Molecular Structure, Spectroscopic(FT-IR,FT-Raman, NMR,UV), HOMO-LUMO Analysis of 1-Bromo-4-Nitrobenzene by Quantum Computational Methods

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Abstract - *This work presents the solid phase FTIR and FT-Raman spectra of 1-Bromo-4-Nitrobenzene (1B4NB) were recorded in the regions 4000-400 cm^{-1} and 3500-50 cm^{-1}, respectively. The fundamental vibrational frequencies and intensities of the vibrational bands were calculated using density functional theory (DFT) with B3LYP method and standard 6-311++G (d, p) basis set combinations. The infrared and Raman spectra were also predicted from the calculated intensities. The vibrational spectra were interpreted with the aid of normal coordinate analysis based on a scaled quantum mechanical force field. Comparison of simulated spectra with the experimental spectra provided important information about the ability of the computational method to describe the vibrational modes. The calculated and observed frequencies are found to be in good agreement. The theoretical UV-Vis spectrum of the compound and the electronic properties, such as HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energies were obtained by TD-DFT approach. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of 1B4NB were calculated using the Guauge Independent Atomic Orbital (GIAO) method. The Mullikan charges of the molecule were computed using DFT calculations. The chemical reactivity and Thermodynamic properties of 1B4NB at different temperatures were also calculated. Information about the size, shape, charge density distribution and site of chemical reactivity of the molecule has been obtained by mapping molecular electron density isosurface with the molecular electrostatic potential.*

Key Words: Vibrational spectra, 1B4NB, FTIR, FT Raman, TD-DFT, HOMO, LUMO.

1. INTRODUCTION

Nitrobenzene is a yellowish, oily, aromatic nitro-compound with an almond-like odour that emits toxic fumes of nitrogen oxides upon combustion. Nitrobenzene is primarily used in the manufacture of aniline, but is also used in the manufacture of lubricating oils, dyes, drugs, pesticides, and synthetic rubber.[1] Nitrobenzene is also used to mask unpleasant odors in shoe and floor polishes, leather dressings, paint solvents, and other materials. Redistilled, as oil of membrane, nitrobenzene has been used as an inexpensive perfume for soaps. The majority of nitrobenzene is used to manufacture aniline, which is a chemical used in the manufacture of polyurethane. [2] The physical and chemical properties of 1-Bromo-4-Nitrobenzene are given below. It is an organic compound with the chemical formula $C_6H_4BrNO_2$. It is also named as p-Bromonitrobenzene and the molecular weight is 202.01 g/mol. This is soluble in ethanol, ethyl ether and benzene .The density of this compound is 1.948 g/mL. It belongs to the product categories of Nitro Compounds; Nitrogen Compounds; Organic Building Blocks. This chemical should be sealed and stored in a cool and dry place. Moreover it should be protected from oxides and light. The vapour pressure of this compound is 0.03 mmHg at 25°C. The Molar refractivity is 40.488 cm^3 and the Molar Volume is 117.46 cm^3.The surface tension of this sample is 50.59 dyne/cm. The boiling point of this sample is 252.635˚C at 760 mmHg

2. EXPERIMENTAL DETAILS

The fine sample of 1-Bromo-4-Nitrobenzene was obtained from Sigma Aldrich, UK, and used as such for the spectral measurements. The room temperature FTIR spectrum of the compound was measured in the 4000–400 cm^{-1} region at a resolution of ±1 cm^{-1}, using a BRUKER IFS-66V vacuum Fourier transform spectrometer equipped with a Mercury Cadmium Telluride (MCT) detector, a KBr beam splitter and global source.

The FT-Raman spectrum of 1B4NB was recorded on a BRUKER IFS–66V model interferometer equipped with an FRA–106 FT-Raman accessory. The spectrum was recorded in the 3500–50 cm^{-1} Stokes region using the 1064 nm line of an Nd: YAG laser for the excitation operating at 200 mW powers. The reported wave numbers are expected to be accurate to within ±1 $cm^{-1.}$

3. COMPUTATIONAL DETAILS

The quantum chemical calculation of 1B4NB has been performed using the B3LYP level of theory supplemented with the standard density functional triply parameter hybrid model DFT/ B3LYP. The 6-311++G(d,p) basis set have been employed using the Gaussian 09 program [3].Density functional theory calculations are reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity. The optimized geometry corresponding to the minimum on the potential energy surface have been obtained by solving self consistent field equation iteratively. Harmonic vibrational wave numbers have been calculated using analytic second derivatives to confirm the convergence to minima on the potential energy surface and to evaluate the zero-point vibrational energy [4]. These force fields obtained in Cartesian coordinates and dipole derivatives with respect to atomic displacements were extracted from the archive section of the Gaussian 09 output and transformed to a suitably defined set of internal coordinates. The optimized geometrical parameters, IR intensity, Raman intensity, the atomic charges, reduced mass, force constant and other thermodynamic parameters were also calculated. Scaling of the force field was performed according to the SQM procedure [5,6] using selective scaling in the natural internal coordinate representation[7,8]. Transformation of the force field and subsequent normal coordinate analysis including the least square refinement of the scale factors, calculation of the potential energy distribution (PED) and the prediction of IR and Raman intensities were done on a PC with the MOLVIB program written by Sundius [9,10]. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1}. The symmetry of the molecule was also helpful in making vibrational assignments. By combining the results of the Gauss view program [11] with symmetry considerations, vibrational frequency assignments were made with a high degree of confidence. The defined local symmetry coordinates form complete set and matches quite well with the motions observed using the Gauss view program. ^{1}H and ^{13}C NMR chemical shifts were calculated with GIAO [12,13] approach by applying B3LYP method [14,15].

4. PREDICTION OF RAMAN INTENSITIES

The Raman activities (Si) calculated with the GAUSSIAN 09 program and adjusted during the scaling procedure with MOLVIB were subsequently converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering [16, 17].

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i\left[1 - \exp\left(\frac{-hc\nu_i}{kT}\right)\right]}$$

Where ν_0 is the exciting frequency (in cm^{-1} units); ν_i is the vibrational wave number of the of the ith normal mode, h, c and k are fundamental constants and f is a suitably chosen common normalization factor for all peaks intensities. Raman activities and calculated Raman intensities are reported in TABLE 2

5. RESULTS AND DISCUSSION

5.1Molecular geometry

The molecular structure of 1B4NB belongs to C_1 point group symmetry. The optimized most stable structure of title molecule is obtained from Gaussian 09 and gauss view 05 programs are shown in Fig1.

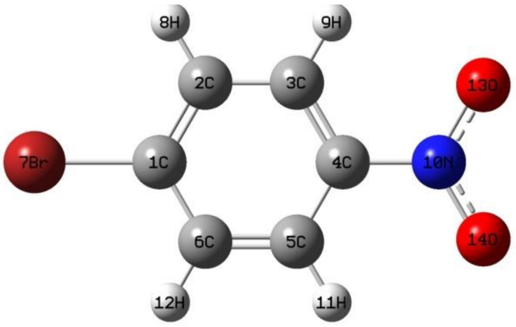

Fig.1. Optimized Structure of 1B4NB along with numbering of atoms

The calculated bond lengths, bond angles and dihedral angles are given in Table1.The calculated geometric parameters represent a good approximation and they are the bases for calculation of other parameters like vibrational frequency. Many Authors explained the changes in the frequency or bond length of C-H bond on substitution due to change in charge distribution on the carbon atom of the benzene ring [18, 19]. The comparative IR and Raman spectra of experimental and calculated frequencies are given in the Fig.2 and Fig.3

TABLE 1-Optimized geometrical parameters of 1B4NB obtained by B3LYP/6-311++G(d,p) density functional calculations

Bond length	Angstrom (Å)	Bond angle	Degree	Torsional angle	Degree
C2-H8	1.081863	C1-C6-C5	119.28	H8-C2-C1-C6	-180
C3-H9	1.081295	H8-C2-C1	120.43	H9-C3-C4-N10	0
C5-H11	1.081295	H9-C3-C2	121.24	H11-C5-C6-C1	-180
C6-H12	1.081863	H11-C5-C6	121.24	H12-C6-C1-C2	-180
O13-N10	1.224458	H12-C6-C1	120.43	O13-N10-C4-C2	-0.01
O14-N10	1.224458	O13-N10-C4	117.6	C6-C5-C4-C3	0
C3-C2	1.390182	O14-N10-O13	124.8	C1-C6-C5-C4	0
C6-C5	1.390182	C6-C5-4C	118.99	C5-C4-C3-C2	0
C1-C6	1.394383	C4-C3-C2	118.99	O14-C4-O13-N10	0
C4-C3	1.391061	C5-C4-C3	121.99	Br7-C2-C6-C1	0
C5-C4	1.391061	N10-C4-C5	119	N10-C3-C5-C4	0
N10-C4	1.478016	Br7-C1-C6	119.27		
Br7-C1	1.908822				

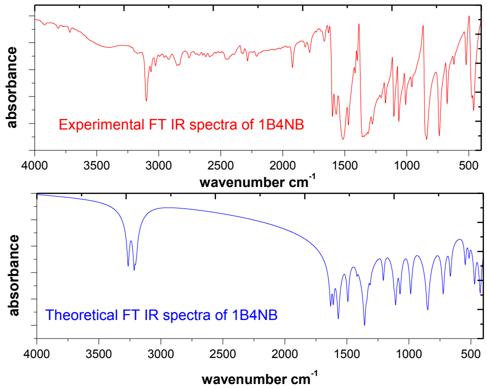

Fig.2. Comparison of Theoretical and experimental FTIR spectrum of 1B4NB.

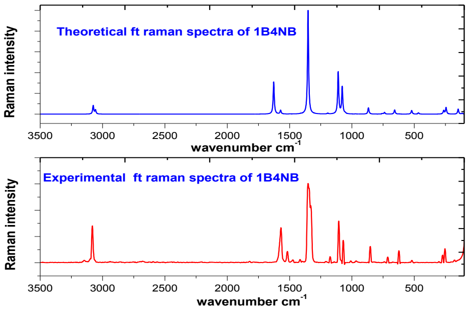

Fig.3. Comparison of Theoretical and experimental FT-Raman spectrum of 1B4NB.

5.2 Vibrational Assignments

The title molecule consists of 14 atoms, which undergoes 36 normal modes of vibrations,25 modes of vibrations are in-plane and remaining 11 are out-of-plane. The bands that are in the plane of molecule is represented as A' and out-of-plane as A''. Thus the 36 normal modes of vibrations in title molecule are distributed as Γvib = 25 A'(in-plane bending) +A''(out-of-plane bending) vibrations. The harmonic vibrational frequencies calculated for 1B4NB at DFT B3LYP levels using the triple split valence basis set along with the diffuse and polarization functions 6-311++G(d, p) observed FTIR and FT-Raman frequencies for various modes of vibrations are presented in Table2.

Comparison of frequencies calculated at DFT (B3LYP) with the experimental values reveals the over estimation of the calculated vibrational modes due to the neglect of anharmonicity in real system. Inclusion of electron correlation in the DFT to certain extends makes the frequency values bigger. Reduction in the computed harmonic vibration, although basis set sensitive are only marginal as observed in the DFT (B3LYP) using 6-311++G(d,p) anyway notwithstanding the level of calculations , it is customary to scale down the calculated harmonic frequencies in order to develop the agreement with the experiment, the scaled calculated frequencies minimize the root-mean square difference between calculated and experimental frequencies for bands with definite identifications. The descriptions concerning the assignment have also been indicated in Table 2.

TABLE 2.Observed and B3lyp /6-311++g(d,p) level calculated vibrational frequencies (in cm^{-1}) of 1-Bromo-4-Nitrobenzene

No	symmetry species	Observed frequency		Calculated frequency (cm^{-1})with B3LYP/6-311++G(d,p) force field					Characterisation of normal modes with PED%
		IR (cm^{-1})	Raman (cm^{-1})	Unscaled (cm^{-1})	Scaled (cm^{-1})	IR intensity	Raman activity Si	Raman intensity (Ii)	
1	A"	-	-	51.719	61	0	0.0017	33.5919	tNO2 (99)
2	A"	-	80.93	79.530	78	2.9449	0.042	348.154	tring(56),gCH(19),tNO2(12),
3	A'	-	-	170.28	148	2.5953	0.6828	1202.20	bCBr (48), bCN (44)
4	A'	-	253.9	248.58	245	0.6865	2.363	1907.87	υCBr (49), bring (25), υCN (15),
5	A"	-	-	258.93	263	1.972	1.183	877.638	gCN(37),tNO2(25),tring(17),gCBr(13),
6	A'	-	273.09	307.41	272	0.312	0.2763	143.346	bCBr(46), bCN (36), bCNO (10)
7	A"	-	-	419.26	389	0	0.0007	0.18882	tring (75), gCH (19)
8	A"	461.02	-	466.46	460	10.0696	0.0105	2.25597	tring(44),gCN(25),tNO2(16),gCBr(12)
9	A'	474.64	-	479.80	467	12.8384	0.3392	68.6034	υCN (43), υCBr (39)
10	A'	521.61	-	532.44	521	1.5004	2.4366	393.857	bCNO (87)
11	A"	-	623.31	636.50	627	0.7426	6.326	693.223	tring (64), gCBr (17), gCH (11)
12	A'	674.47	-	672.37	658	2.3038	0.0578	5.61396	bring (85), υCC (6)
13	A"	-	712.95	720.03	722	24.2362	1.1817	98.6268	tNO2(61), gCN(17), gCH(14)
14	A'	737.87	-	726.23	739	2.2992	3.0988	253.749	bring (57), CBr (13)
15	A"	839.95	-	837.88	841	0	0.0192	1.14093	gCH (99)
16	A"	-	852.97	852.50	855	45.6382	0.2533	14.4737	gCH (73), tring (10)
17	A'	-	-	867.82	868	71.3689	17.0123	933.599	bCNO(51), υ CN(17),υCC(10),bring(10)
18	A"	959.03	-	977.91	972	0.9035	0.4522	18.8788	gCH(86), tring(11)
19	A"	1009.22	-	994.91	993	0	0.0131	0.52554	gCH (93)
20	A'	1064.6-5	-	1026.8	1055	31.3823	2.3487	87.5583	bring (49), υCC (34), bCH (16)
21	A'	-	1069.63	1079.5	1078	42.8837	44.6876	1482.39	υCC (62), υCBr (18), bring(11)
22	A'	1103.85	-	1117.7	1110	42.7895	111.565	3409.92	bring(37),υCN(27), υCC(22), bCH(12)
23	A'	-	1105.63	1124.9	1117	7.3836	0.1621	4.88043	bCH(64), υCC (32)
24	A'	-	1175.03	1198.0	1194	6.6081	3.0957	80.2710	bCH (76), υCC(21)
25	A'	1310.97	-	1313.7	1304	2.1121	0.2531	5.25675	bCH (84), υCC (11)
26	A'	1343.72	-	1340.6	1341	14.555	0.068	1.34431	υCC (91)
27	A'	1356.83	1351.65	1368.1	1352	402.369	417.639	7856.98	NO(72), CN(13),bCNO(12)
28	A'	1416.65	-	1424.9	1410	2.3495	1.1785	20.0616	υCC (53), bCH (41)
29	A'	1514.4	1517.77	1502.1	1497	42.2303	2.1465	32.0550	bCH (62), υCC (35)
30	A'	1569.05	1569.39	1577.8	1572	213.359	16.6403	219.594	υNO (79), bCNO (13)
31	A'	1598.91	-	1614.0	1627	69.6066	172.938	2154.81	CC(68),bCH (19), bring (11)
32	A'	1631.0-1	-	1641.5	1632	71.0629	1.8056	21.5490	υCC(63),bCNO(10)
33	A'	-	3081.52	3204.7	3057	0.3446	41.3678	73.2806	υCH (99)
34	A'	3062.25	-	3205.2	3058	0.5129	52.245	92.5034	υCH (99)
35	A'	3100.13	-	3223.1	3074	2.6354	13.8671	24.1089	υCH (99)
36	A'	-	-	3224.6	3075	4.0079	179.817	312.458	υCH (99)

(υ) stretching (b)bending; (g) scissoring and wagging ; (t) torsion ;PED values are greater than 10% are given

5.2.1 C-H Stretching Vibrations

The hetero-aromatic compounds shows the presence of C-H stretching vibrations in the region 3100-3000 cm^{-1} which is the characteristic region for the ready identification of the C-H stretching vibration [20]. They are not appreciably affected by nature of substituent. In our title compound, there are three CH stretching modes of 1B4NB have been assigned at 3062 and 3100 cm^{-1} in IR spectrum and one C-H stretching mode in Raman spectrum is observed at 3081 cm^{-1}. It's theoretically computed values for C-H stretching vibrations are found to be 3205, 3223, 3224 cm^{-1} respectively. These stretching vibrations are scaled to 3057, 3058, 3074, 3075 cm^{-1} with a maximum 99% PED contribution.

The C-H in-plane-bending vibrations in aromatic heterocyclic compounds characterized by several medium to strong intensity bands in the region between 1300 and 1000 cm^{-1}.When there is in-plane interaction above 1200 cm^{-1}, a carbon and its hydrogen usually move in opposite direction [21]. Accordingly for our title compound 1B4NB, the C-H in-plane bending vibrations occur at 1310 and 1514 cm^{-1} respectively in IR spectrum.

The out-of plane bending vibration gives rise to intense bands in the region between 1000 and 650cm-^{1}.In this work, the C-H out-of-plane bending vibrations occur at 1009 and 959,839 cm^{-1} in IR spectrum and 852 cm^{-1} in Raman spectrum. Here we have theoretically calculated values such as 994, 977, 852 and 837cm^{-1} which shows that the predicted values are coinciding very well with the observed frequencies.

5.2.2 C-Br Vibrations

Strong characteristic absorption due to the C-Br stretching vibration is observed with the position of the band being influenced by neighbouring atoms(or) groups .The smaller the halide atom, the greater the influence of the neighbour. Bands of weak to medium intensity are also observed for the C-Br stretching vibrations .According to these early reports [22,23] the C-Br stretching vibration gives generally strong band. In the present study, a strong band is observed at 253 cm^{-1} in FT-Raman spectrum is assigned to C-Br stretching vibrations for 1B4NB and the theoretically computed value is observed at 245 cm^{-1} respectively.

The C-Br in-plane bending modes are observed at 273 cm^{-1} in FT Raman spectrum. The C-Br out of plane bending (gCBr) mode is observed at 461in FTIR and 623 cm^{-1} in FT- Raman spectrum and its theoretically computed value using B3LYP method is found to be 460 and 636 cm^{-1} in FT-Raman respectively which implies good agreement with the experimental findings. This shows that the other vibrations can hold back the C-Br vibrations due to its weak force constant. The influence of other substitution on C-Br stretching deformation band is significant in this compound.

5.2.3 C-N Vibrations

In aromatic compounds, the C-N stretching vibrations usually lay in the region 1400-1200cm^{-1}. The identification of C-N stretching frequencies was a rather a difficult task since the mixing of vibration was possible in this region (24).In this study, the bands observed at 1356cm^{-1} in FTIR and 1351cm^{-1} Raman spectrum had been assigned to C-N stretching vibrations. The in-plane and out-of-plane bending C-N vibrations had also been identified and presented in Table2.

5.2.4 C-C Vibrations

The bands 1430-1650cm^{-1} in benzene derivatives are assigned to C-C stretching modes [25]. In this title compound, the FTIR and Raman peaks observed at 1598, 1514, 1416 in FTIR and 1517cm^{-1} in FT-Raman are assigned to C-C stretching vibrations respectively. This shows good agreement with the experiment results.

5.2.5 Nitro group Vibrations

The asymmetric and symmetric stretching vibrations of NO2 generally give rise to bands in the regions 1500-1570 cm^{-1} and 1300-1370 cm^{-1} to nitrobenzene and substituted nitrobenzene respectively. In 1B4NB,asymmetric and symmetric stretching modes of NO_2 group found to be at 1569 and 1356 cm^{-1} in FTIR and 1351cm^{-1} in FT-Raman spectrum respectively.

6.2.6. Ring Vibrations:

Usually an in-plane deformation vibration is at higher frequencies than the out of plane vibration [26]. In the present study, the bands observed at 737 cm^{-1} and 674 cm^{-1} in IR respectively attributed to ring in-plane bending modes .The ring out- of- plane bending mode frequencies are observed at 461 cm^{-1} in IR 623 cm^{-1} in Raman spectra as shown in Table2.

6. THERMODYNAMIC ANALYSIS

Based on the vibrational analysis of title molecule at B3LYP/6-311++ G (d,p) basis sets, the thermodynamic analysis has been carried out. The thermodynamic properties such as heat capacity at constant volume (C_V) and Entropy(S) were calculated for different temperatures and listed in the Table 3.

The thermodynamic functions are increasing with increase in temperature which may be due to the fact that the molecular vibrational intensities increase with temperature. Accordingly for our present work, when the temperature increases from 100 to 1000 K, the thermodynamic functions like total energies, Specific heat capacity at constant volume (C_V) and Entropy (S) are also increases [27]. The entropy revealed that the molecule possesses more flexibility of changing its own thermodynamic system with respect to the temperature. The correlation graphics of temperature dependence of thermodynamic functions for title molecule are shown in Fig.4, Fig.5, and Fig.6 respectively.

Table 3.The Temperature dependence of Thermodynamic parameters of 1B4NB

Temperature [T]	Energy[E] (KCal/Mol)	Heat capacity [Cv] (Cal/Mol-kelvin)	Entropy[s] (Cal/Mol-kelvin)
100	52.665	14.245	70.615
200	54.555	23.712	84.722
300	57.413	33.328	96.983
400	61.175	41.614	108.320
500	65.675	48.105	118.778
600	70.745	53.075	128.371
700	76.253	56.922	137.160
800	82.103	59.961	145.232
900	88.225	62.406	152.674
1000	94.569	64.403	159.566

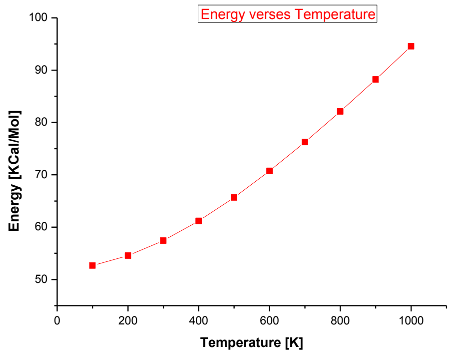

Fig.4.Temperature dependence of energy of 1B4NB

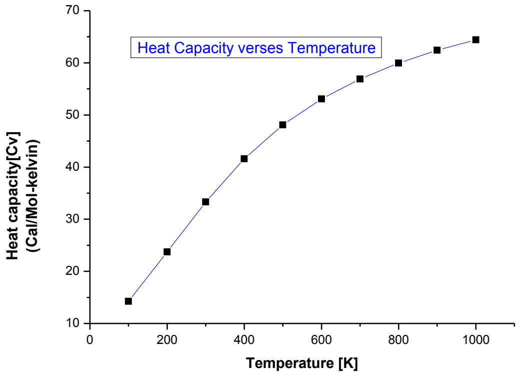

Fig.5.Temperature dependence of Heat capacity at Constant Volume of 1B4NB

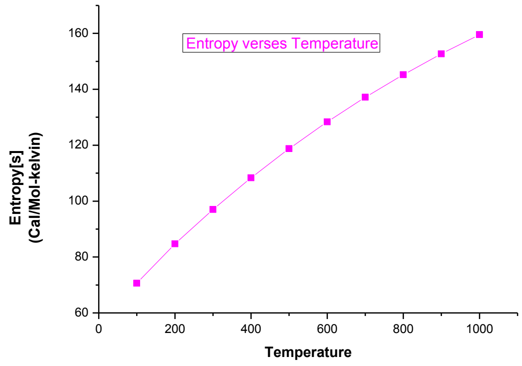

Fig.6. Temperature dependence of Entropy of 1B4NB

The zero point vibrational energy and rotational constants in GHz obtained for optimized geometry with B3LYP/6-311++G(d,p) basis set are presented in Table 4.While performing DFT Calculations the molecule was considered to be at room temperature (298.15K) and at a pressure of 1atm.

TABLE 4.The calculated Thermodynamical parameters of 1B4NB

Parameters	B3LYP/6-31G(d,p)
Zero-point vibrational energy (Kcal/Mol)	57.88016
Rotational constants (GHz):	A 3.7843543 B 0.3600525 C 0.3287724

8. UV SPECTRAL ANALYSIS

Ultraviolet spectra analyses of 1B4NB have been investigated by theoretical calculation. This method is able to detect accurate absorption wavelengths at a relatively small computing time which is correspond to vertical electronic transitions computed on the ground state geometry. Thus TD-DFT method is used with B3LYP function and 6-311++G (d, p) basis set for vertical excitation energy of electronic spectra. The UV-VIS spectrum is shown in Fig.7.

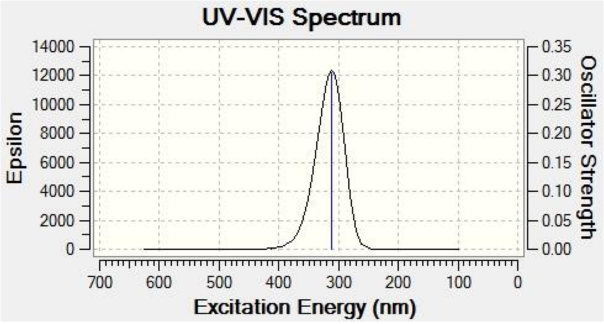

Fig.7.The UV-Visible Spectrum and excitation energy v/s oscillator strength of 1B4NB

Calculations of the molecular orbital geometry show that the visible absorption maxima of this molecule correspond to the electron transition between frontier orbitals such as translation from HOMO to LUMO. The calculated visible absorption maxima of wavelength which are a function of the electron availability have been reported in Table 5.

Table 5.Theoretical electronic absorption spectra values of 1B4NB

Excited State	Energy (eV)	Wavelength λ (nm)	Oscillator strengths (f)
1	2.9994	413.36	0.0011
2	3.982	311.36	0.3049
3	3.9842	311.19	0.0003

9. NMR ANALYSIS

NMR spectroscopy is the most important tool for structure elucidation. By far, the most common nuclei studied in the NMR are the ^1H and ^{13}C. The wide array of available techniques yields wealth of information, not only in the form of just chemical shifts and coupling constants of the involved nuclei, but also as through-bond and through-space connectivity between them [28]. Therefore a full geometry optimization of title molecule was performed by using B3LYP/6-311++G (d,p).

Table.6 Theoretically calculated NMR spectra of ^1H and ^{13}C 1-Bromo-4-nitrobenzene

Atom	Chemical Shift(ppm)
C1	160.6459
C2	137.7438
C3	128.0938
C4	154.9125
C5	134.9037
C6	138.7539
H8	7.4262
H9	7.778
H11	8.5041
H12	7.4873

Then, gauge including atomic orbital (GIAO) ^1H and ^{13}C chemical shift calculations of the compound have been made by the same method. The calculated values for ^1H and ^{13}C are shown in Table 6.Considering that the range of ^{13}C NMR chemical shift for organic molecules is usually greater than 100 ppm, this ensures that reliable interpretation of spectroscopic parameters. Also in this work, ^{13}C NMR chemical shifts in the ring for the title molecule are greater than 100 ppm. Because the bromine and nitrogen atoms are more electronegative, the chemical shift of carbon atoms C1 and C4 next to bromine and nitrogen falls in the region of higher ppm values, than those of other carbon atoms.

Usually the hydrogen atom shows the chemical shifts below 10ppm.In our present work, all the hydrogen atoms attached to benzene ring are below 10ppm.The theoretically calculated ^{13}C and ^1H NMR spectrum are shown in Fig.8.

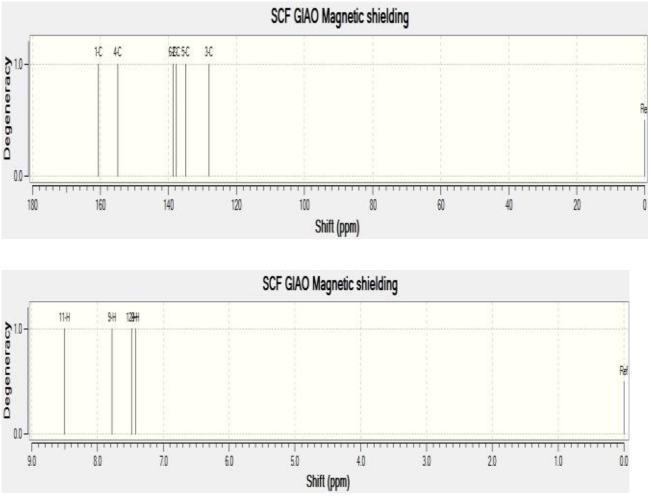

Fig.8.Theoretically calculated NMR spectrum of ^{13}C (above) and ^1H (below) for 1B4NB

10.HOMO-LUMO ENERGY GAP AND RELATED MOLECULAR PROPERTIES

Homo and Lumo are very important parameters for chemical reaction. We can determine the way the molecule interacts with other species ; hence they are called Frontier Orbitals. 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[29].The energy gap between the highest occupied and the lowest unoccupied molecular orbitals is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity [30].Surface for the Frontier orbitals were drawn to understand the bonding scheme of our present compound. The atomic orbital compositions of the frontier molecule orbital are sketched in Fig.9.

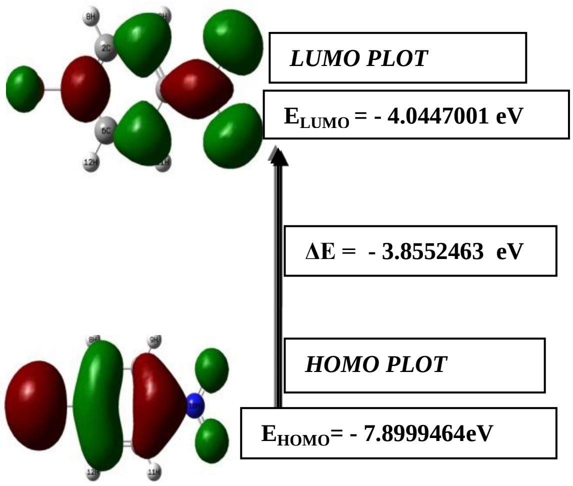

Fig.9.The atomic orbital compositions of the frontier molecular orbital(HOMO-LUMO) for 1-Bromo-4-Nitrobenzene.

The analysis of wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).The HOMO, LUMO and HOMO-LUMO Energy Gap reveals that the energy gap reflects the chemical activity of the molecule.

According to B3LYP/6-311++G(d,p) calculation, the energy band gap (translation from HOMO to LUMO) of the molecule is about -3.8552463 eV

HOMO energy = - 7.8999464eV

LUMO energy = - 4.0447001 eV

HOMO-LUMO energy gap = -3.8552463 eV

The calculated values of the chemical Hardness, Softness, Chemical potential, Electronegativity and Electrophilicity index values for our molecule 1B4NB is given in Table.7.

TABLE7.Energy values of 1B4NB by B3LYP/6 311++G(d,p) method

Energies	Values
E_{HOMO} (eV)	-7.8999
E_{LUMO} (eV)	-4.0447
E_{HOMO} - E_{LUMO} gap (eV)	-3.8552
Chemical hardness (η)	1.9276
Softness (S)	0.2594
Chemical potential (μ)	-5.9723
Electronegativity (χ)	5.9723
Electrophilicity index (ω)	9.2520

11.MULLIKEN ANALYSIS

The total atomic charges of 1B4NB obtained by Mulliken population analysis with B3LYP-6311++G (d,p) basis set combinations are collected in Table 8.From the result , it is clear that the substitution NO_2 atom in the aromatic ring leads to a redistribution of electron density[31]. The σ-electon withdrawing character of the nitrogen atom in 1B4NB is demonstrated by the decrease of C4 atom. The atomic charges in the NO_2 are almost identical. The Mulliken charge obtained from 6-311++G(d,p) basis set shown in Fig.10 and that indicates H9 and H11 atoms are more acidic due to more positive charge.[31]The Histogram of the Mulliken charges is shown in Fig.11

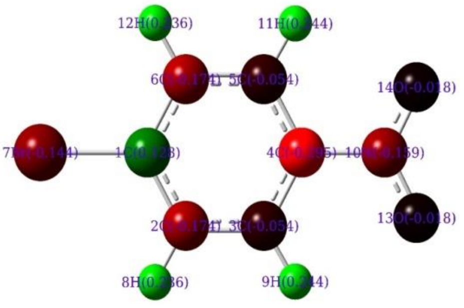

Fig10.Mulliken atomic charges

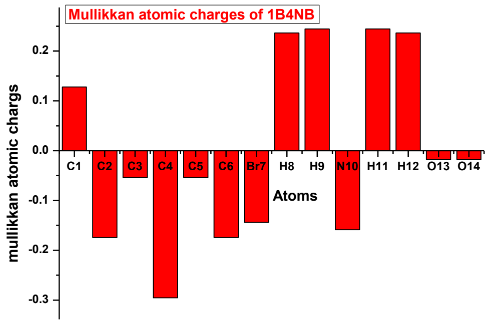

Fig.11.The Histogram of calculated Mulliken charges of 1B4NB

Table 8. Atomic Charges for optimized geometry of 1B4NB using DFT-B3LYP/6-311++G(d,p)

Atoms	Mullikkan Atomic Charges
C1	0.127999
C2	-0.1743
C3	-0.05393
C4	-0.29536
C5	-0.05394
C6	-0.1743
Br7	-0.14406
H8	0.236457
H9	0.244427
N10	-0.15854
H11	0.244427
H12	0.236457
O13	-0.01767
O14	-0.01767

12. MOLECULAR ELECTOSTATIC POTENTIAL

Molecular Electrostatic potential is useful for understanding and predicting the reactive behaviour of wide verity of chemical systems, in both electrophilic and nucleophilic reactions.[32] The MESP simultaneously displays molecular size , shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading and is very useful in research of molecular structure with its physiochemical property relationship. Molecular electrostatic potential (MESP) at a point around a molecule gives an indication of the net electrostatic effect produced at that point by total charge distributions (electron+ nuclei) of the molecule. The mesh view with the colour grading is shown in Fig.12.

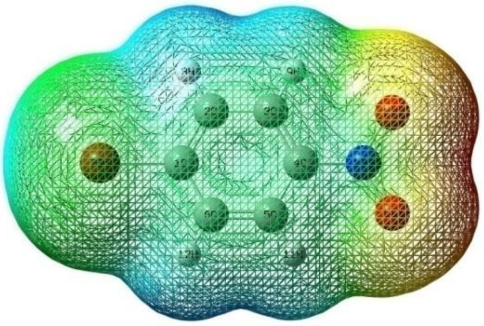

Fig.12.Electron density from total SCF density mapped with esp

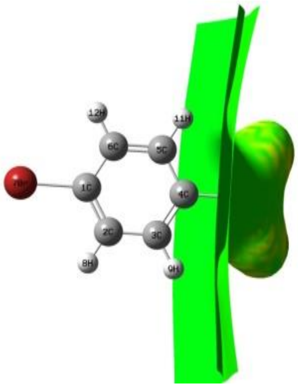

Fig.13. Electrostatic Potential from Total SCF Density mapped with esp

The different values of the electrostatic potential at the surface are represented by different colours. Potential increases in the order Red<yellow<green<blue where blue and yellow (negative region) are related to electrophilic reactivity. The maximum positive regions are localized on the oxygen atom of nitro group which can be considered as possible sites for nucleophilic attack. The mesh view clearly shows that the negative potential sites are on the electronegative atoms while the positive potential sites around oxygen atoms. Green area covers parts of the molecule where electrostatic potentials are nearly equal to zero [33].This is a region of zero potential enveloping the л systems of aromatic ring leaving a more electophilic region in the plane of hydrogen atom. The Electrostatic Potential from Total SCF Density mapped with esp is shown in Fig.13 and the contour map of positive and negative potential for 1B4NB is shown in Fig.14.

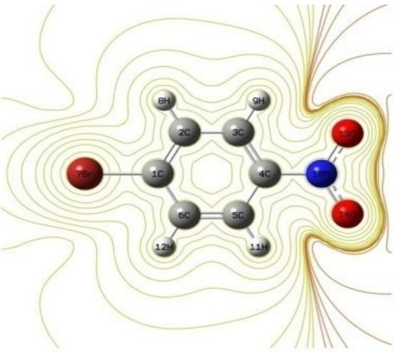

Fig.14. Contour map of 1B4NB

13. CONCLUSION

A complete Vibrational analysis, thermodynamic properties, HOMO and LUMO analysis, performed by DFT-B3LYP methods with 6-311++G (d,p) basis sets. The vibrational frequencies of the title compound were discussed. The calculated values are scaled to rationalize the experimental values. The theoretical UV-Visible spectrum was recorded. The calculated Homo and Lumo energies show that charge transfer occurs within the molecule. The ^1H and ^{13}C NMR chemical shifts of the title compound were calculated using GIAO method. The Mulliken charges of the molecule were reported. The thermodynamic properties (Energy, Heat capacity and Entropy changes) in temperature ranges from 100 to 1000K, Rotational constants, and zero point vibrational energies were also calculated. The molecular electrostatic potential MESP is carried out and the aromatic ring shows more electrophilic region in the plane of hydrogen atom. The positive potential sites found to be around the oxygen atom of nitro group.

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