia, 1999).

**Vibrational assignments:** There are 41 vibrational assignments are assigns for the 2B4MBN molecule. In the 41 assignments C1 point group symmetry includes the 36 in-plane ( $\beta$ ) and 6 out-of-plane ( $\gamma$ ) bending vibrations. The experimental and calculated graphical representations of both spectra (FTIR & FTR) are illustrated in the Figure.2 and 3. The molecule vibrational modes have been separated by 16 stretching, 13 bending, 13 torsion and 18 CH modes are tabulates in Table.3.

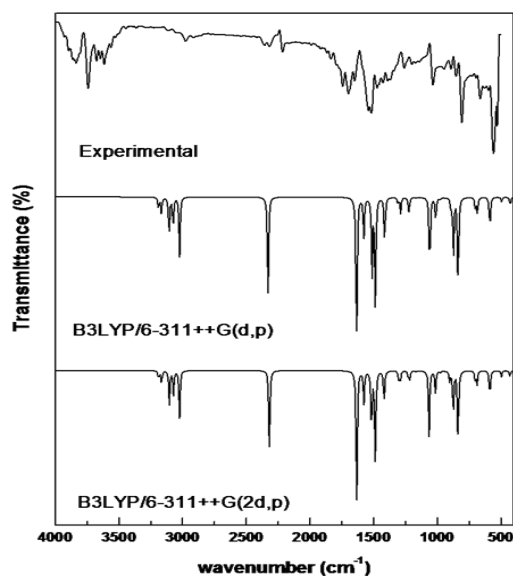


Figure.2. FTIR spectra of 2B4MBN

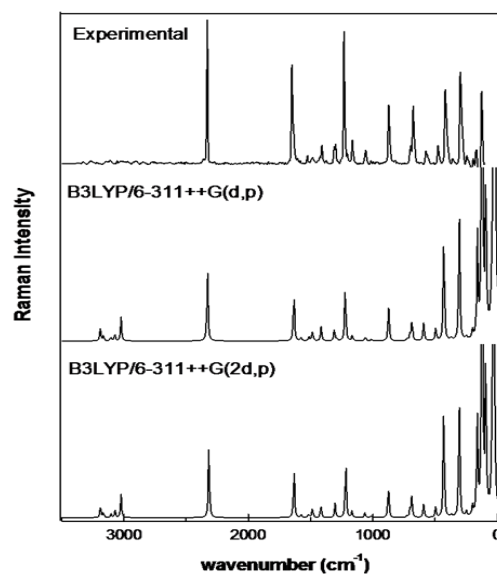


Figure.3. FTR spectra of 2B4MBN

Table.3. Vibrational assignments with TED% of 2B4MBN molecule

Mode	IR	FTR	(2d,p)		(d,p)		(2d,p)		(d,p)		Assignments with TED (%) <sup>a</sup>
			US	S	US	S	IR <sub>act</sub>	R <sub>int</sub>	IR <sub>act</sub>	R <sub>int</sub>	
v1	3563		3196	3180	3198	3056	1.62	311.91	1.95	316.58	vCH (91)
v2			3193	3177	3195	3053	1.25	41.45	1.52	48.84	vCH (91)
v3			3172	3156	3173	3032	5.02	152.75	5.27	152.69	vCH (99)
v4			3111	3095	3113	2975	12.5	114.45	13.3	117.90	vCH (81)
v5	2976		3079	3063	3081	2944	8.9	209.44	10.1	211.18	vCH (98)
v6	2916		3030	3015	3030	2896	17.3	678.80	18.6	685.46	vCH (99)
v7	2319	2333	2323	2311	2334	2231	30.5	2148.5	33.5	2190.5	vNC (89) + vCH (10)
v8	1649	1652	1637	1629	1638	1565	53.5	1457.6	54.1	1544.1	vCC (52) + βHCC (10)
v9	1541		1580	1572	1581	1511	12.2	84.66	13.7	87.80	vCC (59)
v10	1519		1520	1512	1516	1449	25.2	110.73	25.0	115.98	βHCC (62) + vCC (30)
v11			1492	1484	1491	1425	28.7	176.79	29	169.98	βHCH (68)
v12	1473		1486	1479	1486	1420	7.27	128.48	8.1	152.51	δCHCH (65) + βHCC (31)
v13	1426		1422	1415	1419	1356	9.88	224.78	6.7	379.39	δCHHH (35) + βHCC(16) + vCC(13)
v14			1418	1411	1415	1352	3.20	153.52	8.8	42.22	δCHHH (48) + βHCH (19)
v15			1307	1300	1312	1254	2.89	419.79	2.1	389.68	vCC (58)
v16	1259		1294	1288	1290	1233	4.87	25.25	5.1	43.32	βHCC (55)
v17		1232	1233	1226	1231	1176	1.97	26.77	1.3	90.32	βHCC (30) + βCCC (23) + vCC (13)
v18	1201		1220	1214	1224	1170	3.73	1669.0	4.6	1613.4	vCC (81)
v19			1170	1164	1168	1116	0.36	192.09	0.3	187.52	βHCC (48) + vCC (34)
v20	1089		1067	1062	1062	1015	20.7	137.57	21.7	129.49	βCCC (43) + vCC (13) + βHCC (10)
v21			1065	1060	1062	1014	4.36	9.60	4.6	4.76	βHCC (56) + δCHCH (26)
v22	1035		1017	1012	1015	970	8.37	50.04	8.3	48.13	βHCC (68) + vCC (17)
v23	948		980	975	981	938	0.69	3.35	0.8	4.21	δCCCH (59) + τHCCC (32)
v24	892		905	900	894	854	3.83	0.74	3.6	2.37	τHCCC (76)
v25		874	877	872	876	837	18.2	1026.5	19.5	1064.6	vCC (51) + vBrC (12)
v26	854		839	835	839	801	29.2	2.30	32.5	0.59	τHCCC (54) + δCCCH (31)
v27	808		729	725	726	693	0.00	54.76	0.0	74.77	τCCCC (85)
v28	697		703	700	703	672	3.94	295.12	3.7	241.14	vCC (57) + βCCC (21)
v29	664	676	689	685	687	656	4.91	589.84	5.8	634.84	βCCC (69)
v30	598		593	591	594	568	1.13	364.15	1.3	491.06	βCCC (40) + βCCN (36)

v31			589	586	588	562	9.76	29.91	9.7	60.03	$\tau$ CCCC (46) + $\tau$ CCCN (22)
v32			497	495	495	473	2.23	299.02	1.6	374.48	$\tau$ CCCC (41) + $\tau$ CCCN (29)
v33	560		432	429	431	412	0.78	2925.4	0.9	2898.1	$\nu$ CC (41) + $\beta$ CCC (31)
v34		420	430	428	428	409	1.58	247.37	2.0	325.80	$\tau$ CCCC (77) + $\tau$ CCCN (10)
v35	531		372	370	371	355	0.88	88.98	0.9	80.28	$\beta$ CCC (59) + $\beta$ CcBr (13)
v36		298	306	305	306	293	4.54	3594.2	4.4	3894.1	$\nu$ BrC (57) + $\beta$ CCN (15) + $\beta$ CCC (12)
v37			250	249	251	240	3.15	173.85	3.18	100.08	$\tau$ CCCC (67) + $\tau$ CCCN (23)
v38			199	198	200	191	0.13	288.59	0.09	233.14	$\beta$ CcBr (51) + $\beta$ CCC (21)
v39			162	161	160	153	0.21	3081.9	0.23	2917.4	$\tau$ CCcBr (70) + $\tau$ CCCC (12)
v40		126	123	122	123	118	3.06	12273	2.90	14153	$\beta$ CCC (43) + $\beta$ CCN(31)+ $\beta$ CcBr(20)
v41			93	93	93	89	1.62	5174.6	1.57	5527	$\tau$ CCCC (77) + $\tau$ CCCN (11)

$\nu$ -stretching;  $\beta$ -in plane bending;  $\delta$ -Out-of-plane bending;  $\tau$ -torsion;TED-Total Energy Distribution; US-Unscaled; S-Scaled; IR act- IR activity; R Int- Raman Intensity; 6-311++G(2d,p)-2dp; 6-311++G(d,p)- dp

**CH vibrations:** Four kinds of CH moieties are calculated in the title compound 2B4MBN. In this CH moieties have been listed, six CH stretching and CH in plane as well as three torsion and out of plane 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 $\text{cm}^{-1}$  (Socrates, 2001; Premkumar, 2014). The calculated stretching vibrations of the title compound region, in between 3198-3030 $\text{cm}^{-1}$ . The experimental frequencies have been observed at the regions 2916, 2976, 3563 $\text{cm}^{-1}$ . The CH stretching and in-plane bending vibrations are incorporate with each other. The calculated CH in-plane bending vibrations of 2B4MBN occurs in the region of 1233-1017 $\text{cm}^{-1}$  and observed FTIR and FTR spectra at 1035, 1089, 1201 $\text{cm}^{-1}$  and 1232 $\text{cm}^{-1}$ , respectively. The CH out-of-plane bending occurs at the region 950-800 $\text{cm}^{-1}$  generally. The calculated out-of-plane bending vibrations of 2B4MBN are found at 839, 980, 1065 $\text{cm}^{-1}$  and observed in FTIR occurs in the region 854, 948 $\text{cm}^{-1}$ . In this case, the out-of-plane bending has been merged with the torsion vibrations. Calculate and observed values good agreement with each other.

**CBr vibrations:** CBr moieties have been tabulated on the basis of calculated energy distribution and separated three kinds of modes. 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 1129–480  $\text{cm}^{-1}$  while the Carbon interactions with others heavy atoms like Cl, Br, I (Mooney, 1963; Monney, 1964). The 2B4MBN compound has the strong stretching vibrations in the region of 298 and 874  $\text{cm}^{-1}$  found from Raman spectrum. Bending vibrations in the FTIR spectra occurs in the range of 531 $\text{cm}^{-1}$  and the calculated frequency of the title molecule transpire in the range at 123, 199, 372 $\text{cm}^{-1}$ . 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 2220-2240 $\text{cm}^{-1}$  (Dollish, 1974). IR intensity modulated depends upon add the substituent to the benzonitrile. In this research compound has been identified at 2219 and 2233 $\text{cm}^{-1}$  in Raman and FTIR spectra respectively. The calculated wavenumbers of stretching vibrations at 2223 $\text{cm}^{-1}$  coincide with the FTIR value. This is the ideal frequency of the whole molecule which confirmed the CN stretching with 89% assignment. The bending vibrations ( $\beta$ ) of the title molecule for the Raman and FTIR spectra at 598 $\text{cm}^{-1}$  and 298, 126 $\text{cm}^{-1}$ , respectively. The bending vibrations ( $\gamma$ ) of FTIR spectra fall in the region at 420 $\text{cm}^{-1}$  (Bellamy, 1975). These experiment values are well agreement with the calculated frequencies.

**CC vibrations:** There are six equivalents and two out of CC bonding in the 2B4MBN compound and totally eight CC stretching vibrations exist. Generally, the benzene ring CC stretching vibrational modes fall in the region 1650–1200 $\text{cm}^{-1}$  (Lin-Vien, 1991; Varsanyi, 1974). The title compound CC stretching vibrations are found in the regions at 1201, 1519, 1541, 1649 $\text{cm}^{-1}$  and 1652 $\text{cm}^{-1}$  (1220, 1307, 1520, 1580, 1637 $\text{cm}^{-1}$  by theoretically) through IR & Raman

spectra, correspondingly. In addition, some other modes are couples with CC bending vibrations ( $\beta$ ) are found in the regions at  $560,697\text{cm}^{-1}$  and  $874\text{cm}^{-1}$  ( $432, 703, 877\text{cm}^{-1}$  by theoretically) through spectra respectively.

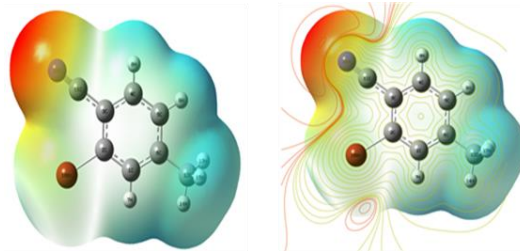
**CCCC torsional vibrations:** The ring torsions have been assigned in the region at below  $800\text{cm}^{-1}$  which is discussed in present paper referred by earlier reports (Rastogi, 2010). The IR and Raman spectra peak observe in the region at  $808$  and  $420\text{cm}^{-1}$  respectively. These peaks have been calculated at the region at  $93, 250, 430, 497, 589, 729\text{cm}^{-1}$  by B3LYP methods which are well merge with observed values. And these wavenumbers are mixed with CCCN torsions in the investigated molecules.

**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 (Nuha A Wazzan, 2016), hydrogen bonding interactions and biological detection methods (Shana Parveen, 2016). The electrophilic and nucleophilic attacks are demonstrated by two different colors. The MEP's of 2B4MBN calculated and drawn by the computational method in Figure 4. 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 ( $-0.0542$  to  $0.0542$ ) 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 and NPA analysis are showing the electronic charges distribution of the molecules which identified the support of MEP maps.

**Thermodynamical parameter:** Several calculated thermodynamic parameters of 2B4MBN 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 2B4MBN at room temperature at different basic sets are also tabulated. These parameters are helpful for the future applications for the researchers and the scientists.

**Table.4. Thermodynamical parameters of 2B4MBN**

Thermal Parameters	6-311g++(2d,p)	6-311g++(d,p)
SCF(a.u)	-2937.4462	-2937.4442
Zero point vibrational Energy(Kcal/Mol)	72.6671	72.62862
Rotational Constant(GHz)	1.37163	1.36752
	0.71946	0.71755
	0.4733	0.47199
Rotational Temperatures(kelvin)	0.06583	0.06563
	0.03453	0.03444
	0.02271	0.02265
<b>Thermal (KCal/Mol)</b>		
Total	78.586	78.564
Transitional	0.889	0.889
Rotational	0.889	0.889
Vibrational	76.809	76.787
<b>Specific heat capacity at constant volume (cal/mol K)</b>		
Total	33.548	33.598
Transitional	2.981	2.981
Rotational	2.981	2.981
Vibrational	27.586	27.637
<b>Entropy (S) (cal/mol K)</b>		
Total	99.142	99.647
Transitional	41.708	41.708
Rotational	30.91	30.918
Vibrational	26.524	27.02
Gibbs Free Energy	0.079074	0.078799
Enthalpy	0.126179	0.126144



**Figure.4. Electrostatic potential map & Counter map for 2B4MBN**

#### 4. CONCLUSION

The 2B4MBN 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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