

## CONFORMATION DEPENDENT VIBRATIONAL MODES IN 2-(2-HYDROXYPHENYL) BENZOTHAZOLE MOLECULE

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### ABSTRACT

Optimized structures for all the four possible conformers of 2-(2-hydroxyphenyl) benzothiazole have been computed using the DFT method at the B3LYP/6-311++G\*\* level. With these optimized structures vibrational parameters have also been computed. Comparative studies of conformer dependent vibrational fundamentals have been carried out.

**KEYWORDS:** Conformational Study, Vibrational Study, 2-(2-Hydroxyphenyl) Benzothiazole

### INTRODUCTION

Heterocyclic compounds are of great interest in the field of pharmaceutical chemistry. Benzothiazole (a heterocyclic) moiety is part of compounds showing various biological properties e.g., as antimicrobial [1-5], anticancer [6-9], anthelmintic [10], antidiabetic [11], antifungal and antiviral activities. We have planned to study the vibrational spectra of some heterocyclic compounds and results of our investigations on 2-(2-hydroxyphenyl) benzothiazole (abbreviated as HBT) and 2-(2-hydroxyphenyl) benzoxazole have already been communicated [12, 13]. In the present work we present the results of our study of the conformer dependent vibrational modes of HBT using the DFT - B3LYP method employing the 6-311++g\*\* basis set.

### COMPUTATIONAL DETAILS

There are two  $C_2$  (2 - fold) axis in the HBT molecule, hence, it has four conformers. The atomic numbering scheme and front and lateral views of all the four conformers of HBT are shown in Figure 1 and Figure 2. The symmetries of the four possible conformers, their total energies and energy differences from the lowest energy conformer (C-I) are given in Table 1. The fundamental vibrational wavenumbers along with their corresponding intensities in IR spectrum, Raman activities and depolarization ratios of the Raman bands for the four conformers of HBT have been computed as described earlier [12,13].

### RESULTS AND DISCUSSIONS

In the following, the changes noticed in the vibrational characteristics of the four conformers (C-I, C-II, C-III and C-IV) of the HBT molecule are discussed which are dependent on the molecular conformations. The conformer dependent vibrational modes are collected in Table 2.

### O-H Modes

The frequencies corresponding to the O<sub>24</sub>-H<sub>25</sub> stretching vibrations are calculated to be 3165, 3662, 3577 and 3659 cm<sup>-1</sup> in the C-I, C-II, C-III and C-IV conformers, respectively. The magnitude of the frequency corresponding to the O<sub>24</sub>-H<sub>25</sub> stretching vibration is the lowest (3165 cm<sup>-1</sup>) in the C-I conformer in comparison to the C-II, C-III and C-IV conformers because of the possibility of H-bonding in the C-I conformer. The IR intensity for this mode is the highest for the C-I conformer whereas it is the lowest in the C-IV conformer. In the present calculation the O<sub>24</sub>-H<sub>25</sub> in-plane bending mode i.e.  $\alpha$  (C<sub>16</sub>-O<sub>24</sub>-H<sub>25</sub>) corresponds to the frequencies 1378, 1136, 1148 and 1139 cm<sup>-1</sup> in the C-I, C-II, C-III and C-IV conformers, respectively. Its magnitude is the highest in the C-I conformer. The IR intensity for this mode increases by a factor of  $\sim 2$  in the C-I and C-II in comparison to the C-III while Raman activity is the highest for the C-II conformer. Moreover, Raman bands are weakly polarized for the C-II and C-III conformer in comparison to the C-I and C-IV conformers. The frequency corresponding to  $\tau$ (C<sub>16</sub>-O<sub>24</sub>-H<sub>25</sub>) is 781 cm<sup>-1</sup> in the C-I conformer which is the highest amongst the four conformers.

### C-H Modes

The mode  $\nu$  (C<sub>19</sub>-H<sub>22</sub>) is calculated to be 3055, 3009, 3053 and 3007 cm<sup>-1</sup> in the C-I, C-II, C-III and C-IV conformers respectively. The vibrational characteristics for this mode is almost the same for the C-II and C-IV conformers, however, Raman activity increases by a factor of  $\sim 2$  and Raman band is strongly polarized for the C-I in comparison to the C-III conformer. The  $\nu$  (C<sub>15</sub>-H<sub>18</sub>) mode in the C-I, C-II, C-III and C-IV conformers is calculated to be 3025, 3068, 3061 and 3031 cm<sup>-1</sup> respectively. Raman activity is the highest in the C-III conformer whereas the IR intensity is the highest in the C-III conformer. The Raman band is highly polarized in the C-IV conformer for this mode. The vibrational characteristic for C-H bending mode of the C<sub>6</sub>-H<sub>11</sub> bond is the highest in the C-I conformer (1400 cm<sup>-1</sup>) while C-II and C-III it differs by 4 cm<sup>-1</sup>. The IR intensity, Raman activity and polarization ratio are the highest for C-I. The  $\beta$  (C<sub>15</sub>-H<sub>18</sub>) mode corresponds to the frequencies 1225, 1270, 1302 and 1298 cm<sup>-1</sup> in the C-I, C-II, C-III and C-IV conformers. The IR intensity and Raman activity for this mode are comparatively higher in the C-II conformer. The mode  $\beta$ (C<sub>19</sub>-H<sub>22</sub>) in the C-I conformer has the highest frequency (1181 cm<sup>-1</sup>) while the mode  $\beta$ (C<sub>17</sub>-H<sub>21</sub>) in the C-III has the highest frequency (1422 cm<sup>-1</sup>). The out-of- plane bending  $\gamma$ (C<sub>6</sub>-H<sub>11</sub>) frequency is calculated to be nearly the same for the C-I, C-II and C-IV conformers whereas it is the highest for the C-III conformer.

### C-OH Modes

The stretching frequency for the  $\nu$  (C<sub>16</sub>-O<sub>24</sub>) mode corresponds to the frequencies 1242, 1208, 1203 and 1225 cm<sup>-1</sup> in the C-I, C-II, C-III and C-IV conformers, respectively. The magnitude of the frequency corresponding this vibration is the highest for the C-I conformer. The IR intensity for C-I conformer and Raman activity for the C-III conformer are the highest and the Raman bands in the C-I conformer is highly polarized amongst all the conformers. The C<sub>16</sub>-O<sub>24</sub> in-plane bending mode corresponds to the frequency 494 cm<sup>-1</sup> in the C-I conformer which is the highest amongst the four conformers. The IR intensity corresponding to this mode is the same in the C-II and C-IV conformers while it decreases by factors of  $\sim 1.5$  and  $\sim 2$  in the C-III and C-I conformers respectively.

### C-N Modes

The stretching frequencies corresponding to the  $\nu$ (C<sub>7</sub>-N<sub>12</sub>) and  $\nu$ (C<sub>2</sub>-N<sub>12</sub>) modes are 1473, 1444, 1480 and

1497  $\text{cm}^{-1}$  and 1209, 1191, 1187 and 1184  $\text{cm}^{-1}$  in the C-I, C-II, C-III and C-IV conformers, respectively. The magnitude of the frequency corresponding to the  $\nu(\text{C}_7\text{-N}_{12})$  mode is the highest and the lowest in the C-IV and C-II conformers, respectively. The IR intensity and Raman activity are the highest and Raman bands are strongly polarized in the C-III conformer.

### Ring Modes

The stretching frequency corresponding to the  $\text{C}_{14}\text{-C}_{15}$  bond corresponds to the frequencies 1290, 1299, 1272 and 1265  $\text{cm}^{-1}$  in the C-I, C-II, C-III and C-IV conformers, respectively. It is the highest in the C-II conformer in comparison to C-I, C-III and C-IV conformers. The IR intensity and Raman activity are the highest in the C-IV and C-I conformers, respectively while the Raman bands are highly polarized in the C-II conformer. The frequency corresponding to one of the  $\Phi(\text{R}_1)$  modes is 551, 425, 457 and 558  $\text{cm}^{-1}$  in the C-I, C-II, C-III and C-IV conformers, respectively. The frequency corresponding to the other  $\Phi(\text{R}_1)$  mode is 420, 315, 414 and 425  $\text{cm}^{-1}$  in the C-I, C-II, C-III and C-IV conformers, respectively. The frequency corresponding to one of the  $\Phi(\text{R}_3)$  mode is the highest (453  $\text{cm}^{-1}$ ) and the lowest (139  $\text{cm}^{-1}$ ) in the C-IV and C-III conformers, respectively. Similarly, for the other  $\Phi(\text{R}_3)$  mode, the corresponding frequency is the lowest (160  $\text{cm}^{-1}$ ) in the C-III conformer. The IR intensity is the highest for the C-IV conformer while the Raman activity is the highest for the C-III conformer. The frequency corresponding to the  $\Phi(\text{R}_2)$  mode is 144, 550, 553 and 1555  $\text{cm}^{-1}$  in the C-I, C-II, C-III and C-IV conformers, respectively.

### CONCLUSIONS

For the first time DFT calculations have been carried out for the four conformers of HBT. The present calculation predicts that amongst the four conformers of HBT two possess planar ( $\text{C}_s$ ) and two possess non-planar ( $\text{C}_1$ ) structures. The C-I is found to be the most stable conformer of HBT. The intramolecular hydrogen bonding is expected between the N atom of the thiazole ring and H of the OH group in the C-I conformer only. The magnitude of frequency corresponding to the  $\text{O}_{24}\text{-H}_{25}$  stretching vibration is the lowest (3165  $\text{cm}^{-1}$ ) in the C-I conformer in comparison to the C-II, C-III and C-IV conformers while the magnitudes of  $\alpha(\text{C}_{16}\text{-O}_{24}\text{-H}_{25})$  and  $\tau(\text{C}_{16}\text{-O}_{24}\text{-H}_{25})$  mode are the highest in the C-I conformer in comparison to the C-II, C-III and C-IV conformers.

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## APPENDICES

**Table 1: Conformers, Their Total Energies and Point Groups for HBT**

S. No.	Conformers	Point Groups	Total Energy (Hartree)	Relative Energy Kcal/Mol
1	C-I	C <sub>s</sub>	-1029.18488483	0
2	C-II	C <sub>s</sub>	-1029.17129414	8.534
3	C-III	C <sub>1</sub>	-1029.17011280	9.287
4	C-IV	C <sub>1</sub>	-1029.16592044	11.923

**Table 2: Calculated Conformer Dependent Vibrational Modes for the Four Conformers of HBT**

Mode	C <sub>s</sub> Point Group		Species	C <sub>1</sub> Point Group		Species	Normal Mode Assignment
	C-I <sup>§</sup> Scaled Freq (cm <sup>-1</sup> )	C-II <sup>§</sup> Scaled Freq (cm <sup>-1</sup> )		C-III <sup>§</sup> Scaled Freq (cm <sup>-1</sup> )	C-IV <sup>§</sup> Scaled Freq (cm <sup>-1</sup> )		
v <sub>1</sub>	117 (1,0)0.10	116 (3,1)0.75	a <sup>+</sup>	96 (1,3)0.71	82 (2,3)0.71	a	β(C <sub>7</sub> -C <sub>14</sub> )
v <sub>2</sub>	144 (0,4)0.75	550 (0, 0)0.75	a <sup>+</sup>	553 (2,2) 0.75	155 (0,3)0.70	a	Φ(R <sub>2</sub> )
v <sub>3</sub>	235 (0,1)0.75	453 (7, 0)0.75	a <sup>+</sup>	213 (2,1)0.63	204 (0,1)0.71	a	γ(C <sub>7</sub> -C <sub>14</sub> )
v <sub>4</sub>	260 (2,3)0.1	270 (1, 3)0.13	a <sup>+</sup>	248 (1,3)0.14	246 (0,3)0.14	a	ν(C <sub>7</sub> -C <sub>14</sub> )
v <sub>5</sub>	291 (5,2)0.72	244 (2,0)0.36	a <sup>+</sup>	275 (4,3)0.27	280 (9,1)0.75	a	β(C <sub>7</sub> -C <sub>14</sub> )
v <sub>6</sub>	311 (0,0)0.75	236 (6,1)0.75	a <sup>+</sup>	160 (0,3)0.68	332 (46,2)0.48	a	Φ(R <sub>3</sub> )
v <sub>7</sub>	420 (2,0)0.75	315 (1, 0)0.75	a <sup>+</sup>	414 (51,1)0.55	425 (7,1)0.36	a	Φ(R <sub>1</sub> )
v <sub>8</sub>	447 (7,0)0.75	139 (1,5)0.75	a <sup>+</sup>	320 (2,2)0.57	453 (5,3)0.48	a	Φ (R <sub>3</sub> )
v <sub>9</sub>	494 (4,5)0.19	467 (9, 0)0.74	a <sup>+</sup>	475 (6,4)0.67	471 (9,8)0.18	a	β(C <sub>16</sub> -O <sub>24</sub> )
v <sub>10</sub>	551 (0,0)0.75	425 (2, 0)0.75	a <sup>+</sup>	457 (9,0)0.69	558 (1,1)0.57	a	Φ(R <sub>1</sub> )
v <sub>11</sub>	781 (63,1)0.75	266 (90,2)0.75	a <sup>+</sup>	437 (23,2)0.50	320 (2,2)0.57	a	τ(C <sub>16</sub> -O <sub>24</sub> -H <sub>25</sub> )
v <sub>12</sub>	841 (2,0)0.75	841 (1, 0)0.75	a <sup>+</sup>	935 (2,0)0.71	846 (1,0)0.45	a	γ(C <sub>6</sub> -H <sub>11</sub> )
v <sub>13</sub>	1092 (34,25)0.34	1064 (80,1)0.42	a <sup>+</sup>	1066 (4,3)0.16	1074 (50,5)0.27	a	β(C <sub>20</sub> -H <sub>23</sub> )
v <sub>14</sub>	1129 (28,17)0.33	1414 (70,104)0.32	a <sup>+</sup>	1422 (51,20)0.30	1408 (41,25)0.26	a	β(C <sub>17</sub> -H <sub>21</sub> )
v <sub>15</sub>	1181(118,75)0.23	1130 (11,32)0.52	a <sup>+</sup>	1126 (22,32)0.32	11851132 (8,)0.53	a	β(C <sub>19</sub> -H <sub>22</sub> )
v <sub>16</sub>	1209(41,404)0.27	1191 (9,604)0.26	a <sup>+</sup>	1187 (86,193)0.31	1184 (59,451)0.24	a	ν(C <sub>2</sub> -N <sub>12</sub> )
v <sub>17</sub>	1225 (12,23)0.21	1270 (71,135)0.34	a <sup>+</sup>	1302 (16,13)0.71	1298 (41,10)0.58	a	β(C <sub>15</sub> -H <sub>18</sub> )
v <sub>18</sub>	1242 (39,10)0.63	1208 (19,89)0.21	a <sup>+</sup>	1203 (30,463)0.25	1225 (29,29)0.17	a	ν(C <sub>16</sub> -O <sub>24</sub> )
v <sub>19</sub>	1290 (14,223)0.28	1299 (42,15)0.74	a <sup>+</sup>	1272 (41,10)0.71	1265 (46,61)0.26	a	ν(C <sub>14</sub> -C <sub>15</sub> )
v <sub>20</sub>	1378 (31,7)0.29	1136 (34,59)0.19	a <sup>+</sup>	1148 (61,7)0.05	1139 (25,3)0.29	a	α(C <sub>16</sub> -O <sub>24</sub> -H <sub>25</sub> )
v <sub>21</sub>	1400 (58,702)0.37	1220 (16,91)0.27	a <sup>+</sup>	1216 (24,3)0.26	1213 (17,27)0.35	a	β(C <sub>6</sub> -H <sub>11</sub> )
v <sub>22</sub>	1473(66,1019)0.31	1444 (33,811)0.31	a <sup>+</sup>	1480(91,1876)0.33	1497(48,1593)0.32	a	ν(C <sub>7</sub> -N <sub>12</sub> )
v <sub>23</sub>	3025 (1,20)0.52	3068 (5,73)0.14	a <sup>+</sup>	3061 (7,165)0.12	3031 (1,76)0.53	a	ν(C <sub>15</sub> -H <sub>18</sub> )
v <sub>24</sub>	3055 (9,397)0.12	3009 (12,116)0.38	a <sup>+</sup>	3053 (7,184)0.20	3007(12,112)0.38	a	ν(C <sub>19</sub> -H <sub>22</sub> )
v <sub>25</sub>	3165(493,137)0.26	3662 (89,170)0.23	a <sup>+</sup>	3577(173,178)0.20	3659 (71,148)0.23	a	ν(O <sub>24</sub> -H <sub>25</sub> )

<sup>§</sup>Number outside bracket is frequency in cm<sup>-1</sup> unit, numbers within the bracket are IR intensity and Raman activity and number outside bracket is depolarization ratio (from left to right)

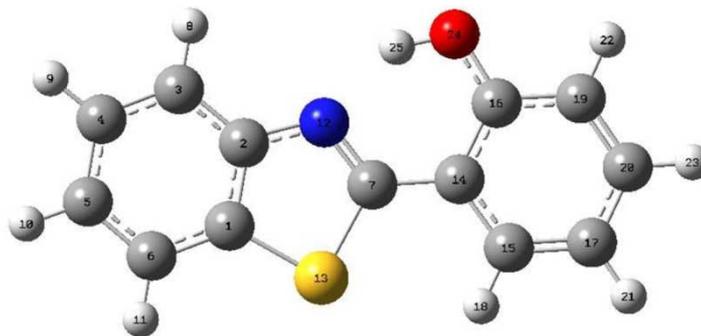


Figure 1: Atomic Numbering Scheme of HBT

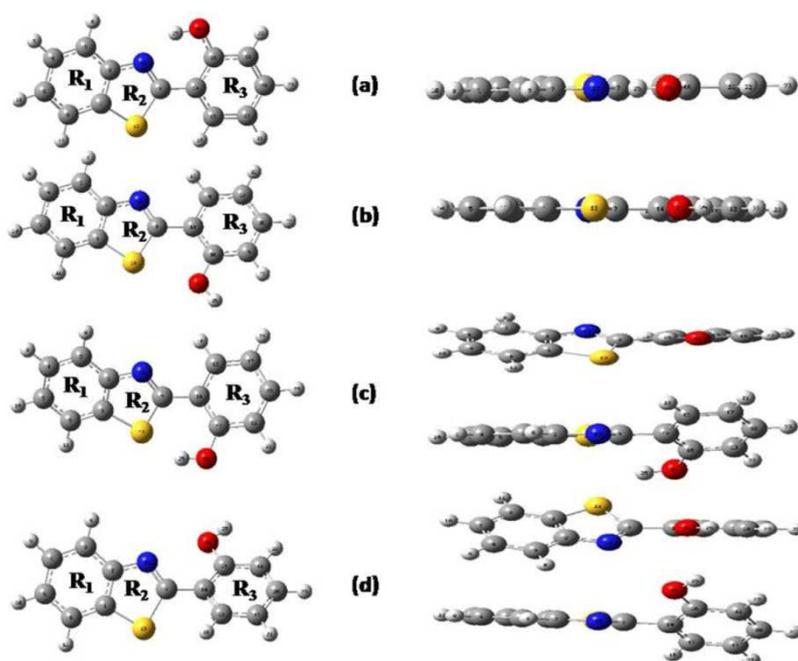


Figure 2: Front and Lateral View of (a) Conformer C-I, (b) Conformer C-II, (c) Conformer C - III, and (d) Conformer C-IV of HBT

