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Experimental spectroscopic studies and Hartee-Fock *ab initio* calculations of 2-bromo-4, 6-dinitro aniline

Munish K Yadav, Bandana Sharma*

D N (PG) Bio-Physics Lab, Meerut.

**Department of Physics, Ajay Kumar Garg Engg. College, Ghaziabad.*

ABSTRACT

The FT-IR and FT-Raman spectra of 2-bromo-4, 6-dinitro aniline have been recorded in the region 4000-400 cm^{-1} and 2000-100 cm^{-1} , respectively. The molecular geometry and vibrational frequencies and intensity of 2-bromo-4, 6-dinitro aniline in the ground state have been calculated by using the Hartee-Fock method with 6-31+G (d, p) as the basis set. The optimized geometric bond lengths and bond angles were obtained using HF method. The harmonic vibrational frequencies were calculated and scaled values have been compared with experimental FT-IR and FT-Raman spectra. The observed and experimental calculated frequencies are found to be in good agreement.

Keywords: FT-IR spectra, FT-Raman spectra, Ab-initio, 2-bromo-4, 6-dinitroaniline, vibrational analysis.

INTRODUCTION

Aniline is the simplest of the primary aromatic amines, an organic base used to make dyes, drugs, explosives, plastics and rubber chemicals. Aromatic amines are very important in biology and chemical industry. Aniline and its derivatives are used in the production of dyes, pesticides and antioxidants. Some of the para-substituted derivatives of aniline are local anesthetics and in these molecules the amino group plays an important role in the interaction with the corresponding receptor. The conducting polymer of aniline namely polyaniline is used in microelectronics devices diodes and transistors [1]. Due to all these applications of the substituted anilines the understanding of their molecular structure as well as spectral analysis has great importance and has been the subject of many experimental and theoretical studies. A systematic study on the vibrational spectra of simple primary, secondary and tertiary amines received considerable attention in view of their importance to biological importance systems and industrial significance. The inclusion of substituent in the aniline leads to the variation of charge distribution in the molecule and consequently affects the structural, electronic and vibrational parameters. The position of the substituents in the benzene ring as well as its electron

donor/acceptor capabilities plays a very important role on the structural and electronic properties of the molecules [1].

Vibrational assignments based on FT-IR in the vapour, solution, liquid phases and Raman spectra in the liquid state were reported for aniline. Vibrational spectra of 2,6-dibromo-4-nitro aniline and 2-(methylthio) aniline have been studied by applying the DFT calculations based on Becke-3-Lee-Yang-Parr (B3LYP) level with 6-31G* basis sets by Krishna Kumar *et al.*[3] Honda *et al.* [9] studied the NH stretching vibrations of the aniline and its derivatives (including p-flouroaniline) by using the IR-UV double resonance spectroscopy.

Few reports are available on infrared and Raman studies of anilines and its derivatives [1], but the vibrational spectroscopic analysis of 2-bromo-4,6-dinitroaniline has not been carried out. Literature survey reveals that neither the complete Raman and IR spectra nor the *ab-initio* calculations for 2-bromo-4, 6-dinitro aniline have been reported so far. The aim of present study is to give a complete description of the molecular geometry and molecular vibrations of the title molecule. Theoretical *ab-initio* calculations have been carried out at HF level with 6-31+G (d, p) as the basis set. These calculations have been performed to support our wave number assignments.

MATERIALS AND METHODS

Experimental Details

The compound 2-bromo-4, 6-dinitro aniline in the solid form was purchased from Sigma Aldrich Chemical Pvt. Ltd. West Germany with a stated purity of greater than 98% and was used as such without further purification. The FT-IR spectrum of this compound was recorded in the region 4000-400 cm^{-1} using KBr pallets. The laser Raman spectrum of the title compound was recorded in the region 2000-100 cm^{-1} . The observed experimental FT-IR and laser Raman spectra are shown in figure 2 and 3. The spectral measurements were carried out at USIC, New Delhi.

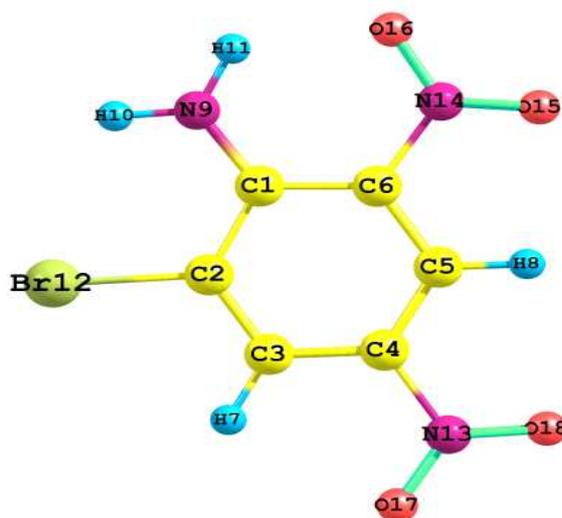


Figure 1 Numbering system adopted in the study for 2-bromo-4, 6-dinitroaniline

Computational Details

The calculations of vibrational wave numbers and geometrical parameters were carried out by using *ab-initio* method at HF level adopting 6-31+G(d, p) as the basis set. The entire calculations were performed on a Pentium IV personal computer using Gaussian 03W program package, invoking gradient geometry optimization. Initial geometry generated from standard geometrical

parameters were minimized without any constraint in the potential energy surface at Hartee-Fock level. The optimized structural parameters were used in the vibrational frequency calculations. Finally, these calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics. By combining the results of the GAUSSVIEW program with symmetry considerations along with available related molecules [22], vibrational frequency assignments were made with high degree of accuracy. Experimental and theoretical vibrational frequencies were compared and these values are found to be in good agreement with each other. Theoretical spectrum are shown in figure (4) and (5).

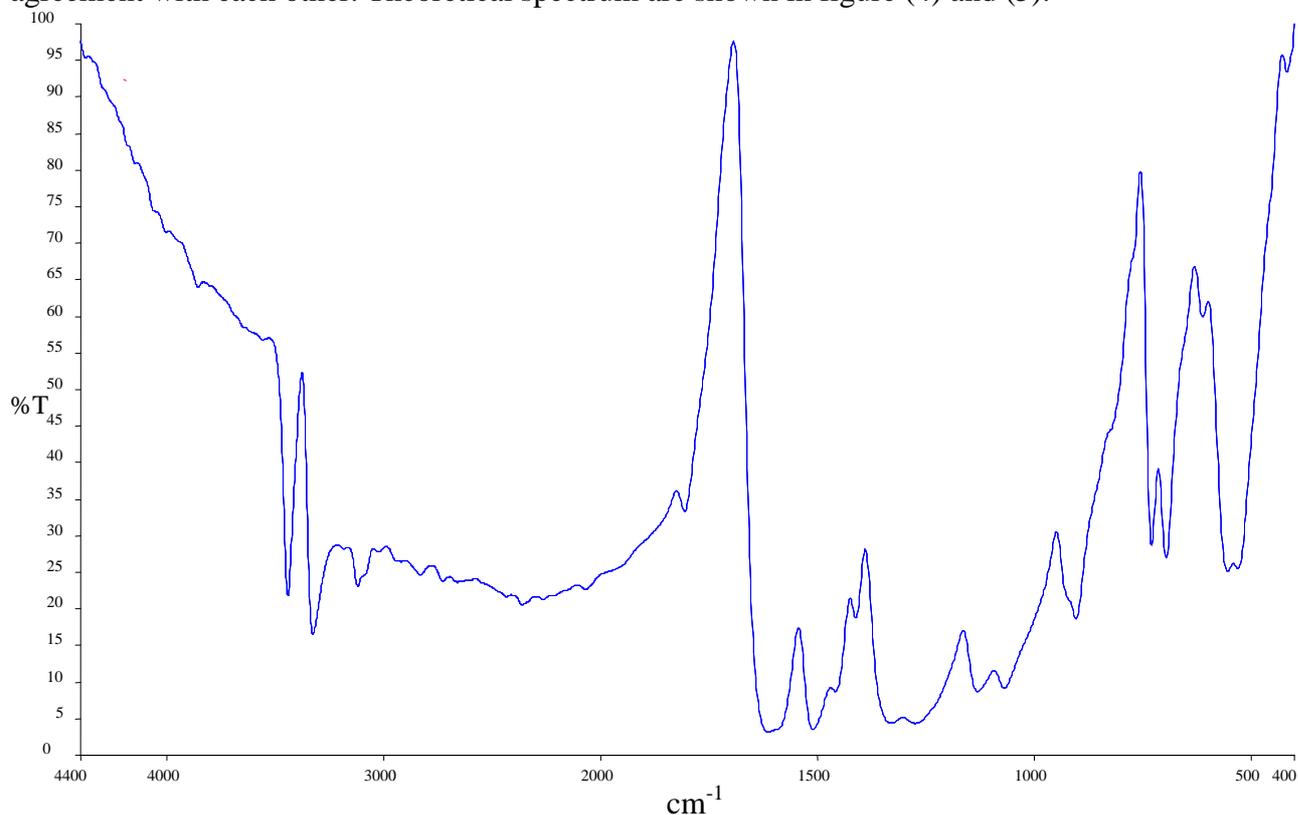


Figure 2 FT-IR spectrum of 2-bromo-4, 6-dinitroaniline

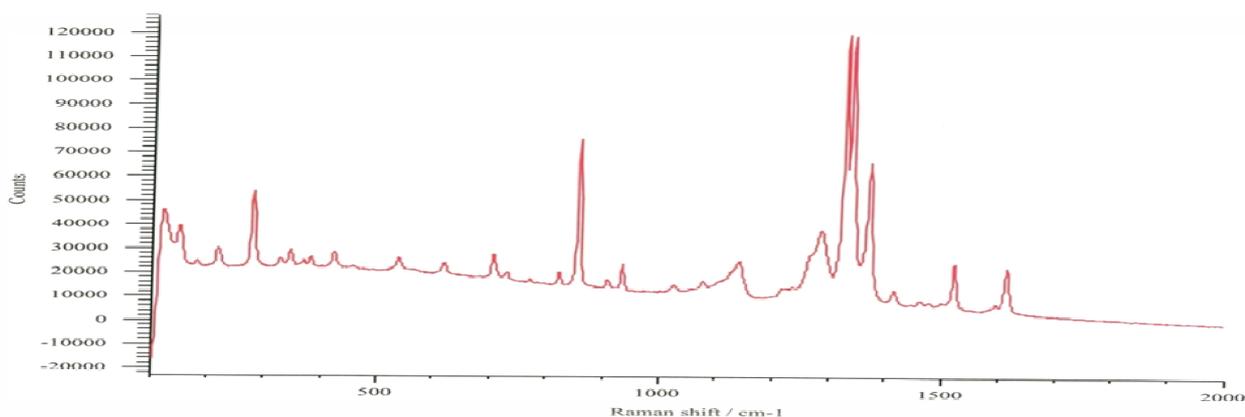


Figure 3 FT-Raman spectrum of 2-bromo-4, 6-dinitro aniline

RESULTS AND DISCUSSIONS

Geometry Optimization

The optimized structural parameters of 2-bromo-4, 6-dinitroaniline using HF/6-31+G (d, p) are listed in table 1 in accordance with the atom numbering scheme given in Figure 1. To the best of our knowledge experimental data on the geometric structure of the title compound are not available. The optimized bond lengths of C-C phenyl ring falls in the range of 1.363-1.424 Å for HF/6-31+G(d, p) which are in good agreement with the experimentally reported values for C-C bond length of the phenyl ring of the similar molecules. Also it is evident from the Table 1 the both C-NO₂ bonds have identical bond length of 1.448 Å and 1.451 Å. This is also evident from the Table 1 that both the N-H bond has same bond length of 0.992 Å. Bond angles are also shown in the table 1. The structural changes on the carbon skeleton concern both the bond distances and bond angles. They are most pronounced at the place of substitution and depend on the electro negativity as well as on the acceptor/donor character of the substituent [2], [3].

Vibrational Analysis

The molecule 2-bromo-4, 6-dinitro aniline has 18 atoms with 48 normal modes of fundamental vibration. All the 48 fundamental vibrations are active in both IR and Raman. Vibrational assignments are based on the comparison of calculated and observed Raman & IR frequencies and activities as well as the depolarization ratios of Raman bands. The assignments are shown in Table 2 for several of phenyl ring modes along with substituents. The harmonic vibrational frequencies calculated for 2-bromo-4,6-dinitro aniline at HF level using 6-31+G(d,p) as the basis set and observed FT-IR & FT-Raman frequencies for various modes of vibrations have been collected in Table 2. Comparison of the frequencies calculated with experimental values reveals the overestimation of calculated vibrational modes. The vibrational frequencies were scaled down by a factor of 0.8923 for HF computation [3].

Table 1: Optimized bond lengths and bond angles of 2-bromo-4, 6-dinitroaniline at HF/6-31+G (d,p) level.

S. No.	Parameters		Parameters		Parameters	
	Bond Lengths	(Å)	Bond Angle		Bond Angle	Degree
1	(C1-C2)	1.424	(C2-C1-C6)	115.2	(C4-N13-O17)	117.3
2	(C1-C6)	1.418	(C2-C1-N9)	120.2	(C4-N13-O18)	117.8
3	(C1-N9)	1.332	(C1-C2-C3)	122.7	(C6-C5-H8)	119.8
4	(C2-C3)	1.363	(C1-C2-Br12)	119.1	(C5-C6-N14)	115.8
5	(C2-Br12)	1.891	(C6-C1-N9)	124.6	(C6-N14-O15)	117.9
6	(C3-C4)	1.394	(C1-C6-C5)	122.3	(C6-N14-O16)	118.5
7	(C3-H7)	1.071	(C1-C6-N14)	121.9	(H10-N9-H11)	120.1
8	(C4-C5)	1.368	(C1-N9-H10)	119.8	(O17-N13-O18)	125
9	(C4-N13)	1.448	(C1-N9-H11)	120.1	(O15-N14-O16)	123.6
10	(C5-C6)	1.387	(C3-C2-Br12)	118.2		
11	(C5-H8)	1.07	(C2-C3-C4)	119.5		
12	(C6-N14)	1.451	(C2-C3-H7)	120.7		
13	(N9-H10)	0.992	(C4-C3-H7)	119.8		
14	(N9-H11)	0.992	(C3-C4-C5)	120.9		
15	(N13-O17)	1.196	(C3-C4-N13)	119.4		
16	(N13-O18)	1.194	(C5-C4-N13)	119.7		
17	(N14-O15)	1.191	(C4-C5-C6)	119.5		
18	(N14-O16)	1.202	(C4-C5-H8)	120.8		

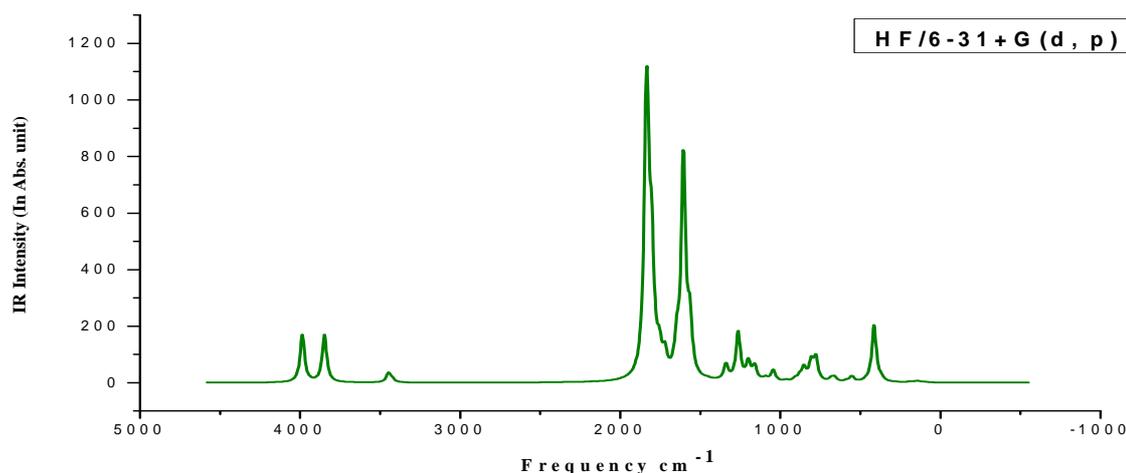


Figure 4 Theoretical FT-IR spectrum of 2-bromo-4, 6-dinitro aniline

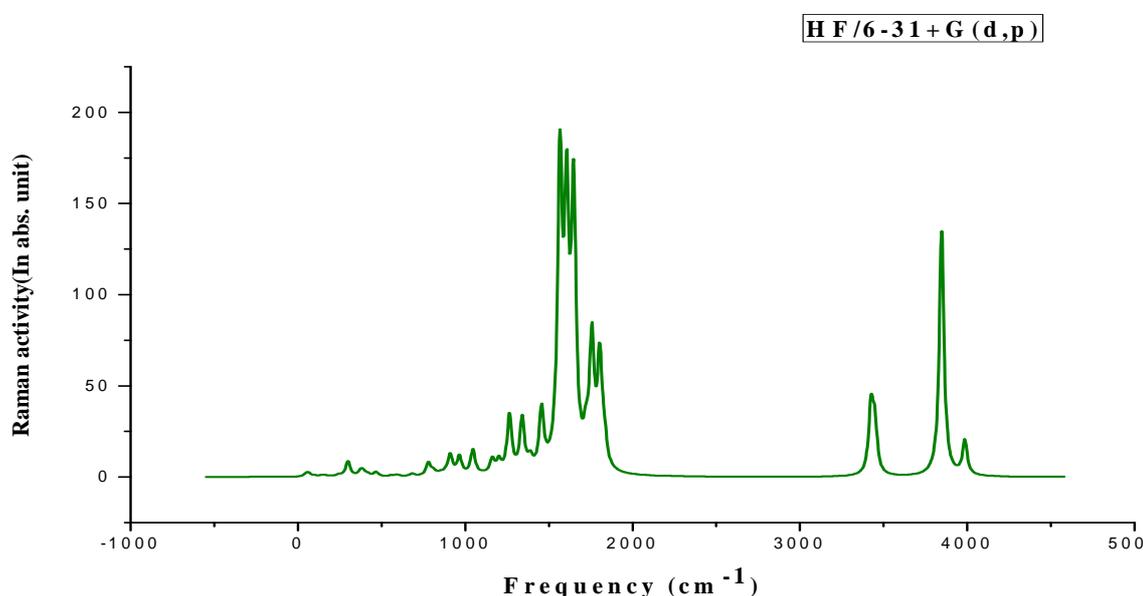


Figure 5 Theoretical FT-Raman spectrum of 2-bromo-4, 6-dinitro aniline

C-H vibrations:

The hetero atomic structure 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 C-H stretching vibrations [1]. In this region, the bands are not affected, appreciably by the nature of the substituent [1], [3], [4], [12]. The titled compound is tetra-substituted aromatic system; it has two hydrogen atoms on the ring. The C-H stretching modes usually appear with the strong Raman intensity and are highly polarized [9], [10]. May be owing to this high polarization, Raman bands have not been observed in experimental spectra [1]. The C-H stretching vibrations of benzene derivatives generally appear above 3000 cm^{-1} . In the experimental IR spectrum of the titled compound, the bands at 3045, 3080, 3121, 3180 cm^{-1} are assigned as C-H stretching vibrations [10], [4], [6], [9]. Scaled frequency 3069 cm^{-1} at the HF/6-31+G(d, p) level corresponds to C5-H8 stretching vibration and the frequency 3048 cm^{-1} corresponds to C3-H7 stretching vibration. From the above discussion this is clear that experimental and theoretical C-H stretching vibrations are in close agreement with each other. The C-H out of plane-bending and in plane aromatic C-H bending vibrations corresponds to C3-H7 & C5-H8 unit. The in-plane bending vibrations appear in the range 1300-1000 cm^{-1} for the substituted benzenes and the out of plane bending vibrations occur in the frequency range 1000-750 cm^{-1} even though found to be

contaminated by C-N and C-NH₂ stretching are in the range found in the literature [1], [12]. The bands are sharp but are of weak to medium intensity [5], [6]. The medium and strong intensity bands at 770 , 904 cm⁻¹ in IR spectrum and 810 , 900 cm⁻¹ in Raman spectrum are assigned as C-H out of plane bending , these bands falls in the IR/Raman values of 770-990cm⁻¹. The C-H in plane bending vibrations falls in the IR / Raman values of 1121-1250 cm⁻¹. The experimentally recorded C-C-C out of plane & C-C-C in plane bending modes have been found to be consistent with the available data [12], [13]. The C-C-C out of plane & in plane bending vibrations is given in the table 3.

Table 2: Experimental and HF level computed vibrational frequencies (cm⁻¹) obtained for 2-bromo-4, 6-dinitro aniline

Mode No.	Experimental		HF/6-31+G(d,p)				Depol.	Vibrational Assignments
	FT-IR	FT-Raman	Unscaled	Scaled	I _{IR}	I _{Raman}		
1			49	44	0	2	0.7500	τ(NO ₂)
2			64	57	0	2	0.7500	τ(NO ₂)
3		120 (vs)	101	89	2	0	0.7500	τ(NH ₂)
4			140	125	4	1	0.7500	γ(C- C-C)
5			159	142	2	1	0.7301	β(C-NO ₂), β(C-Br)
		150 (vs)						γ(C-Br)
6			191	170	2	0	0.6470	β(C-NO ₂), β(C-Br)
		180 (w)						γ(C- NH ₂)
7			243	217	0	1	0.7500	γ(C- C-C), γ(C-H)
		222 (vs)						β(C-Br), γ(C- NO ₂)
8		277(vs)	298	266	0	8	0.1539	ν(C-Br)
9		322(w)	370	329	9	0	0.7500	γ(C- NH ₂), β(C-C-C)
10			374	333	1	2	0.7089	β(C-NO ₂)
11			387	345	1	2	0.3176	β(C-C-C)
12		340(s)	415	369	199	0	0.7500	γ(C-NH ₂)
13			415	370	2	1	0.5692	ω(NH ₂)
		355(w)						β(C-C-C)
		370(w)						β(C-C-C)
14	417 (s)	415(s)	465	414	4	2	0.4899	β(C-NH ₂)
		448(w)						γ(C-C-C)
15		480(vw)	554	493	19	0	0.7500	γ(C-C-C), γ(C-H)
16			589	524	5	1	0.4575	β(C-C-C), ρ(NO ₂)
	545 (s)	538(s)						ρ(NO ₂)
17			610	543	0	0	0.7500	γ(C-H),t(NH ₂)
	555 (vs)	602(s)						ρ(NO ₂)
18			662	589	15	0	0.7500	t(NH ₂)
19			683	608	11	1	0.3670	β(C-C-C), β(C-NH ₂)
	612 (vs)	670(vw)						β(C-C-C), β(C-NO ₂)
20	695 (vs)		779	693	79	7	0.1230	ω(NO ₂)
		700(s)						ω(NO ₂)
	729 (vs)	715(s)						ω(NO ₂)
21			808	719	66	2	0.2550	β(C-C-C)
22			833	741	0	0	0.7500	γ (C-C-C), ω(NO ₂)
23			853	760	46	1	0.7500	γ(C-H), ω(NO ₂)
	770 (w)	770(w)						γ(C-H)
		780(vw)						β(C-C-C),γ(C-H)
24			881	784	16	1	0.7500	γ (C-C-C), ω(NO ₂)
25			909	809	8	11	0.0824	β(C-H)
		810(s)						γ(C-H)
		840(vw)						γ(C-H)
26	830 (w)	852 (vs)	965	858	5	10	0.0477	δ(NO ₂)

	904 (vs)	900 (s)						$\delta(\text{NO}_2), \gamma(\text{C-H})$
27	935 (w)	935 (vs)	1045	930	39	14	0.4227	$\nu(\text{C-NO}_2)$
28		970(vw)	1092	972	11	0	0.7500	$\gamma(\text{C-H})$
29		990(vw)	1113	991	2	0	0.7500	$\gamma(\text{C-H})$
		1022(w)						ring breathing
30			1161	1033	51	8	0.2184	$\beta(\text{C-H}), t(\text{NH}_2)$
31			1201	1068	65	7	0.6358	$\beta(\text{C-H}), t(\text{NH}_2)$
	1069 (vs)	1068(w)						$t(\text{NH}_2)$
		1119(w)						trigonal bending
32		1121(w)	1264	1125	172	32	0.3037	$\beta(\text{C-H})$
	1131(s)	1140 (s)						$\beta(\text{C-H})$
		1142(w)						$\beta(\text{C-H})$
33		1145(vw)	1340	1193	56	29	0.4997	$\beta(\text{C-H})$
34			1388	1236	0	6	0.7490	$\beta(\text{C-H})$
		1209(w)						$\beta(\text{C-H})$
35		1250(w)	1456	1296	3	32	0.1143	$\beta(\text{C-H})$
	1275 (w)	1285 (s)						$\nu(\text{C-C}), \nu(\text{C-NH}_2)$
36			1565	1393	106	30	0.1745	$\nu(\text{C-C}), \beta(\text{C-H})$
37			1566	1393	81	133	0.1807	$\nu(\text{C-C}), \nu(\text{C-NH}_2), \beta(\text{C-H})$
38	1340(w)	1326(vs)	1606	1429	775	135	0.6961	$\nu_s(\text{NO}_2)$
39		1372(vs)	1647	1466	108	146	0.1935	$\nu_s(\text{NO}_2)$
40	1411 (vs)	1418(s)	1722	1532	69	14	0.7482	$\nu(\text{C-C})$
41	1460 (s)	1470 (w)	1757	1563	85	69	0.6894	$\nu(\text{C-C})$
		1480(w)						$\nu_s(\text{C-C})$
42	1511 (vs)	1510(vw)	1828	1627	382	58	0.6041	$\nu_{as}(\text{NO}_2), \nu(\text{C-H})$
43		1524 (s)	1838	1636	390	14	0.5758	$\nu_{as}(\text{NO}_2), \nu(\text{C-H})$
	1570 (w)	1590 (w)						$\nu_{as}(\text{NO}_2)$
44	1615 (vs)	1618 (s)	1803	1605	726	2	0.3965	$\delta(\text{NH}_2)$
		1620(w)						$\nu(\text{C-C})$
		1622(w)						$\nu(\text{C-C})$
45	3045(w)		3425	3048	11	36	0.2998	$\nu(\text{C-H})$
	3080(w)							$\nu(\text{C-H})$
	3121 (vs)							$\nu(\text{C-H})$
46	3180(w)		3448	3069	32	26	0.2435	$\nu(\text{C-H})$
47	3327 (vs)		3848	3424	168	135	0.1126	$\nu_s(\text{N-H})$
48	3444 (vs)		3986	3547	168	19	0.7322	$\nu_{as}(\text{N-H})$

Where *s*-strong; *vs*-very strong; *w*-weak; *vw*-very weak; *v*-stretching; ν_s -symmetric stretching; ν_{as} -asymmetric stretching; β -in-plane-bending; γ -out-of-plane bending; ω -wagging; ρ -rocking; *t*-twisting; τ -torsion; δ -scissoring; I_{IR} -IR Intensities; I_{Raman} -Raman Intensities; *Depol.*-Depolarization

Phenyl ring vibrations

The vibrational motions of a benzene ring are not isolated but involve the entire molecule. These vibrations are usually observed between 1650-1400 cm^{-1} and often lead to four observable absorptions of variable intensity [8], [12]. As a result of symmetry, benzene, generally does not exhibit these bands. However most benzene derivatives do and usually 2 or 3 of these bands are sufficiently separate from other absorptions that they can be identified with a reasonable degree of confidence. In general the bands around 1650-1400 cm^{-1} in benzene derivatives are assigned to skeletal stretching C – C bands [12], [9]. The bands observed at 1412 ,1460 cm^{-1} in IR spectrum and 1418 , 1470 , 1480 , 1620 , 1622 cm^{-1} in Raman spectrum are assigned to C-C stretching vibrations for the titled compound [6], [7], [15]. At the HF/6-31+G (d, p) level scaled frequencies at 1393, 1532 and 1563 are assigned as C-C stretching vibrations. It means the experimental and theoretical C-C stretching is in good agreement with each other.

NH₂ group vibration

The NH₂ group has two N-H stretching vibrations, one being symmetric and other asymmetric. The frequency of asymmetric vibration is higher than that of symmetric one [1]. The NH₂ group will involve the symmetric and asymmetric N-H stretching vibrations. In the case of nearly all the primary aromatic amines [1], two bands occur in the region 3500-3300 cm⁻¹ (Bellamy 1959) [14], [1], [22]. The bands around 3500 cm⁻¹ have been assigned by a large number of workers as asymmetric N-H stretching and that is appearing around 3400 cm⁻¹ as symmetric N-H stretching vibration. So the band observed at 3444 cm⁻¹ has been assigned as N-H asymmetric stretching (NH₂ asymmetric stretching) vibration and the band observed at 3327 cm⁻¹ has been assigned as N-H symmetric stretching (NH₂ symmetric stretching) vibration. At the HF/6-31+G (d, p) level asymmetric N-H stretching is observed at 3547 cm⁻¹ and symmetric N-H stretching at 3424 cm⁻¹.

Bellamy [7], [8] suggested that the NH₂ scissoring mode lies in the region of 1700-1600 cm⁻¹ in nearly all primary aromatic amines. In this region C-C stretching modes also give rise to absorption, however, in almost all the aniline derivatives the scissoring mode is found at a higher frequency than C-C stretching [11]. In accordance with their conclusions, the scissoring mode due to one NH₂ group in the present compound is identified at 1615 cm⁻¹ in IR spectra & the band at 1618 cm⁻¹ in Raman spectra is also assigned for the NH₂ scissoring mode. According to the theoretical calculations this scissoring identified at 1605 cm⁻¹. NH₂ twisting frequency is expected to occur in the region 1170-1060 cm⁻¹ [1], [12]. So the strong band observed at 1069 cm⁻¹ in the IR spectrum and a weak band at 1068 cm⁻¹ in Raman spectra are assigned for NH₂ twisting mode of the mentioned compound. This twisting mode observed at 1033, 1068 cm⁻¹ at HF/6-31+G (d, p) level.

Similarly the NH₂ wagging modes lies in the region [1], [2], [18] between 678-631 cm⁻¹, so the wagging mode due to presence of one NH₂ group is identified at 695 cm⁻¹ in the IR spectra and at 700 cm⁻¹ in the Raman spectra of the above mentioned compound whereas at the theoretical level this band observed at 370 cm⁻¹. In the present work, the strong band observed in Raman spectra at 120 cm⁻¹ is assigned to NH₂ torsional mode and the same band at 89 cm⁻¹ at the theoretical level. A band at 1275 cm⁻¹ in the IR spectra of the mentioned compound and the strong band at 1285 cm⁻¹ in the Raman spectra are assigned to the C-NH₂ stretching mode. This stretching vibration observed at 1393 cm⁻¹ at the theoretical level.

C-Br Vibrations

In the titled compound there is one bromine group at the second position. In the earlier vibrational studies of bromoanilines, dibromoanilines, 4-amino-3-bromotoluene and 5-amino-2-bromotoluene (1) the C-X stretching vibration mode of a heavy substituent lies in the low frequency region 200-480 cm⁻¹ (10), (13). So the sharp band which is observed at 277 cm⁻¹ in the Raman spectra of the titled compound associated with the C-Br stretching mode by way of comparison with the C-Br stretching frequencies reported in number of bromobenzenes (8), [15], [16]. At the Hartee-Fock level C-Br stretching observed at 266 cm⁻¹, found to be in good agreement with the experimental results. The C-Br in plane bending mode lies in the low frequency region below 440 cm⁻¹. The assignments made for these vibrations are given in the table and are in agreement with those reported in a number of related molecules [8], [12], [23]. The C-Br out of plane bending vibrations lies in the low frequency region below 350 cm⁻¹. Theoretical and experimental vibrational frequencies are in close agreement with each other.

Internal vibrations of NO₂ group

There are two NO₂ groups at the 4th and 6th position. The most characteristic bands in the spectra of nitro compounds are due to NO₂-stretching vibrations, which are two useful group wave

numbers, not only because of their spectral position but also for their strong intensity[7], [14]. The bands seen at 1524, 1590 cm^{-1} in the Raman spectrum and 1511, 1570 cm^{-1} in the IR spectrum is assigned as $\nu_{\text{as}}(\text{NO}_2)$ for the title compound. The bands at 1340 cm^{-1} in IR spectrum and 1326, 1372 cm^{-1} in the Raman spectrum is assigned as $\nu_{\text{s}}(\text{NO}_2)$ modes. For the titled compound 2B46DNA, the bands observed at 830, 904 cm^{-1} in case of IR spectrum and a very strong band at 852 and a weak band at 900 cm^{-1} in case of Raman spectrum are assigned for the nitro scissoring mode, $\nu_{\text{sc}}(\text{NO}_2)$. For the above mentioned compound the bands at 695, 729 cm^{-1} in the IR spectrum and the bands at 700, 715 cm^{-1} in the Raman spectrum are assigned as $\nu_{\text{w}}(\text{NO}_2)$ wagging mode, $\nu_{\text{w}}(\text{NO}_2)$. In aromatic compounds the $\nu_{\text{r}}(\text{NO}_2)$ rocking mode, $\nu_{\text{r}}(\text{NO}_2)$ is active in the region $540 \pm 70 \text{cm}^{-1}$ [20], [21], [22]. Nitrobenzene [3] show this rocking mode at 531 cm^{-1} . In the present case, the bands at 545, 555, 612 cm^{-1} in case of IR spectrum and the bands at 538, 602 cm^{-1} in Raman spectrum are the $\nu_{\text{r}}(\text{NO}_2)$ rocking band, $\nu_{\text{r}}(\text{NO}_2)$ (11),(12). In the above mentioned compound torsion of NO_2 is missing in both IR and Raman spectrum. Using 3D Gauss view visualization programme asymmetric NO_2 stretching [22], [18], [12] are observed at 1627, 1636 cm^{-1} whereas the symmetric stretching appeared at the lower scaled frequencies 1429, 1466 cm^{-1} . At the HF/6-31+G (d, p) level scissoring of NO_2 appeared at 858 cm^{-1} and wagging as strong bands at 693, 760, 784 cm^{-1} . Rocking vibrations of NO_2 group identified at 524 cm^{-1} . Torsional mode also appeared in this theoretical calculation at 44, and 57 cm^{-1} . From all this discussion it is clear that the internal vibrations of nitro group from theoretical and experimental calculations are close to each other.

CONCLUSIONS

In the present work we have performed the experimental and theoretical vibrational analysis of 2B46DNA for the first time. The equilibrium geometry computed by HF level for both the bond lengths and bond angles performed better. The vibrational frequencies analysis by HF method agrees satisfactorily with experimental results. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of 2B46DNA were examined and proposed in this investigation. The difference between the observed and calculated wave number values of most of the fundamentals is very small and therefore, the assignment seems to be correct.

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