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## Vibrational Spectroscopy

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# Molecular structure, vibrational spectroscopic studies and HOMO-LUMO analysis of 2-bromo-4, 6-dinitroaniline

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#### Introduction

One of the most important aromatic amines is aniline. Aniline and its derivatives are of great industrial importance and it is widely used as starting materials in a vast amount of pharmaceutical, electro optical, dye manufacturing industry and many other industrial processes [1-6]. The conducting polymer of aniline namely polyaniline is used in Microelectronic devices as diodes and transistor [7-10].

A systematic study of the vibrational spectra of simple primary, secondary and tertiary anilines received considerable attention in the spectroscopic literature in view of their obvious importance for biological systems and their industrial significance. The introduction of one or more substituent in aniline leads to the variation of charge distribution in the molecule and consequently, this greatly affects the structural, electronic and vibrational parameters [11]. Amino groups are generally referred as electron donating substituent in aromatic ring systems.

Fourier transform infrared spectroscopy (FT-IR) is a technique that is widely used to identify organic and some inorganic materials. Infrared spectrometry (IR) provides a useful way for the identification of drugs. FT-IR and FT-Raman spectra of BDNA have been recorded in the regions 4000-400 cm<sup>-1</sup> and 3500-100 cm<sup>-1</sup>.

Hence, the present work has been undertaken to give a complete description of the molecular geometry and molecular vibrations of the title compound. The complete vibrational analysis of BDNA was performed by combining the experimental and theoretical information using HF and DFT based scaled quantum chemical approach [12]

#### ABSTRACT

The molecular vibrations of 2-bromo-4,6-dinitroaniline (BDNA) were investigated in solid phase, at room temperature by FT-IR and FT-Raman spectroscopy. The molecular geometry and vibrational frequencies of BDNA in the ground state were calculated by using the Hartree-Fock (HF) and density functional theory (DFT) methods (B3LYP) with 6-311++G\*\* as basis set. Comparison of the observed fundamental vibrational frequencies of BDNA with calculated results by HF and density functional methods indicates that B3LYP is superior to HF method for molecular vibrational problems. The Mulliken atomic charges have also been computed at HF/6-311++G\*\* and B3LYP/6-311++G\*\* level. Finally the calculated HOMO and LUMO energies show that charge transfer occur in the molecule.

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#### **Experimental details**

The compound BDNA was obtained from Lancaster Chemical Company, UK and used as such for the spectral measurements. The room temperature Fourier Transform infrared spectrum of the title compound was measured with KBr pellet technique in the 4000-400 cm<sup>-1</sup> region at a resolution of 1 cm<sup>-1</sup> using BRUKER IFS 66V spectrophotometer equipped with He-Ne laser source. The FT-Raman spectrum of BDNA was recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory in the 3500-100 cm<sup>-1</sup> stoke region using the 1064 nm line of a Nd:YAG Laser for excitation operating at 200mW power. The reported wave numbers are believed to be accurate within  $\pm 1$  cm<sup>-1</sup>. **Computational details** 

The molecular geometry optimization vibrational frequency calculations were carried out for BDNA with GAUSSIAN 09W software package [13] using HF and B3LYP functional method combined with standard 6-311++G\*\* basis set [14,15] was applied to represent the molecular orbital. The IR and Raman wave numbers and intensities were computed at the same level of theory using the harmonic approximation and the analytical derivatives procedure incorporated in the Gaussian program.

The vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program [16]. The symmetry of the molecule was also helpful in making vibrational assignments. The symmetry of the vibrational modes were determined by using standard procedure [17,18] of decomposition the traces of the symmetry operations in to the irreducible representations. The Raman activities (*Si*) calculated by the Gaussian-09 program were converted to relative Raman

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intensities (*Ii*) using the following relationship derived from the basic theory of Raman scattering,

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 s_i}{\upsilon_i [1 - \exp(-hc \upsilon_i)]/kT}$$
(1)

where  $v_0$  is the exciting frequency (in cm<sup>-1</sup> units),  $v_i$  the vibrational wave number of the *i*<sup>th</sup> normal mode, *h*, *c* and *k* are the universal constants, and *f* is the suitably chosen common normalization factor for all the peak intensities.

### **Results and discussion**

#### **Geometry optimization**

The molecular structure of BDNA belongs to C<sub>s</sub> point group symmetry and is shown in Fig 1. The 48 normal modes of vibrations are distributed among the symmetry species as  $\Gamma$ vib=33A (in plane)+15A" (out of plane). All vibrations are active in both the Raman scattering and infrared absorption. The A' modes be polarized bands in the Raman spectrum. The optimized structural parameters calculated by HF and B3LYP level with the  $6-311++G^{**}$  basis set are listed in Table 1. From the optimized geometry the C1-C2 and C1-C6 bond length values are found to be very high in both HF and B3LYP methods due to polarizability of amino group. These corresponding values are 1.4242Å, 1.4168Å in HF and 1.4297 Å, 1.4294Å in B3LYP method. In amino group N7-H8 and N7-H9 parameters can accommodate low bond length value. It clearly indicates that these parameters occupies the higher energy level. The lowest value of bond length N12-O13 (1.0077Å) compare than all other band lengths and highest value of band length have been C2-Br10 (1.9147Å). The dihedral angle of N7-C1-C6-C5 is -179.99<sup>0</sup> by HF and B3LYP method. The hydroxyl proton was localized near the N16-O17 oxygen and hydrogen bonded to the C5-H15 oxygen of the symmetry related molecule. The N16-O17 bond length is 1.2242Å and C5-H15 bond length is 1.4683Å by B3LYP method. The dihedral angles C2-C1-C6-N16, C2-C1-N7-H9 and C1-C2-C3-H11 are coplanar angle.



#### Vibrational spectra

Detailed description of vibrational mode can be given by means of normal coordinate analysis (NCA). For this purpose, the set of 60 standard internal coordinates containing 12 redundancies are defined as given in Table 2. From these a nonredundant set of local symmetry coordinates were constructed by suitable linear combination of internal coordinates following the recommendations of Fogarasi *et al.* [12] are summarized in Table 3. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

For visual comparison, the observed and stimulated FT-IR and FT-Raman spectra of the title compound are presented in Fig 2 and 3, respectively. Comparison between calculated and observed vibrational spectra helps us to understand the observed

spectral features. The results of our vibrational analysis, viz., calculated vibrational frequencies, IR intensities and assignment of the fundamentals for the title compound are collected in Table 4.

#### Amino group vibrations

The  $NH_2$  group gives rise to six internal modes of vibrations such as; the symmetric stretching, the asymmetric stretching, the symmetry deformation or the scissoring , the rocking, the wagging and torsional mode. The frequency of symmetry vibration in higher than that of symmetry one. If the two NH bonds of the  $NH_2$  group are symmetric, these modes satisfy an empirical relation as suggested by Bellamy and Williams [19] as

 $v_{sy} = 345.5 + 0.876 v_{asy}$ 

 $v_{asy}$  asymmetry wave number.

In our present work BDNA observed values of  $NH_2$  asymmetric and symmetric stretching modes are in the range 3450-3333 cm<sup>-1</sup> is in agreement with experimental value of 3964-3544 cm<sup>-1</sup>[20].

The internal deformation vibrations known as NH<sub>2</sub> scissoring frequency is found at 1650 cm<sup>-1</sup> is well within the range (1590-1650 cm<sup>-1</sup>) reported for aniline by Thompson [21] and this observation is in conformity with the calculated values are found at 1746, 1569  $\text{cm}^{-1}$  in both HF and B3LYP, respectively. The wagging and torsion modes have been observed at  $620-200 \text{ cm}^{-1}$  with strong and medium intensity respectively [22]. The NH<sub>2</sub> torsion mode has been computed to be at 646 cm<sup>-1</sup> and 626 cm<sup>-1</sup> in both HF and B3LYP method have been assigned to NH2 torsion mode. The calculated values at 355 and 342 cm<sup>-1</sup> in HF and B3LYP are assigned to  $NH_2$ wagging mode. This is also found at 346 cm<sup>-1</sup> in Raman spectrum. However, the recorded spectral data 632, 634 cm<sup>-1</sup> do support the vibration. The calculated values at 1154 and 1055 cm<sup>-1</sup> in HF and B3LYP are assigned to NH<sub>2</sub> rocking mode. These also observed at 1131, 1140 cm<sup>-1</sup> in IR and Raman mode. These vibrations show good agreement with computed harmonic frequency as well as recorded spectral data.

#### **C-H vibrations**

The assignments of the carbon-hydrogen stretching modes are straight forward on the basis of the HF/6-311++G\*\* and B3LYP/6-311++G\*\* predicted wavenumbers. The BDNA molecule gives rise to two C-H stretching, two C-H in-plane bending and two C-H out-of-plane bending vibrations. Aromatic compounds commonly exhibit multiple weak bands in the region 3100-3000 cm<sup>-1</sup> due to aromatic C-H stretching vibration [23]. The aromatic C-H stretching vibrations are observed in the region 3125-3060 cm<sup>-1</sup> are in agreement with recorded FT-IR and FT-Raman spectrum at 3120 and 3080 cm<sup>-1</sup>. The two C-H in-plane bending vibrations appears in the range 1000-1300 cm<sup>-1</sup> in the substituted benzenes and the two out of plane bending vibrations occurs in the wave number range 750-1000 cm<sup>-1</sup> are usually weak. The C-H in-plane bending vibrations are assigned at 1340 cm<sup>-1</sup> in infrared and 1348cm-1 and 1170 cm<sup>-1</sup> in Raman. The computed wave numbers 1379, 1192 cm<sup>-1</sup> are calculated by HF/6-311++G\*\* method 1301, 1083 cm<sup>-1</sup> by B3LYP/6- $311++G^{**}$  method. The infrared bands are observed at 1080 and 1040 cm<sup>-1</sup> are assigned to C–H out-of-plane bending vibrations. The calculated values are found at 1086, 1056 and 956, 943 cm<sup>-1</sup> by HF and B3LYP, respectively, are assigned to C-H out-ofplane bending vibrations. These observed values of C-H

vibrations of BDNA are assigned within the characteristic region and is presented in Table 4.

#### **C-Br** vibrations

The vibrations belonging to the bond between the ring and the bromine atom are important as mixing of vibrations are possible due to the presence of heavy atoms [24]. Bromine compounds absorb strongly region 650-485 cm<sup>-1</sup> due to C–Br stretching vibrations [25]. In the observed Raman spectrum, the band identified at 276 cm<sup>-1</sup> has been assigned to C–Br stretching vibration. The bending vibrations arising from C–Br bands are observed in their respective characteristic regions, of BDNA and they are listed in Table 4.

#### C-NO<sub>2</sub> vibrations

The aromatic nitro compounds have strong absorption due to the asymmetric and symmetry stretching vibrations of the NO<sub>2</sub> group at 1570-1485cm<sup>-1</sup> and 1370-1320cm<sup>-1</sup>, respectively. Hydrogen bonding has little effect on the NO<sub>2</sub> asymmetric stretching vibrations [25, 26].The nitro group substituted at the fourth and sixth position of BDNA gives rise to C–NO<sub>2</sub> stretching vibrations in addition to the internal vibrations is possible. The bands appeared at 1690, 1671, and 1498, 1482 cm<sup>-1</sup>

<sup>1</sup> are unambiguously assigned to  $C-NO_2$  asymmetric and symmetric stretching vibrations, respectively. The calculated stretching modes are found at 1826, 1816 and 1637, 1598 cm<sup>-1</sup> in HF/6-311++G\*\* and 1651, 1622 and 1481, 1438 cm<sup>-1</sup> in B3LYP/6-311++G\*\* are assigned to  $NO_2$  asymmetric and symmetric stretching vibrations, respectively. These vibrations show good agreement with experimental as well as observed spectral data.

#### **C-N** vibration

The identification of C–N vibrations is found to be difficult tasks because of the mixing of several vibrations possible in this region. Yadav et al and Silverstein et al [27, 28] assigned the C-N stretching absorption in the range 1266-1382 cm<sup>-1</sup>. Our calculation followed by Gaussview visualization showed by B3LYP method 1151, 837 and 735 cm<sup>-1</sup> frequency corresponding to a mixed mode stretching frequencies due to C-NO<sub>2</sub> and C-NH<sub>2</sub>. The other C-N out-of-plane bending vibrations are found to be at 336, 216, 130 cm<sup>-1</sup>in HF/6-311++G\*\* basis set and 309, 198, 117 cm<sup>-1</sup> in B3LYP/6-311++G\*\* basis set during computation while the experimentally assigned values are observed at 320, 250 in Raman spectrum. The C-N in-plane bending vibrations are observed at 475,420 and 380 cm<sup>-1</sup>. The computed values for the C–N in plane bending vibrations by B3LYP method are at 423, 384 and 353 cm<sup>-1.</sup>

#### **C–C** vibration

The ring carbon-carbon stretching vibrations occur in the region 1625-1430 cm<sup>-1</sup>. In General, the bands are of variable intensity and are observed at 1625-1590, 1590-1575, 1540-1470, 1465-1430 and 1380-1780 cm<sup>-1</sup> from the frequency ranges given by Varasanyi [29] for the five bands in the region. In the present work, the frequencies observed in the FT-IR spectrum at 1600 and 1331 cm<sup>-1</sup> have been assigned to C–C stretching vibrations. The corresponding vibrations appear in the FT-Raman spectrum at 1598, 1522, 1461, 1414, 1369 and 1335 cm<sup>-1</sup>. The theoretically computed values at 1569, 1556, 1385, 1358, 1349 and 1241 cm<sup>-1</sup> show good agreement with experimental data by B3LYP/6-311++G\*\* method. The in plane deformation vibration is at higher frequencies than the out-of-plane

vibrations. Shimonouchi *et al* [30] gave the frequency data for these vibrations for different benzene derivations as a result of normal coordinate analysis.

#### Mulliken population analysis

The population analysis in the molecule was calculated using the HF/6-311++G\*\* and B3LYP/6-311++G\*\* level. The charge distribution structure and chart of warfarin are shown in Fig 2. The O18 oxygen atom has more negative charge, whereas the hydrogen atom H9 has more positive charge than the other hydrogen atoms. The result suggests that the atoms bonded to the hydrogen atom and all oxygen atoms are electron acceptor and the charge transfer takes place from hydrogen to oxygen. The carbon atom C2 is more positive than the other carbon atoms due to electron donating substitution at that position. The C2 atom of BDNA can accommodate high positive charge and become high acidic as compared to other carbon atoms while in the presence of NO<sub>2</sub> group in C6 atom is less acidic (is less positive charge). The charge on Br10 atom is less negative and become less base.



#### **HOMO-LUMO** analysis

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability [31]. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron the HOMO and LUMO energy calculated by B3LYP/6-311++G\*\* method as shown in Fig 4. The HOMO-LUMO transition implies an electron density transfer to ring from Br atom. Moreover, the orbital significantly overlap in their position for BDNA. HOMO and LUMO energies calculated by B3LYP/6-311++G\*\* are HOMO energy -0.38920a.u

LUMO energy = 0.00017a.u

HOMO-LUMO energy gap =-0.38937a.u.



#### Other molecular properties

Several calculated thermodynamic parameters are presented in Table 6. Scale factors have been recommended [32] for an accurate prediction in determining the zero point vibration energies (ZPVE), and the entropy,  $S_{vib}(T)$ .

The variations in the ZPVE seem to be insignificant. The total energies are found to decrease with the increase of the basis set dimension. The changes in the total entropy of BDNA at room temperature at different basis set are only marginal.



#### Conclusion

Attempt has been made in the present work for the proper

frequency assignments for the compound BDNA from the FTIR and FT-Raman spectra. The equilibrium geometries and harmonic frequencies of BDNA were determined and analyzed both at HF/B3LYP method of theories utilizing  $6-311++G^{**}$  basis set giving allowance for the lone pairs through diffuse functions. The difference between the observed and calculated B3LYP method wavenumber values of most of the fundamentals is very small.

Comparison between the calculated vibrational frequencies and the experimental values indicate that both the methods of B3LYP/6-311++G\*\* and HF/6-311++G\*\* can predict the IR and Raman spectra of the title compound well. The optimized geometry parameters calculated at B3LYP/6-311++G\*\* are slightly larger than those calculated at HF/6-311++G\*\* level and the B3LYP calculated values coincides well compared with the experimental data on the whole.

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Table 1 Optimized geometrical parameters of 2-bromo- 4,6-dinitro aniline based	ł
on HF/6-311++C** and B3LVP /6-311++C**	

Bond length	Value(Å)		Bond angle	Value(degrees)		
	HF B3LYP			HF	B3LYP	
C1-C2	1.4242	1.4297	C2-C1-C6	115.1397	115.2611	
C1-C6	1.4168	1.4294	C2-C1-N7	120.2719	120.689	
C1-N7	1.3331	1.3422	C6-C1-N7	124.5884	124.0499	
C2-C3	1.3618	1.3726	C1-C2-C3	122.5793	122.7984	
C2-Br10	1.8994	1.9147	C1C2Br10	119.4547	118.6738	
C3-C4	1.393	1.3726	C2-C3-C4	1197389	119.1422	
C3-H11	1.0712	1.9147	C2-C3-H11	120.6699	121.3578	
C4-C5	1.3664	1.3998	C4-C3-H11	119.7389	119.5	
C4-N12	1.4525	1.0808	C3-C4-C5	120.8491	121.2466	
C5-C6	1.3858	1.3783	C3-C4-N12	119.408	119.156	
C5-H15	1.0697	1.4683	C5-C4-N12	119.7429	119.5973	
C6-N16	1.4559	1.3915	C4-C5-C6	119.4811	119.3611	
N7-H8	0.9912	1.0801	C4-C5-H15	120.7798	120.8877	
N7-H9	0.9913	1.4657	C6-C5-H15	119.7391	1197512	
N12-013	1.1869	1.0077	C1-C6-N16	122.3596	121.5806	
N12-014	1.1888	1.0100	C5-C6-N16	115.8277	116.2288	
N16-017	1.1835	1.2242	C1-N7-H8	119.7526	119.4503	
N16-018	1.1955	1.2263	C1-N7-H9	120.2236	118.9538	
			H8-N7-H9	120.0222	121.5958	
			C4-N12-O13	117.675	117.7027	
			C4-N12-O14	117.2755	117.3299	
			O13-N12-O14	125.0495	124.9674	
			C3-C2-Br10	117.966	118.5278	
			C1-C6-C5	122.3596	122.1906	
			C6-N16-O17	117.8771	118.2539	
			C6-N16-O18	118.4003	118.3619	
			O17-N16-O18	123.7226	123.3841	
			C6-C1-C2-C3	0.0449	-0.0034	
			C6-C1-C2-Br10	-0.0289	-0.0052	
			C2C1C6C5	-0.0593	0.0045	
			C2-C1-C6-N16	179.9929	180.0031	
			N7-C1-C6-C5	-179.9969	-179.9919	
			N7-C1-C6-N16	0.0554	0.0067	
			C2C1N7H8	0.1920	0.0163	
			C2C1N7H9	179.7274	179.9902	
			C6-C1-N7-H8	-179.8735	-179.9875	
			C6-C1-N7-H9	-0.3381	-0.0136	
			C1C2C3C4	-0.0147	0.0014	
			C1-C2-C3-H11	179.9744	180.0013	
			Br10-C2-C3-C4	179.9994	179.9995	
			Br10-C2-C3-H11	-0.0044	-0.0004	
			C2-C3-C4-C5	-0.0046	0.0003	
			C2-C3-C4-N12	179.9744	-179.9995	
			H11-C3-C4-C5	-180.0009	-80.0002	
			H11-C3-C4-N12	-0.0219	0.00004	
			C3-C4-C5-C6	-0.0095	0.0008	

For numbering of atom refer Fig.1.

Table2 Definitions of internal coordinates of 2-bromo-4,6-dinitro aniline							
NO	Symbol	Туре	Definition				
			Stretching				
1-6	ri	C-C	C1-C2, C2-C3, C3-C4, C4-C5, C5-C6, C6-C1				
7	Ri	C-N	C1-N7				
8-9	Pi	N-H	N7–H8, N7–H9				
10-11	Qi	C-H	C3-H11, C5-H15				
12	qi	C-Br	C2-Br10				
13-14	Ti	C-N	C4–N12, C6–N16				
15-18	Di	N-O	N12-O13, N1-O14, N16-O17, N16-O18				
			Bending(in plane)				
19-24	αί	Ring	C1-C2-C3,C2-C3-C4, C3-C4-C5,				
			C4-C5-C6, C5-C6-C1, C6-C1-C2				
25-30	βi	CCN	C2-C1-N7,C6-C1-N7,C3-C4-N12,				
			C5-C4-N12, C5-C6-N16, C1-C6-N16				
31-34	δί	CCH	C2-C3-H11, C4-C3-H11,				
			C4-C5-H15, C6-C5-H15				
35-36	ρί	CCBr	C1-C2-Br10, C3-C2-Br10				
37-40	πi	CNO	C4-N12-O13, C4-N12-O14				
41-42	φi	O-N-O	O13-N12-O14, O17-N16-O18				
43-44	ψi	CNH	C1-N7-H8, C1-N7-H9				
45	ψi	H-N-H	H8-N7-H9				
			Out of plane bending				
46-47	ωi	CH	H11-C3-C2-C4, H15-C5-C4-C6				
48	ωi	CBr	Br10-C2-C1-C3				
49-50	ωi	$NO_2$	C4-N12-O13-O14, C6-N16-O17-O18				
51-53	ωi	CN	N7-C1-C2-C6, N12-C4-C3-C5, N16-C6-C5-C1				
54	ωi	NH	С1-N7-Н8-Н9				
Torsion							
55-60	τί	τRing	C1-C2-C3-C4, C2-C3-C4-C5, C3-C4-C5-C6, C4-C5-C6-C1, C5-C6-C1-C2, C6-C1-C2-C3				
Een mum	haming of	ctom not	han Dia 1				

For numbering of atom refer Fig.1.

Table3 Definitions of local symmetry coordinates of 2-bromo-4,6-dinitroaniline

No	Symbol	Definition				
1-6	CC	r1, r2, r3, r4, r5, r6				
7	CN(amino)	R7				
8–9	NH <sub>2</sub> ss	$(p8 + p9)/\sqrt{2}$				
	NH <sub>2</sub> asyms	$(P8 - p9)/\sqrt{2}$				
10-11	CH	Q10, Q11				
12	CBr	q12				
13-14	CN(Nitro)	T13, T14				
15-18	NO <sub>2</sub> ss	$(D15 + D16)/\sqrt{2}, (D17 + D18)/\sqrt{2}$				
	NO2 asyms	$(D15 - D16)/\sqrt{2}, (D17 - D18)/\sqrt{2}$				
19	Rtrigd	$(\alpha 19 - \alpha 20 + \alpha 21 - \alpha 22 + \alpha 23 - \alpha 24)/\sqrt{6}$				
20	Rsymd	$(-\alpha 19 - \alpha 20 + 2\alpha 21 - \alpha 22 - \alpha 23 + 2\alpha 24)/\sqrt{12}$				
21	Rasymd	$(\alpha 19 - \alpha 20 + \alpha 22 - \alpha 23)/2$				
22-24	bCN	$(\beta 25 - \beta 26)/\sqrt{2}, (\beta 27 - \beta 28)/\sqrt{2}, (\beta 29 - \beta 30)/\sqrt{2}$				
25-26	bCH	$(\delta 31 - \delta 32)/\sqrt{2}, (\delta 33 - \delta 34)/\sqrt{2}$				
27	bCBr	$(\rho 35 - \rho 36)/\sqrt{2}$				
28-29	NO2 rock	$(\pi 37 - \pi 38)/\sqrt{2}, (\pi 39 - \pi 40) \sqrt{2}$				
30-31	NO2 twist	$(\pi 37 + \pi 38)/\sqrt{2}, (\pi 39 + \pi 40)/\sqrt{2}$				
32-33	NO <sub>2</sub> sciss	$(2\varphi 41 - \varphi 37 - \varphi 38)/\sqrt{6}, (2\varphi 42 - \varphi 39 - \varphi 40)/\sqrt{6}$				
34	NH <sub>2</sub> rock	$(\psi 43 - \psi 44)/\sqrt{2}$				
35	NH2 twist	$(\psi 43 + \psi 44)/\sqrt{2}$				
36	NH <sub>2</sub> sciss	$(2\psi 45 - \psi 43 - \psi 44)/\sqrt{6}$				
37-38	ωCH	ω46, ω47				
39	ωCBr	ω48				
40-41	ωNO <sub>2</sub> wag	ω49, ω50				
42-44	ωCN	ω51, ω52, ω53				
45	NH <sub>2</sub> wag	ω54				
46	tRtrig	$(\tau 55 - \tau 56 + \tau 57 - \tau 58 + \tau 59 - \tau 60)/\sqrt{6}$				
47	tRsym	$(-\tau 55 - \tau 56 + 2\tau 57 - \tau 58 - \tau 59 + 2\tau 60)/\sqrt{12}$				
48	tRasy	$(\tau 55 - \tau 56 + \tau 58 - \tau 59)/2$				

ss-symmetric stretching; asyms-asymmetric stretching; trigd-trigonal deformation; b-bending in-plane; ω-bending out-ofplane; asymd-asymmetric deformation; symd-symmetric deformation t-*torsiong;* ω-*bending out-of-plane*.

# Table 4 Assignment of fundamental vibration of 2 bromo-4,6-dinitro aniline by normal mode analysis based on SQM force field calculations using HF/6-311++G\*\* and B3LYP/6-311+G\*\* force field.

Symmetr y	Observed	value(cm <sup>-1</sup> )	Ca val	lculated ue(cm <sup>-1</sup> )	IR in	tensity	Rama (arbitra	an active ary units)	Force	constant	Redu	iced Mass	Assignments
Species	IR	Raman	HF	B3LYP	HF	<b>B3LYP</b>	HF	<b>B3LYP</b>	HF	B3LYP	HF	B3LYP	
A'	3443	3450	3964	3680	160.25	144.81	17.40	19.89	10.25	8.82	1.1072	1.1051	NH2 asym stretching
A'	3330	3333	3832	3544	166.16	141.95	134.81	235.03	9.04	7.74	1.0451	1.0459	NH <sub>2</sub> s stretching
A'	3125	3120	3423	3241	31.37	29.64	25.7	26.43	7.55	6.76	1.0937	1.0912	CH stretching
A'	3060	3080	3400	3229	10.45	11.79	35.37	41.45	7.46	6.71	1.0947	1.0922	CH stretching
A'	1690	-	1826	1651	719.83	385.64	2.38	76.85	15.28	8.56	7.7734	5.3298	NO <sub>2</sub> asym stretching
A'	1671		1816	1622	398.44	219.14	14.23	2.04	17.81	11.68	9.1616	7.5286	NO <sub>2</sub> asy stretching
A'	1650		1795	1615	396.3	31.82	56.92	4.70	3.05	3.15	1.6064	2.0561	NH <sub>2</sub> scissoring
A'	1600	1598	1746	1569	91.39	101.53	62.57	62.13	8.09	13.09	4.5030	9.0253	CC stretching
A'	-	1522	1712	1556	96.5	209.92	13.48	45.90	11.18	9.66	6.4721	6.7666	CC stretching
A'	-	1498	1637	1481	111.4	45.28	143.24	10.12	10.64	3.79	6.7337	2.9321	NO2 s stretching
A'	1480	1482	1598	1438	785.03	25.30	120.74	13.21	19.84	6.2	13.1741	5.0843	NO <sub>2</sub> s stretching
A'	-	1461	1556	1385	10.31	43.46	60.14	127.77	7.74	6.66	5.4226	5.8871	CC stretching
A'	-	1414	1556	1358	163.4	396.84	83.26	335.72	6.32	10.12	4.4277	9.3164	CC stretching
A'		1369	1444	1349	3.655	258.39	33.66	152.1	3.85	4.06	3.1357	3.7829	CC stretching
A'	1340	1348	1379	1301	0.508	315.35	4.74	138.86	1.83	7.05	1.6367	7.0623	CH in plane bending
A'	1331	1335	1326	1241	45.26	17.93	31.90	5.69	3.69	1.2	3.5631	1.327	CC stretching
A'		1239	1253	1151	171.92	149.25	28.75	57.41	3.76	4.1	4.0677	5.2371	CN stretching
A'		1170	1192	1083	64.64	80.61	6.77	4.05	1.61	1.31	1.9195	1.8919	CH in plane bending
A'	1131	1140	1154	1055	53.06	34.13	8.18	10.87	1.56	1.12	1.9925	1.7111	NH <sub>2</sub> rocking
A″	1080		1086	956	1.45	5.71	0.13	0.08	0.92	0.71	1.3297	1.3231	CH out of plane bending
A″	1040	022	1056	943	17.25	58.27	0.22	14.59	0.88	4.68	1.3321	8.9282	CH out of plane bending
A'	920	933	1044	931	42.96	18.88	12.23	0.12	4.83	0.67	/.5148	1.3231	NO <sub>2</sub> scissoring
A'	850	-	972	868	/.06	2.23	9.26	31.75	0.48	4.76	( 1209	10./161	NO <sub>2</sub> scissoring
A	-	821	908	837	8.85	4.70	2.05	8.03	2.98	2.40	0.1308	5.9723	CN stretching
A'	-	-	824 810	735	1.79	0.52	2.05	5.69	2.69	3.10	15.1441	9.8005	NO <sub>2</sub> wagging
A'	725	- 724	810	755	27.20	0.55	0.07	0.88	5.00 1.79	3.69	9.0119	12.2175	NO wegging
A A'	735	734	800 777	712	17.71	17.10	7.57	13.24	4.70	2.46	0.24	0.0804	Ring in plane bending
A \	682	-	740	671	4.61	42.82	0.14	0.04	3.29	2.90	9.24	9.1485	Ring inplane bending
A'	640	_	678	650	12.07	14 168	1 31	0.0045	1 13	0.26	4.15	1 0521	Ring in plane bending
А	010		070	050	12.07	8	1.51	0.0045	1.15	0.20	1.15	1.0521	iting in plane bending
A'	632	634	646	624	14.40	8.92	0.0383	1.4187	0.2602	0.9587	1.0558	4.1684	NH <sub>2</sub> torsion
A'	555	-	589	539	4.43	1.96	0.9425	1.9962	1.6961	1.4153	8.2818	8.2554	Ring out of plane
													bending
Α"	540	535	523	500	18.39	8.55	0.2033	0.1112	0.5736	0.5559	3.5494	3.7698	Ring out of plane
													bending
A″	490	-	485	449	6.51	9.68	0.1479	0.13	0.6333	0.5675	4.5517	4.7639	Ring out of plane
	175		161	100	2.52	0.40	0.1166	2 0011	0.6550	0.5402	5 1507	5 2040	bending
A'	475	-	464	423	3.52	2.42	2.4466	3.0911	0.6552	0.5492	5.1507	5.2040	CN in plane bending
A'	-	420	412	384	1.61	1.68	1.2067	1.0757	0.8965	0.655	8.9344	1.53353	CN in plane bending
A'	-	380	385	333	0.73	0.09	2.224	1./38	0.8/91	0.738	10.0472	10.0465	CN in plane bending
A'	-	300	3/3	347	1.37	157.49	2.1858	0.1848	0.7511	0.08	9.1251	1.1589	NO <sub>2</sub> focking
A'	-	340	333	342	197.81	0.8145	0.1800	5.7475	0.0885	0.61	1.184	8.//8/	NH <sub>2</sub> wagging
A.	-	520 276	204	270	4.62	0.58	0.4045	0.1298	0.0030	0.38	9.0855	10.2729	CR stretching
A'	-	270	294	270	0.41	0.0857	0.5157	9.1232	0.9132	0.78	17.9023	16.0000	CN out of plana handing
A A'	-	190	189	198	2 38	1.76	0.0474	0.3421	0.1233	0.11	4.4736	4.0093	NO <sub>2</sub> rocking
A ^'	-	176	159	144	2.30	1.62	0.5725	1 2067	0.2585	0.27	17.66	17 6047	CBr in plane bending
A \	-	120	130	117	4 15	3.12	0.5725	0.4680	0.089	0.07	8 99	8 7603	CN out of plane bending
Δ"	-	95	86	83	1.06	0.52	0 4194	0.4000	0.0380	0.04	8.76	10 6855	CBr out of plane
11	-	20	00	05	1.00	0.52	0.11)7	0.17	0.0500	0.0 T	0.70	10.0000	bending
A'	-	-	53	49	0.03	0.012	1.6258	1.5352	0.0263	0.02	16.05	15.9551	NO <sub>2</sub> torsion
A'	-	-	32	43	0.39	0.4695	1.4868	1.4671	0.0088	0.147	14.65	13.0081	NO <sub>2</sub> torsion

s-symmetric; asym-asymmetric.

Atoms	HF/6-311++G**	B3LYP/6-311++G**
C1	-0.824	-1.015626
C2	0.966	0.765854
C3	-0.143	0.414012
C4	-0.583	-0.702808
C5	0.031	0.561768
C6	0.250	0.171387
N7	-0.415	-0.21958
H8	0.306	0.25148
H9	0.378	0.33312
Br10	-0.203	-0.115688
H11	0.354	0.29652
N12	-0.102	-0.184293
O13	-0.050	0.00547
O14	-0.065	-0.010998
H15	0.379	0.32854
N16	-0.158	-0.234136
O17	-0.032	0.027479
018	-0.089	-0.047199

Table5 Mulliken atomic charges for 2- bromo-4,6-dinitroaniline

Table 6 Theoretically computed energies (a.u), zero point vibrational energies (Kcal mol-1), rotational constants (GHZ), entropies (cal mol-1k-1) and dipole moment (Debyes) for BDNA

Parameters	HF/6-311++G**	B3LYP/6-311++G**
Total energy(hartrees)	-3264.63873103	-3270.35682585
Zero point energy(Jmol <sup>-1</sup> /kcalmol <sup>-1</sup> )	317321.1 /75.81456	29116.9/69.57860
Rotational constants(GHz)	0.57008	0.55774
	0.41917	0.41224
	0.24154	0.23704
Entropy Total(cal/molK)		
Translational	42.577	42.577
Rotational	32.988	33.044
Vibrational	35.759	37.893
Dipole moment(Debye)	5.4034	5.6573