



## Molecular structure and vibrational spectra of Benzophenone hydrazone molecule by density functional theory

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### ABSTRACT

Quantum chemistry calculations have been performed to compute optimized geometry, NBO analysis, harmonic vibrational frequency along with intensities in IR spectrum by using B3LYP/6-31G\* and B3LYP/6-311+G\*\* levels for Benzophenone hydrazone (C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>) in the ground state. Theoretical vibrational spectra of the title compound were interpreted by means of PEDs using MOLVIB program. The scaled harmonic vibrational frequencies have been compared with experimental FT-IR spectra. A detailed interpretation of the infrared spectra of the title compound is reported. The shortening of C–H bond length and blue shifting of the CH stretching wavenumber suggest the existence of improper weak C–H...N hydrogen bonding, which is also confirmed by the natural bond orbital analysis. The theoretical spectrograms for FT-IR spectra of the title compound have also been constructed.

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### 1. Introduction

Organic materials with very large second-order nonlinear optical (NLO) susceptibilities have attracted a lot of attention because of their potential applications in electro-optic modulation [1–4], frequency conversion [5,6] and THz wave generation [7]. The above said facts motivated the materials scientists to search the novel materials for nonlinear optical applications. One of the ways in which an organic molecule can have a large optical nonlinearity is by possessing a conjugated system of bonds which gives rise to a strong p-electron localization. The delocalization of the p-electrons can be further enhanced by the addition of donor and acceptor groups at the opposite ends of the conjugated system [8]. The large second order optical nonlinearities, short transparency cut-off wavelength and stable physiochemical performance are needed in the realization of most of the recent electronic applications.

Benzophenone (BP) is one of the potential organic NLO materials, which has NLO efficiency much higher than urea with non-hygroscopic nature [9]. It is known that the crystals of BP are optically active and exist in two enantiomorphous modification [10,11] orthorhombic space group class P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>; they have a strong negative birefringence [12]. Davydova et al. [13] measured the Raman spectra of BP molecule. Tsonko et al. [14] studied the vibrational spectra and structure of benzophenone in solid state and in solution.

Arivanandhan et al. [15] studied the grown benzophenone single crystals. Recently, a derivative of BP molecule, Benzophenone hydrazone (BH, C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>), was synthesized [16]. But so far no theoretical work is done on vibration spectra of the nonlinear optical material because of its high complexity and low symmetry. Therefore, we made an investigation and studied the structure and vibrational frequencies of the title compound.

Density functional theory (DFT) approaches, especially those using hybrid functional, have evolved to a powerful and very reliable tool, being routinely used for the determination of various molecular properties. B3LYP functional has been previously shown to provide an excellent compromise between accuracy and computational efficiency of vibrational spectra for large and medium size molecules [17–20]. It is well known that vibrational frequencies obtained by quantum chemical calculations are typically larger than their experimental counterparts, and thus, empirical scaling factors are usually used to better match the experimental vibrational frequencies [21]. These scaling factors depend both on the method and basis sets used in calculations, they are determined from the mean deviation between the calculated and experimental frequencies. In addition, the standard frequency scaling factor of B exchange functionals is very close to unity so the B-based procedures can often be used without scaling. For this reason, by using the DFT (B3LYP) method with 6-31G\* and 6-311+G\*\* basis sets, we have calculated the geometric parameters and the vibrational spectrum of the title compound in the ground state and compared with the experimental vibrational frequencies. These calculations are expected to provide new insight into the vibrational spectrum and molecular parameters.

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**Table 1**  
Optimized geometrical parameters of BH molecule with 6-31G\* and 6-311+G\*\* basis sets, bond lengths (Å) and bond angles (°).

Parameter	B3LYP		Exp <sub>BH</sub>	Exp <sub>BP</sub>	Parameter	B3LYP		Exp <sub>BH</sub>	Exp <sub>BP</sub>
	6-31G*	6-311+G**				6-31G*	6-311+G**		
N(1)–N(2)	1.370	1.365	1.371(3)	–	C(13)–C(8)–C(9)	118.6	118.88	118.56(2)	–
N(1)–C(7)	1.294	1.289	1.286(2)	–	C(13)–C(8)–C(7)	120.86	120.59	120.49(2)	–
C(9)–C(10)	1.395	1.394	1.384(3)	–	C(9)–C(8)–C(7)	120.53	120.52	120.94(2)	–
C(9)–C(8)	1.405	1.401	1.383(3)	–	N(1)–C(7)–C(8)	123.41	122.44	122.92(2)	–
C(8)–C(13)	1.405	1.401	1.392(3)	–	N(1)–C(7)–C(6)	116.96	117.94	118.26(2)	–
C(8)–C(7)	1.499	1.501	1.496(3)	–	C(8)–C(7)–C(6)	119.63	119.62	118.82(2)	121.6
C(7)–C(6)	1.487	1.485	1.482(3)	1.496	C(1)–C(6)–C(5)	118.21	118.25	118.3(2)	–
C(6)–C(1)	1.408	1.406	1.391(3)	1.388	C(1)–C(6)–C(7)	120.47	120.80	120.92(2)	–
C(6)–C(5)	1.405	1.403	1.390(3)	1.400	C(5)–C(6)–C(7)	121.32	120.96	120.81(2)	118.2
C(1)–C(2)	1.391	1.388	1.377(4)	1.402	C(6)–C(1)–C(2)	120.81	120.74	120.8(2)	119.7
C(10)–C(11)	1.397	1.394	1.381(4)	–	C(11)–C(10)–C(9)	120.14	120.09	120.0(2)	–
C(5)–C(4)	1.396	1.395	1.383(4)	1.408	C(6)–C(5)–C(4)	120.86	120.86	120.5(2)	118.6
C(13)–C(12)	1.396	1.394	1.366(4)	–	C(8)–C(13)–C(12)	120.64	120.51	120.5(2)	–
C(12)–C(11)	1.396	1.394	1.362(4)	–	C(11)–C(12)–C(13)	120.20	120.17	120.9(2)	–
C(4)–C(3)	1.395	1.392	1.383(5)	1.367	C(3)–C(4)–C(5)	120.34	120.31	120.1(2)	120.3
C(3)–C(2)	1.399	1.397	1.363(4)	1.354	C(4)–C(3)–C(2)	119.33	119.34	119.9(3)	120.6
C(1)–H(1)	1.085	1.082	–	–	C(12)–C(11)–C(10)	119.69	119.75	119.7(2)	–
C(2)–H(2)	1.087	1.085	–	–	C(3)–C(2)–C(1)	120.45	120.50	120.4(3)	120.8
C(3)–H(3)	1.087	1.084	–	–	C(1)–C(6)–C(7)–C(8)	–121.0	–106.51	–	–
C(4)–H(4)	1.087	1.084	–	–	N(2)–N(1)–C(7)–C(8)	178.37	177.77	–	–
C(5)–H(5)	1.086	1.083	–	–	N(2)–N(1)–C(7)–C(6)	–2.33	–2.69	–	–
N(2)–N(1)–C(7)	120.0	120.01	119.05(2)	–	C(1)–C(6)–C(5)–C(4)	–0.05	0.16	–	–
C(10)–C(9)–C(8)	120.73	120.59	120.31(2)	–	C(13)–C(8)–C(9)–C(10)	0.12	–0.06	–	–
					C(5)–C(6)–C(7)–C(8)	59.80	74.71	–	–

The present study was undertaken with the following two-fold objectives. One is to predict the IR spectrum of the title compound. The other is to assign all predicted frequencies using normal mode analysis.

## 2. Computational details

All of the electronic structure calculations were performed using density functional theory (DFT) as implemented in the Gaussian'03 suite of programs [22]. The hybrid non-local B3LYP [23,24] functional was used. Optimized geometries were initially calculated using the 6-31G\* [25] basis set before re-optimization with 6-311+G\*\* basis set. Optimized geometries of the molecules were calculated without any geometrical restriction. The title compound was found to be minima on their respective potential energy surfaces as revealed by the lack of imaginary frequencies. The vibrational wavenumber, IR intensity and Raman activities have also been calculated at the DFT-B3LYP level using the 6-31G\* and 6-311+G\*\* basis sets. A uniform scaling factor of 0.98 [26] was adopted for vibrational frequencies obtained from B3LYP/6-311+G\*\* and a scaling factor of 0.96 [27] for B3LYP/6-31G\*. Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of potential energy distribution (PED) with the version V7.0-G77 of the MOLVIB program written by Sundius [28,29].

## 3. Results and discussion

### 3.1. Molecular geometry

The optimized geometrical parameters, namely, bond lengths and angles calculated by B3LYP/6-31G\* and B3LYP/6-311+G\*\* levels listed in Table 1 are in accordance with atom numbering scheme given in Fig. 1. The experimental data obtained by Anandha Babu et al. [16] are also included. In order to have a comparison, the experimental geometrical data of BP molecule [14] are also listed in Table 1. The molecular structure of BP molecule is given in Fig. 1.

Optimizations for model polycyclic aromatic hydrocarbons using the B3LYP/6-31G\* have previously yielded structural bond lengths and angles in good agreement to experiment values [30]. But it is noted that the optimization parameters calculated by

B3LYP/6-311+G\*\* method for BH is superior to that calculated by B3LYP/6-31G\* method, when we compare the computational results with the experimental values.

Optimized structure yields identical bond lengths for the C<sub>5</sub>–C<sub>6</sub> and C<sub>1</sub>–C<sub>6</sub>, C<sub>5</sub>–C<sub>4</sub> and C<sub>4</sub>–C<sub>3</sub> bonds at the two levels of calculations B3LYP/6-31G\* and B3LYP/6-311+G\*\*. The calculated C<sub>5</sub>–C<sub>6</sub> and C<sub>1</sub>–C<sub>6</sub> bonds by B3LYP/6-311+G\*\* are all larger than the experimental C<sub>5</sub>–C<sub>6</sub> and C<sub>1</sub>–C<sub>6</sub> bonds of BH and BP molecules. The bond lengths of these C–C bonds are much shorter than the typical C–C single bond (1.54 Å) and longer than the C=C double bond (1.34 Å) [31]. For BH molecule, it is noted that the experimental C<sub>7</sub>–C<sub>6</sub> bond is 1.482 Å, but the experimental C<sub>7</sub>–C<sub>6</sub> bond of BP molecule is 1.496 Å. This shows the conjugation effect of hydrazone group.

The C<sub>7</sub>=N<sub>1</sub> bond length is 1.289 Å at B3LYP/6-311+G\*\* level, which is shorter than that of the C=N bond (1.33 Å) [32], which result from the conjugation effect of the coplanar atoms, showing the aromaticity of the benzene ring. The N<sub>1</sub>–N<sub>2</sub> bond length is higher at B3LYP/6-31G\* level than that at B3LYP/6-311+G\*\* level and has been calculated to be 1.365 Å at B3LYP/6-311+G\*\* level.

Interesting, the DFT geometry optimization performed on the BH molecule indicated that it exhibits intramolecular hydrogen bond interaction. The magnitudes of bond angles C<sub>2</sub>–C<sub>1</sub>–H<sub>1</sub> and C<sub>6</sub>–C<sub>1</sub>–H<sub>1</sub> are 120.53° and 118.73° at B3LYP/6-311+G\*\* level, respectively, which indicates that the C<sub>1</sub>–H<sub>1</sub> bond is not symmetrically disposed on C<sub>1</sub>, rather it is tilted toward the N<sub>1</sub> atom due to propensity of N<sub>1</sub> atom to form H-bonding with the H<sub>1</sub> atom. It is noted that the distance between N<sub>1</sub> and H<sub>1</sub> atoms is 2.48 Å, while the C<sub>1</sub>–N<sub>1</sub> bond length is 2.81 Å.

All the dihedral angles on the benzene ring are either 0° or 180° with ±0.5° at B3LYP/6-311+G\*\* level. The title compound consists of two benzene rings, each forming a plane with their dihedral angle of 74.4° at B3LYP/6-311+G\*\* level.

### 3.2. Vibrational assignments

The optimized structural parameter were used to compute vibrational frequencies of the compound at the B3LYP/6-31G\* and B3LYP/6-311+G\*\* methods. The goal of the vibrational analysis is to find vibrational modes connected with specific molecular structures of calculated compound.

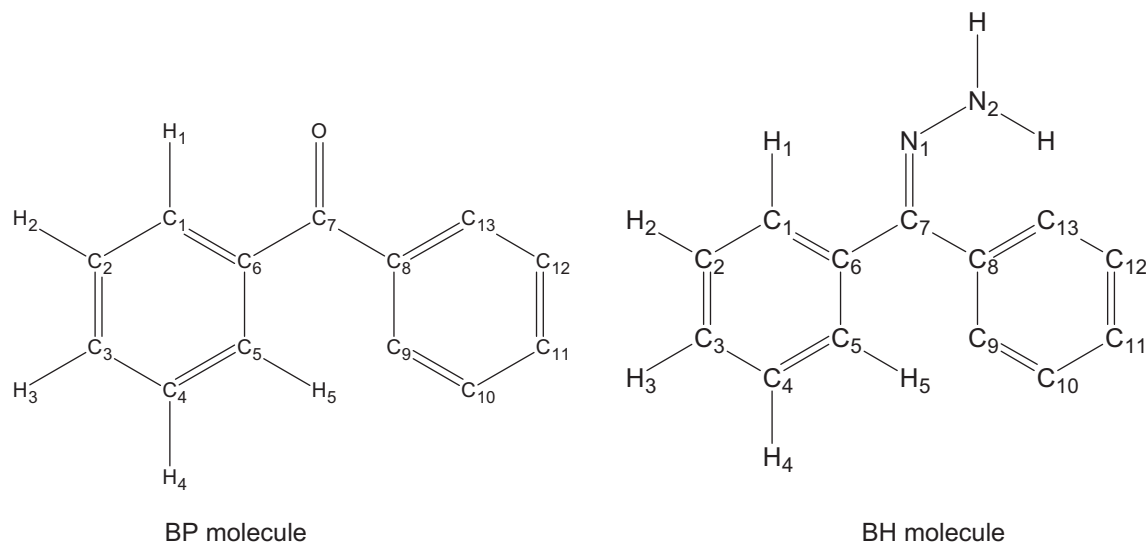


Fig. 1. Molecular structures and atom numbering scheme of BP and BH molecules.

The theoretically calculated DFT force fields were transformed to this latter set of vibrational coordinates and used in all subsequent calculations. Table 2 presents the calculated vibrational frequencies, IR intensities, Raman activity and normal mode descriptions (characterized by PED) of the BH compound studied. The experimental IR intensity of BH and BP molecules are also listed in Table 2.

Comparing the experimental values with the calculated IR intensity, generally, the results calculated by B3LYP/6-311+G\*\* method are closer to the experimental values than those calculated by B3LYP/6-31G\* method. So we will use the results calculated by B3LYP/6-311+G\*\* method to have a vibrational analysis. Calculated IR intensities help us to distinguish and more precisely assign those fundamentals which are close in frequency. Anandha Babu et al. [16] recorded the FT-IR spectra of BH crystals in the range 4000–450  $\text{cm}^{-1}$ , so we only listed the vibrational frequencies which are bigger than 450  $\text{cm}^{-1}$  in Table 2.

### 3.2.1. C–H vibrations

According to Roeges [33], the CH stretching vibrations of the phenyl ring are expected in the region 3120–3000  $\text{cm}^{-1}$ . In this region, the bands are not affected appreciably by the nature of the substituent. In the present theoretical study, the calculated values of these modes for the title compound are 3097, 3098, 3105, 3106, 3112, 3119, 3125, 3127, 3129, 3139  $\text{cm}^{-1}$  at B3LYP/6-311+G\*\* method. Experimentally the bands are observed at 3055  $\text{cm}^{-1}$  in the IR spectrum for BH molecule. For BP molecule, the CH stretching vibrations of the phenyl ring are observed at 3003, 3065, 3069, 3088 and 3102  $\text{cm}^{-1}$ .

The C–H out of plane deformation is observed between 1000 and 700  $\text{cm}^{-1}$  [33]. The DFT calculations give these modes at 767, 775, 840, 849, 914, 918, 953, 971, 973, 986, 990  $\text{cm}^{-1}$  for BH. The C–H out of plane deformation are reported by Anandha Babu et al. [16] at 768  $\text{cm}^{-1}$  for BH molecule, while the C–H out of plane deformation are observed at 812, 850, 948, 970, 993  $\text{cm}^{-1}$  for BP molecule.

The  $\delta(\text{C–H})$  in-plane deformation vibrations are given at 1026, 1031, 1073, 1076, 1156, 1158, 1169, 1177, 1184  $\text{cm}^{-1}$  at B3LYP/6-311+G\*\* method and the experimental values are reported at 1064  $\text{cm}^{-1}$  for BH molecule and 1038, 1078, 1164, 1188  $\text{cm}^{-1}$  for BP molecule.

### 3.2.2. N–H stretching vibration

Hetero aromatics containing an N–H group show its stretching absorption in the region 3500–3220  $\text{cm}^{-1}$ . The position of absorption in this region depends upon the degree of hydrogen bonding, and hence upon the physical state of the sample or the polarity of the solvent [34]. For the title compound, the N–H symmetric stretching mode is observed at 3270  $\text{cm}^{-1}$  and N–H asymmetric stretching is observed at 3421  $\text{cm}^{-1}$ . DFT calculations give the N–H symmetric stretching vibration at 3386  $\text{cm}^{-1}$  and asymmetric stretching vibration at 3558  $\text{cm}^{-1}$ . The N–H symmetric stretching wavenumber is red shifted by 116  $\text{cm}^{-1}$  in the IR with a strong intensity from the computed wavenumber and the N–H asymmetric stretching wavenumber is red shifted by 137  $\text{cm}^{-1}$ .

The bands at 3521 [35], 1493 and 650  $\text{cm}^{-1}$  [36] are assigned to N–H stretching, N–H in-plane bending and out-of-plane bending vibrations. For the title compound, the N–H in-plane bending is observed at 1442  $\text{cm}^{-1}$  and the N–H out of plane bending is observed at 778  $\text{cm}^{-1}$ . While DFT calculations show that the IR bands appearing at 1261, 1316, 1330  $\text{cm}^{-1}$  are assigned to N–H in-plane bending and those appearing at 632, 717  $\text{cm}^{-1}$  are assigned to N–H out of plane bending.

### 3.2.3. C=C stretching

The carbon–carbon stretching modes of the phenyl group are expected in the range from 1650 to 1200  $\text{cm}^{-1}$ . The actual positions of these modes are determined not so much by the nature of the substituents but by the form of substitution around the ring [37], although heavy halogens cause the frequency to diminish undoubtedly [38]. The carbon–carbon stretching bands are observed in the infrared spectrum at 1335, 1492, 1559, 1581  $\text{cm}^{-1}$  for BH molecule and 1452, 1493, 1579, 1598  $\text{cm}^{-1}$  for BP molecule. DFT calculations give the carbon–carbon stretching modes at 1284, 1303, 1325, 1330, 1441, 1445, 1490, 1494, 1577, 1581, 1595, 1606  $\text{cm}^{-1}$ .

### 3.2.4. C=N vibrations

The identification of C=N, C–N vibrations are very difficult task, since the mixing of several bands are possible in the region [39]. Krishnakumar and John Xavier [40] have observed the C–N stretching vibration at 1375  $\text{cm}^{-1}$  in pyrimidines. Subramanian et al. [41] have identified the stretching frequency of C=N bond

**Table 2**  
Calculated and experimental fundamental frequencies ( $\text{cm}^{-1}$ ) for BH compound by B3LYP method.

	Calculated frequencies		Experimental <sub>BH</sub> <sup>a</sup> (IR)	Experimental <sub>BP</sub> <sup>b</sup> (IR)	Assignments[PED]
	6-31G*	6-311+G**			
1	466(24.43,0.99)	474(20.23,0.59)		436	$\Phi$ (ring)[62], $\rho$ (CNN)[31]
2	488(8.96,1.57)	497(7.47,0.75)			$\Phi$ (ring)[74]
3	547(6.19,3.22)	560(9.66,1.36)			$\Phi$ (ring)[84]
4	605(3.75,4.14)	615(32.94,8.95)		618	$\alpha$ (ring)[81]
5	610(0.14,6.21)	621(0.06,5.68)		686	$\alpha$ (ring)[90]
6	637(20.58,1.54)	632(303.11,44.87)			$\delta$ (N–H) <sub>oop</sub> [85]
7	605(51.61,5.98)	654(22.05,1.98)			$\rho$ (CNN)[52]
8	682(17.97,3.64)	674(8.15,2.06)	695		$\rho$ (CNN)[43], $\delta$ (C–H) <sub>oop</sub> [52]
9	685(70.93,4.91)	692(44.42,0.08)			$\delta$ (C–H) <sub>oop</sub> [90]
10	689(118.95,7.20)	703(52.21,0.25)			$\delta$ (C–H) <sub>oop</sub> [90]
11	720(238.69,28.02)	717(20.96,12.08)	778		$\delta$ (N–H) <sub>oop</sub>
12	754(1.68,9.06)	767(18.69,6.65)	768		$\delta$ (C–H) <sub>oop</sub> [85]
13	764(23.58,1.24)	775(23.14,5.39)			$\delta$ (C–H) <sub>oop</sub> [85]
14	828(0.76,4.92)	840(0.41,0.84)		812	$\delta$ (C–H) <sub>oop</sub> [99]
15	833(1.14,6.00)	849(0.23,0.54)		850	$\delta$ (C–H) <sub>oop</sub> [99]
16	896(5.02,2.42)	914(7.28,0.60)			$\delta$ (C–H) <sub>oop</sub> [90]
17	897(3.24,2.57)	918(1.59,0.34)			$\delta$ (C–H) <sub>oop</sub> [95]
18	933(10.03,3.12)	953(15.93,6.04)		948	$\delta$ (NNC)[41], $\delta$ (C–H) <sub>oop</sub> [52]
19	935(5.62,0.49)	971(0.31,0.17)			$\delta$ (C–H) <sub>oop</sub> [99]
20	936(0.99,0.96)	973(0.06,0.09)		970	$\delta$ (C–H) <sub>oop</sub> [95]
21	957(0.38,0.92)	986(0.12,0.31)			$\delta$ (C–H) <sub>oop</sub> [99]
22	959(0.27,0.27)	990(0.08,2.24)		993	$\delta$ (C–H) <sub>oop</sub> [95]
23	975(0.20,49.69)	994(0.44,97.19)			$\alpha$ (ring)[95]
24	977(0.79,34.83)	996(1.00,32.64)			$\alpha$ (ring)[95]
25	1014(2.62,29.35)	1026(5.34,35.83)			$\delta$ (C–H) <sub>ip</sub> [87]
26	1020(3.48,4.31)	1031(6.36,2.30)		1038	$\delta$ (C–H) <sub>ip</sub> [90]
27	1063(14.44,3.41)	1073(26.31,4.10)	1064		$\delta$ (C–H) <sub>ip</sub> [52], $\nu$ (N–N)[36]
28	1067(4.66,0.63)	1076(7.87,0.79)		1078	$\delta$ (C–H) <sub>ip</sub> [92]
29	1086(9.27,4.05)	1096(16.71,5.08)			$\nu$ (N–N)[65]
30	1144(0.75,12.60)	1156(2.21,16.34)			$\delta$ (C–H) <sub>ip</sub> [95]
31	1146(0.00,5.38)	1158(0.03,2.89)		1164	$\delta$ (C–H) <sub>ip</sub> [99]
32	1158(15.35,68.64)	1169(18.81,77.10)			$\nu$ (N–N)[35], $\delta$ (C–H) <sub>ip</sub> [47]
33	1165(2.62,5.20)	1177(1.14,3.94)		1188	$\delta$ (C–H) <sub>ip</sub> [95]
34	1171(11.14,12.86)	1184(14.19,9.08)			$\nu$ (N–N)[37], $\delta$ (C–H) <sub>ip</sub> [50]
35	1252(23.13,70.69)	1261(21.60,38.60)			$\nu$ (C–C)[34], $\delta$ (N–H) <sub>ip</sub> [57]
36	1276(1.52,10.20)	1284(0.27,10.08)			$\nu$ (C=C)[82]
37	1294(6.58,3.46)	1303(3.98,2.33)			$\nu$ (C=C)[80]
38	1308(5.39,46.47)	1316(8.29,113.61)			$\nu$ (C–C)[41], $\delta$ (N–H) <sub>ip</sub> [52]
39	1312(0.40,6.39)	1325(0.58,2.74)	1335		$\nu$ (C=C)[85]
40	1317(7.08,49.26)	1330(4.70,57.19)	1442		$\nu$ (C=C)[37], $\delta$ (N–H) <sub>ip</sub> [45]
41	1430(6.62,1.12)	1441(5.50,0.73)			$\nu$ (C=C)[90]
42	1433(10.95,9.95)	1445(10.67,14.01)		1452	$\nu$ (C=C)[90]
43	1479(3.05,3.09)	1490(4.25,4.84)			$\nu$ (C=C)[88]
44	1482(15.54,40.18)	1494(16.56,51.03)	1492	1493	$\nu$ (C=C)[88]
45	1565(4.82,103.0)	1577(6.06,111.06)	1559		$\nu$ (C=C)[82]
46	1569(1.64,6.04)	1581(2.19,10.89)	1581	1579	$\nu$ (C=C)[90]
47	1584(30.61,470.66)	1595(48.32,594.97)			$\nu$ (C=C)[35], $\delta$ (NH <sub>2</sub> )[28], $\nu$ (C=N)[32]
48	1593(0.07,63.21)	1606(0.26,51.11)		1598	$\nu$ (C=C)[87]
49	1601(4.78,28.02)	1613(11.19,19.49)			$\delta$ (NH <sub>2</sub> )[40], $\nu$ (C=N)[35]
50	1621(12.29,15.85)	1630(11.35,35.30)	1611		$\delta$ (NH <sub>2</sub> )[48], $\nu$ (C=N)[42]
51	3052(1.45,49.49)	3097(1.44,48.00)		3003	$\nu$ (C–H)[100]
52	3055(0.87,30.99)	3098(1.01,19.92)			$\nu$ (C–H)[100]
53	3060(17.73,134.44)	3105(1.22,110.54)		3065	$\nu$ (C–H)[100]
54	3062(5.58,130.32)	3106(12.78,139.90)			$\nu$ (C–H)[100]
55	3072(25.34,61.72)	3112(11.72,75.16)		3069	$\nu$ (C–H)[100]
56	3075(38.08,169.90)	3119(26.46,133.30)		3088	$\nu$ (C–H)[100]
57	3078(21.94,25.58)	3125(18.56,19.35)		3102	$\nu$ (C–H)[100]
58	3084(11.48,277.98)	3127(11.77,319.56)			$\nu$ (C–H)[100]
59	3086(14.09,152.74)	3129(10.95,187.41)			$\nu$ (C–H)[100]
60	3098(6.43,89.00)	3139(5.41,104.30)	3055		$\nu$ (C–H)[100]
61	3294(1.47,262.17)	3386(1.84,275.50)	3270		$\nu_s$ (N–H) [100]
62	3459(11.74,213.99)	3558(31.01,162.22)	3421		$\nu_{as}$ (N–H) [100]

First numbers in the parentheses under the columns 2–3 correspond to the IR intensities and the second numbers to the Raman intensities.  $\alpha$ : planar ring deformation,  $\Phi$ : non-planar ring deformation,  $\nu$ : stretching,  $\delta$ : bending, ip: in-plane deformation, oop: out-of-plane deformation,  $\rho$ : rocking, as: asymmetric, s: symmetric.

<sup>a</sup> Data from Ref. [16].

<sup>b</sup> Data from Ref. [14].

in 2,4-diamino-6-hydroxypyrimidine at  $1459 \text{ cm}^{-1}$ . The C=N vibration is observed at  $1611 \text{ cm}^{-1}$  for BH molecule by Anandha Babu et al. [16], while DFT calculations give the mode at 1595, 1613,  $1630 \text{ cm}^{-1}$ .

### 3.2.5. NH<sub>2</sub> bending

Filip et al. [42] reported the NH<sub>2</sub> bending at the range of  $1660$ – $1650 \text{ cm}^{-1}$ . Hoffmann et al. [43] reported that the NH<sub>2</sub> bending at  $1586 \text{ cm}^{-1}$  is observed in the chitosan spectrum. In the present

**Table 3**

Second-order perturbation theory analysis of Fock matrix in NBO basis at B3LYP/6-311+G\*\* level.

Donor NBO(i)	Acceptor NBO(i)	$E^{(2)}$ (kJ/mol)	$\epsilon_j - \epsilon_i$	$F(i, j)$
LP1 N <sub>1</sub>	$\sigma_{C7-C6}^*$	1.98	0.84	0.037
LP1 N <sub>1</sub>	$\sigma_{C1-H1}^*$	0.62	0.86	0.021
LP1 N <sub>1</sub>	$\sigma_{C7-C8}^*$	11.88	0.82	0.089
LP1 N <sub>1</sub>	$\sigma_{N2-H2}^*$	0.93	0.83	0.025
LP1 N <sub>1</sub>	$\sigma_{N2-H3}^*$	7.41	0.81	0.070
LP1 N <sub>2</sub>	$\sigma_{C7-N1}^*$	21.5	0.35	0.079

study, the NH<sub>2</sub> bending mode is observed at 1611 cm<sup>-1</sup> by Anandha Babu et al. [16]. DFT calculations give the NH<sub>2</sub> bending at 1595, 1613, 1630 cm<sup>-1</sup>.

### 3.2.6. C–H...N hydrogen bonding

Generally a hydrogen bond is formed when the hydrogen atom of a covalent A–H bond of a proton donor molecule interacts with a lone electron pair of an atom of X of a proton acceptor. Recently it has been established that a C–H group can be a hydrogen bond donor. Although the C–H...N interactions are considered weak, these interactions have been shown to be of great importance in biological systems in order to elucidate the structure–activity relationship [44].

Using the results obtained by B3LYP/6-311+G\*\* method, the intramolecular distance between H<sub>2</sub> and N<sub>1</sub> atoms is found to be 2.48 Å. The distance is shorter than that of the van der Waals separation between the N atom and H atom (2.75 Å) [45] indicating the existence of the C–H...N interaction in BH molecule. In addition, it is noted that the C<sub>1</sub>–H<sub>1</sub> bond is shorter than the other C–H bond on benzene ring and the C<sub>1</sub>–H<sub>1</sub> bond length is 1.082 Å at B3LYP/6-311+G\*\* method. The contraction in the C<sub>1</sub>–H<sub>1</sub> bond leads to a 84 cm<sup>-1</sup> blue shift and the decrease in intensity in the observed band [16] of IR spectra.

### 3.3. NBO analysis

The NBO analysis is already proved to be an effective tool for the chemical interpretation of hyperconjugative interaction and electron density transfer from the filled lone pair electron [46]. In order to investigate the various second-order interaction between the filled orbitals of one subsystem and vacant orbitals of another subsystem the DFT/B3LYP level has been used, and it predicts the delocalization or hyperconjugation [47]. The hyperconjugative interaction energy can be deduced from the second-order perturbation approach [48]:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i, j)^2}{\epsilon_j - \epsilon_i} \quad (1)$$

where  $q_i$  is the  $i$  th donor orbital occupancy,  $\epsilon_i, \epsilon_j$  are diagonal elements (orbital energies) and  $F(i, j)$  is the off-diagonal NBO Fock matrix element. The interaction between the nitrogen lone-pair LP<sub>1</sub>N<sub>1</sub> and the anti-bonding orbitals  $\sigma_{C1-H1}^*$  has been calculated using NBO analysis and the results are shown in Table 3. It is noted that the energetic contribution (0.62) of hyperconjugative interaction is weak, the  $E^{(2)}$  value is chemically significant and can be used as a measure of the intramolecular delocalization. The strengthening and contraction of C–H bond is due to rehybridization [49], which reveals the low value of electron density (0.45433) in the  $\sigma_{C1-H1}^*$  orbitals. This indicates the presence of C–H...N hydrogen bonding interaction in the BH molecule.

## 4. Conclusion

The molecular structures, vibrational spectra of BH molecule are performed by density functional theory calculations. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibrational modes of BH molecule were assigned based on the results of the PED output obtained from normal coordinate analysis. The results show that the shortening of C–H bond length and blue shifting of the CH stretching wavenumber suggest the existence of improper weak C–H...N hydrogen bonding, which is also confirmed by the natural bond orbital analysis.

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