



## Molecular structure and vibrational spectra of 2- and 5-methylbenzimidazole molecules by density functional theory

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### ABSTRACT

The FT-IR and FT-Raman spectra of 2-methylbenzimidazole (2-MB) and 5-methylbenzimidazole (5-MB) molecules have been recorded between 400–4000 cm<sup>-1</sup> and 50–3500 cm<sup>-1</sup> region, respectively. The molecular geometry and vibrational frequencies of 2- and 5-MB molecules in the ground state have been calculated by using the density functional methods (B3LYP) with 6-311++G(d,p) and 6-31G(d,p) as basis sets. The total energy distributions (TEDs) for the normal modes were computed for the minimum energy structure of the molecules. Comparison of the observed fundamental vibrational frequencies of 2- and 5-MB molecules with calculated results by density functional B3LYP approach will give better result for our studied molecular vibrational problem.

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### 1. Introduction

Benzimidazoles are heterocyclic compounds that have awakened great interest during the last few years because of their proven biological activity as antiviral, antimicrobial, and antitumor agents. For this reason, the development of a systematic FT-IR, FT-Raman and NMR study of 1- substituted compounds in 2-methylbenzimidazole (2-MB) constitutes a significant tool in understanding the molecular dynamics and structure parameters that govern their behaviors. Two new 1-alkyl-2-MB compounds were synthesized from reaction of 2-MB with primary and secondary alkyl halides using a strong base as a catalyst [1]. Benzimidazole is known for commercial and biological importance as pharmaceuticals, veterinary anthelmintics and fungicides. It is also of a considerable interest as a ligand towards transition of metal ions with a variety of biological molecules including ionheme systems, vitamin B<sub>12</sub> and its derivatives and several metallo-proteins [2]. Recently a number of vitamin B<sub>12</sub> compounds have been isolated in which the 5,6-dimethylbenzimidazole part of the vitamin molecule has been replaced by adenine [3]. Benzimidazole and 1,2,3-benzotriazole have widespread applications in chemical practice as polymers, organic optical bistable switches or corrosion inhibitors [4].

A set of 2-alkylsulfonyl derivatives of 5-MB was synthesized and evaluated for antimycobacterial activity. The structures of the compounds were confirmed by <sup>1</sup>H NMR and IR data and their purity by elemental analysis. Antimycobacterial activities against *Mycobacterium tuberculosis* and nontuberculous mycobacteria were expressed as the minimum inhibitory concentration. These substances exhibited significant antimycobacterial activity, in particular against both strains of *Mycobacterium kansasii*. In order to enhance the activity of benzimidazole, they tried to substitute the hydrogen atoms at 2- and 5-positions. Thus, they synthesized derivatives of benzimidazole in which the CH<sub>3</sub> group on the benzimidazole ring at 5-position is maintained while the benzyl moiety on the sulfur atom at 2-position is further modified by groups with electron-accepting (NO<sub>2</sub>, CN, CF<sub>3</sub>) and electron-donating (Cl, F, Br, OCH<sub>3</sub>) properties in order to optimize the lipophilic and steric characteristic [5]. The purpose of this work is the detailed investigation of the substituent effects on the vibrational spectra of 2- and 5-MB. The clear-cut assignment of the available experimental spectra has been made on the basis of calculated total energy distribution (TED). Particular attention has been paid to the effect of the methyl substituent on the frequencies and the intensities of the corresponding bands in the vibrational spectra of these molecules.

### 2. Experimental

The sample of 2- and 5-MB are in solid form at room temperature was purchased from Sigma Aldrich Chemical Company, USA and was used as such without further purification. The infrared

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spectrums of the samples were recorded between 400–4000  $\text{cm}^{-1}$  on a Mattson 1000 FT-IR spectrometer which was calibrated using polystyrene bands. The samples were prepared as a KBr disc. The FT-Raman spectrums of the samples were recorded between 50–3500  $\text{cm}^{-1}$  region on a Bruker FRA 106/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector. The observed experimental FT-IR and FT-Raman spectra are shown in Figs. 1 and 2.

### 3. Computational details

The molecular structures of 2- and 5-MB (in vacuum) in the ground state are optimized by B3LYP with 6-311++G(d,p) and 6-31G(d,p) as basis sets. Density functional for all studies reported in this paper has the following form

$$E_{XC} = (1 - a_0)E_X^{LSDA} + a_0E_X^{HF} + a_X \Delta E_X^{B88} + a_c E_C^{LYP} + (1 - a_c)E_C^{VWN}$$

where the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke's exchange functional correction, and the gradient corrected correlation functional of Lee, Yang and Parr [6]. RB3LYP with 6-311G(d,p) and 6-31G(d) level of theory with the optimized geometries have been used to calculate all frequencies of 2- and 5-MB molecules. The calculated harmonic frequencies were also scaled by corresponding scaling factor [7]. The TED of vibrational modes was calculated by using the Scaled Quantum Mechanics (SQM) program [8,9]. All the calculations are performed by using Gauss-view molecular visualization program and Gaussian 03 program package on the personal computer [10,11]. The theoretical FT-IR spectra are shown in Figs. 3 and 4.

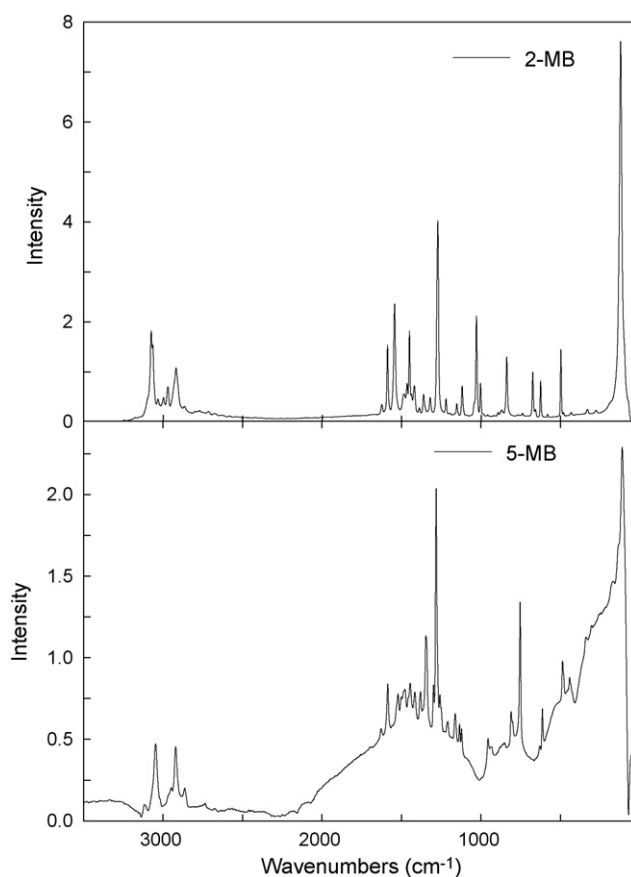


Fig. 2. Experimental FT-Raman spectra of 2- and 5-MB.

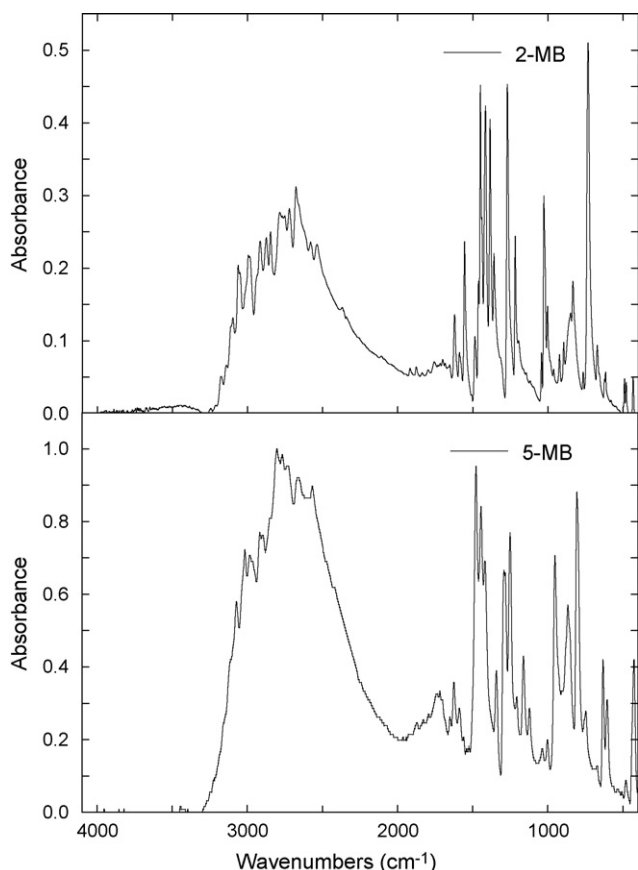


Fig. 1. Experimental FT-IR spectra of 2- and 5-MB.

#### 3.1. Prediction of Raman intensities

The Raman activities ( $S_i$ ) calculated with Gaussian 03 program [11] converted to relative Raman intensities ( $I_i$ ) using the following relationship derived from the intensity theory of Raman scattering

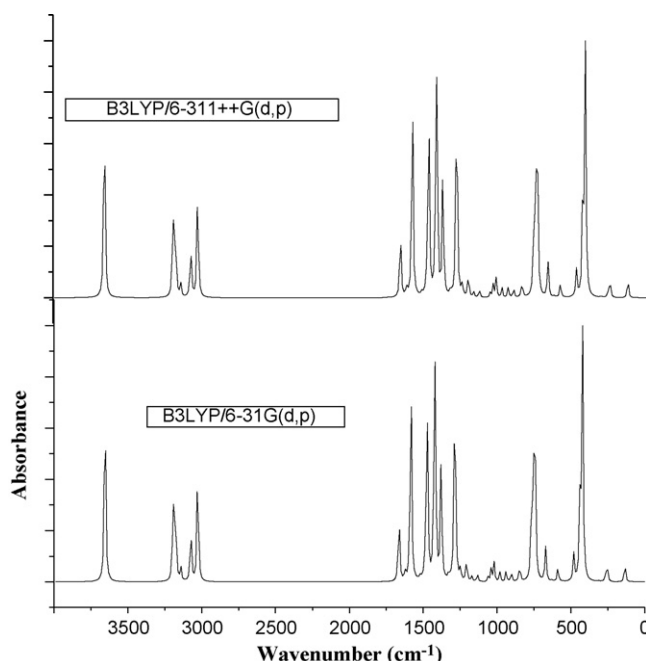


Fig. 3. Theoretical FT-IR spectrum of 2-MB.

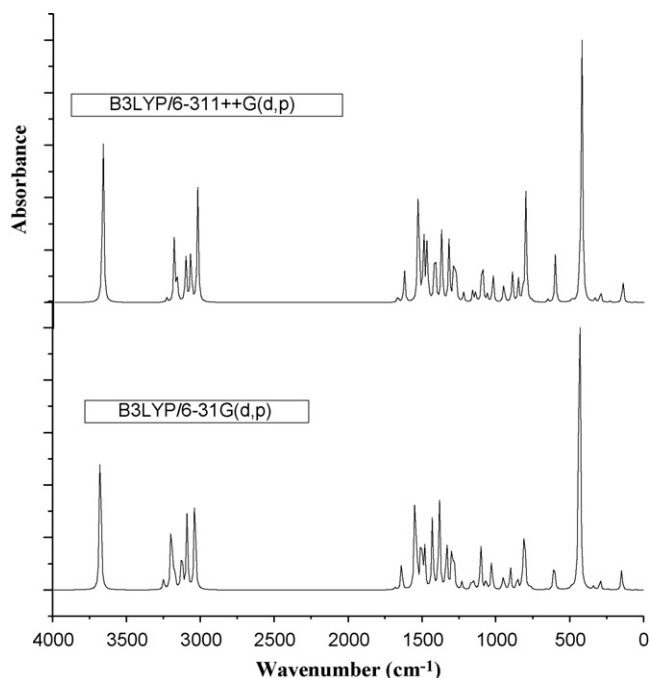


Fig. 4. Theoretical FT-IR spectrum of 5-MB.

[12,13].

$$I = \frac{f(\nu_0 - \nu)^4 S_i}{\nu_i [1 - \exp(-hc\nu_i/kT)]}$$

where  $\nu_0$  is the exciting frequency in  $\text{cm}^{-1}$ ,  $\nu_i$  the vibrational wavenumber of the  $i$ th normal mode,  $h$ ,  $c$  and  $k$  are fundamental constants, and  $f$  is a suitably chosen common normalization factor for all peak intensities. For simulation, the calculated FT-Raman spectra were plotted using pure Lorentzian band shape with a bandwidth of Full Width and Half Maximum (FWHM) of  $10 \text{ cm}^{-1}$  as shown in Fig. 5. In the FT-IR spectra, the theoretically simulated spectra are more regular than the experimental ones, because many vibrations presenting in condensed phase leads to strong perturbation of infrared intensities of many other modes.

## 4. Results and discussion

### 4.1. Geometrical structures

Optimized geometries of 2- and 5-MB in the ground state have belonged to  $C_s$  and  $C_1$  symmetry point group, respectively. Molecules of initial geometry generated from standard geometry parameters were minimized adopting the standard 6-311++G(d,p) basis set. The optimized structures were confirmed to complete for fixed at around of  $-\text{CH}_3$  group itself and also fixed at the position of minima. The atom numbering scheme for 2- and 5-MB are shown in Fig. 6(a) and (b). The optimized bond lengths and angles from the geometry optimizations determined at the DFT/B3LYP levels with 6-311++G(d,p), 6-31G(d), 6-31G(d,p) as basis set for the title molecule are presented in Table 1. The crystal structure of 2-MB was reported by Obodouskaya et al. [14] and compared our calculated structural parameter values with the X-ray data of 2-MB. However the X-ray crystal structure of 5-MB is unknown, it is compared with other similar system such as 5,6-dimethylbenzimidazole [15]. From the theoretical values of both the 2- and 5-MB molecules, we find that most of the optimized bond lengths and angles are slightly smaller, as well as longer than the experimental value; this is due to the fact that the theoretical calculations belong to isolated molecule

in gaseous phase and experimental results belong to molecule in solid state.

2- and 5-MB are heterocyclic compounds and resonance effect is observed in the ring of these molecules. As a result, C–C bond length and C–C–C bond angles in the ring are similar to the benzene molecule. In the benzene ring, C–C bond length is about  $1.396 \text{ \AA}$  [16], our calculations were similar to this value, for example the optimized bond length of C–C in phenyl ring fall in the range  $1.390\text{--}1.413 \text{ \AA}$  at B3LYP/6-311++G(d,p) method show good agreement with X-ray data value of  $1.360\text{--}1.395 \text{ \AA}$  for 2-MB. But in the case of 5-MB the C–C bond distance fall in range  $1.388\text{--}1.415 \text{ \AA}$  also show excellent correlation with experimental data.

C–N bond distance was found to be  $1.47$  for some nitramines [17], but it is about  $1.389 \text{ \AA}$  in both 2- and 5-MB molecules by B3LYP/6-311++G(d,p) method. Moreover, all carbon and nitrogen atoms in the ring are coplanar, as in benzene ring. The N–C–N bond angle of 2-MB appears a little distorted because of substitution of methyl group. The X-ray data of N–C–N bond angles in the case of benzimidazole is  $114^\circ$  [18], where as in our 2-MB molecule it is  $112.4^\circ$  as shown in Table 1.

### 4.2. Vibrational assignments

Vibrational spectral assignments were performed on the recorded FT-IR and FT-Raman spectra based on the theoretically predicted wavenumbers by density functional B3LYP/6-311++G(d,p) method and are collected in Tables 2 and 3. None of the predicted vibrational spectra has imaginary frequencies, implying that the optimized geometry is located at the local lowest point on the potential energy surface. We know that ab initio HF and DFT potentials systematically overestimate the vibrational frequencies. These discrepancies are corrected either by computing anharmonic corrections explicitly or by directly scaling the calcu-

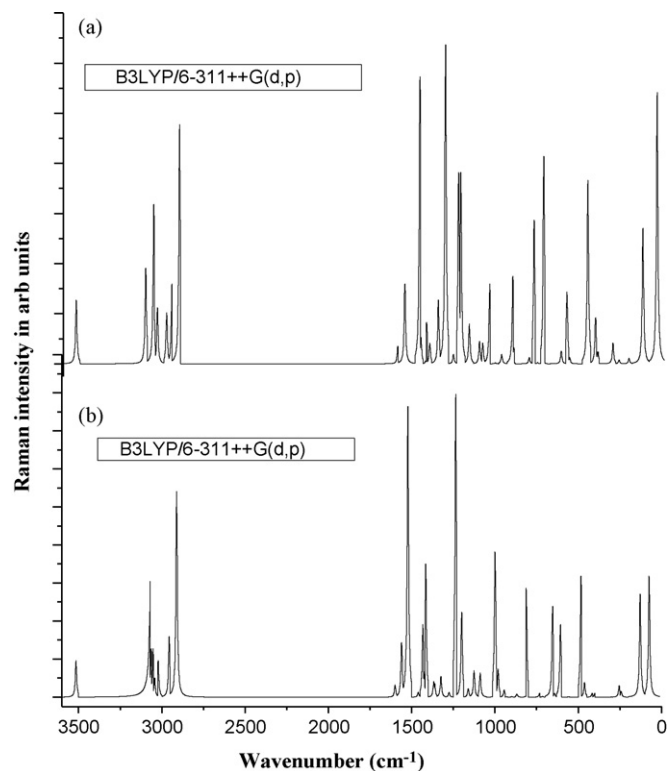


Fig. 5. Theoretical FT-Raman spectrum of (a) 2-MB and (b) 5-MB by B3LYP/6-311++G(d,p) method.

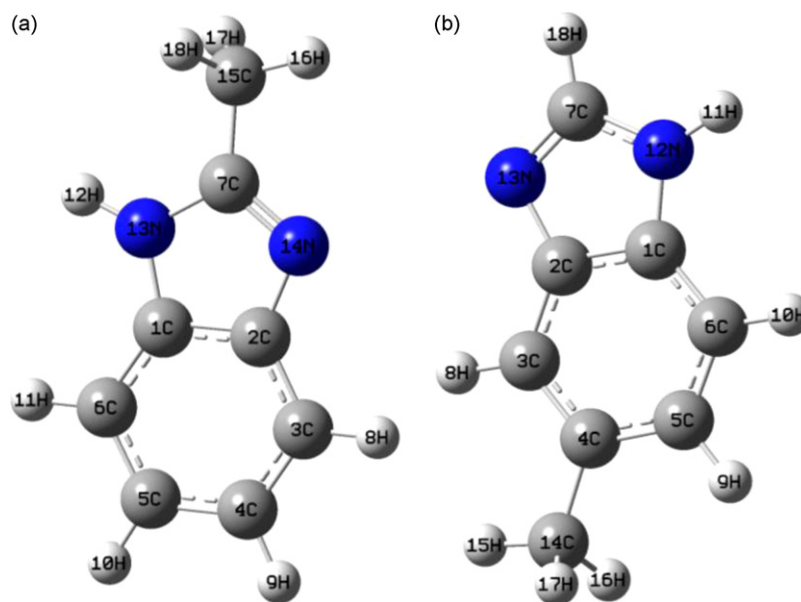


Fig. 6. Atom numbering scheme of (a) 2-MB and (b) 5-MB.

lated wavenumbers with a scaling factor of 0.961 and 0.968 for 6-31G(d,p) and 6-311++G(d,p) method, respectively. After the scaling, the deviation from the experiments is less than  $10\text{ cm}^{-1}$  with a few exceptions.

The title molecule 2- and 5-MB each has 18 atoms. The 48 fundamental vibrations in the case of 2-MB is distributed as 33  $A'$  (in-plane) + 15  $A''$  (out-of-plane) to show as  $C_s$  symmetry. In FT-Raman spectrum, the  $A'$  vibrations give rise to polarized bands while the  $A''$  ones to depolarized bands. All the vibrations are active in both FT-IR and FT-Raman. In the case of 5-MB, there will not be any relevant distribution since it belong to  $C_1$  symmetry. The calculated infrared and Raman frequencies together with experimental data of the title molecules are presented in Tables 2 and 3. The total energy distribution (TED) was calculated by using the Scaled Quantum Mechanics program [8,9] and fundamental vibrational modes were characterized by their TED.

#### 4.2.1. N–H vibrations

It has been observed that the presence of NH atomic group in various molecules may be correlated with a constant occurrence of absorption bands whose positions are slightly altered from one compound to another; this is because the atomic group vibrates independently of the other groups in the molecule and has its own frequency. Normally in all the heterocyclic compounds, the N–H stretching vibration occurs in the region  $3000\text{--}3500\text{ cm}^{-1}$  [18]. Tsuboi [19] reported the N–H stretching frequency at  $3481\text{ cm}^{-1}$  in aniline. In line with his observation, N–H stretching is assigned to the band at  $3460\text{ cm}^{-1}$  in the case of benzimidazole [2]. In our title molecule, 5-MB the weak band at  $3447\text{ cm}^{-1}$  in FT-IR corresponds to N–H stretching vibration. The theoretically calculated harmonic wavenumber at  $3509\text{ cm}^{-1}$  by B3LYP/6-311++G(d,p) shows little deviation on the higher side. The TED of this mode is pure stretching mode as it is evident from Table 2, which it is exactly contributing to 100%. In the case of 2-MB, the same vibration by B3LYP/6-311++G(d,p) method predicted at  $3502\text{ cm}^{-1}$  is also coinciding with literature data [19]. The N–H in-plane and out-of-plane bendings are assigned to the wavenumber at  $1398\text{ cm}^{-1}$  and  $410\text{ cm}^{-1}$  respectively predicted by B3LYP/6-311++G(d,p) for 2-MB. In the case of 5-MB molecule the band observed at  $1324\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  in FT-IR and FT-Raman spectra respectively are assigned to the N–H in-plane bending vibration. The theoretically computed

value by B3LYP/6-311++G(d,p) method at  $1342\text{ cm}^{-1}$  shows better correlation with experimental data.

#### 4.2.2. C–H vibrations

The hetero aromatic structure shows the presence of C–H ring stretching vibrations in the region  $3000\text{--}3100\text{ cm}^{-1}$  which is the characteristic region for the ready identification of C–H stretching vibration. In this region the bands are not affected appreciably by the nature of substituent [20]. The 2-MB has four adjacent C–H moieties in benzene ring. The expected four C–H stretching vibrations correspond to mode nos 2, 3, 4 and 5. The scaled vibration mode nos 2, 3, 4 and 5 (Table 2) corresponds to stretching modes of C3–H, C4–H, C5–H and C6–H units. The calculated frequencies of the C–H stretching vibrations in 2-MB is  $3060, 3052, 3040$  and  $3031\text{ cm}^{-1}$  show very good agreement with experimental data. In the case of 5-MB it has two adjacent and one isolated C–H moieties in the benzene ring and one C–H moieties in the imidazole ring. The expected three C–H stretching vibrations in benzene ring and one C–H stretching in imidazole ring corresponds to mode nos 2, 3, 4 and 5 (Table 3). The scaled vibration modes nos 2, 3, 4 and 5 correspond to stretching modes of C3–H, C5–H, C6–H and C7–H units. The calculated frequencies of the C–H stretching vibrations in 5-MB are at  $3095, 3048, 3045$  and  $3026\text{ cm}^{-1}$  also correlate with experimental observation. The TED of these C–H stretching vibrations is pure and it is almost contributing to 100%.

Substitution sensitive C–H in-plane bending vibrations lie in the region  $1000\text{--}1300\text{ cm}^{-1}$  [20]. In 2-MB four modes are associated mainly with the C–H in-plane bending vibrations, mode nos 21, 24 and 25. These mode numbers are observed at the following wavenumbers at  $1120\text{ cm}^{-1}$  in FT-IR and  $1221, 1119, 1041\text{ cm}^{-1}$  in FT-Raman. Similar observations are also found in the case of 5-MB. The C–H out-of-plane bending vibrations contribute mainly to the mode nos. 30, 31 and 32. The experimental observation for the C–H out-of-plane bending falls in the experimental value of  $730\text{--}930\text{ cm}^{-1}$ .

#### 4.2.3. Methyl group vibration

The title molecules 2- and 5-MB possess a  $\text{CH}_3$  group in the second and fifth position, respectively. For the assignments of  $\text{CH}_3$  group frequencies, basically nine fundamentals can be associated with each  $\text{CH}_3$  group namely,  $\text{CH}_{3\text{as}}$ : asymmetric stretch;  $\text{CH}_3$  ips:

**Table 1**  
Geometrical parameters optimized in 2- and 5-MB; bond lengths and angles.

2-Methylbenzimidazole					5-Methylbenzimidazole				
Bond lengths (Å)	6-31G(d)	6-31G(d,p)	6-311++G(d,p)	2-MB [1]	Bond lengths (Å)	6-31G(d)	6-31G(d,p)	6-311++G(d,p)	5,6-DMB [14]
C1–C2	1.416	1.416	1.413	1.395	C1–C2	1.414	1.414	1.411	1.411
C1–C6	1.395	1.395	1.393	1.389	C1–C6	1.397	1.397	1.395	1.395
C1–N13	1.385	1.385	1.385	1.383	C1–N12	1.386	1.385	1.385	1.385
C2–C3	1.400	1.400	1.398	1.378	C2–C3	1.402	1.402	1.400	1.399
C2–N14	1.390	1.390	1.389	1.389	C2–N13	1.391	1.391	1.389	
C3–C4	1.392	1.392	1.390	1.382	C3–C4	1.393	1.393	1.391	1.392
C3–H8	1.086	1.085	1.084		C3–H8	1.087	1.086	1.084	1.085
C4–C5	1.409	1.408	1.407	1.395	C4–C5	1.417	1.417	1.415	1.427
C4–H9	1.087	1.086	1.084		C7–H18	1.513	1.512	1.512	1.082
C5–C6	1.394	1.393	1.392	1.360	C5–C6	1.390	1.390	1.388	
C5–H10	1.087	1.086	1.084	1.084	C5–H9	1.088	1.087	1.085	
C6–H11	1.087	1.086	1.084	1.084	C6–H10	1.087	1.086	1.084	1.086
C7–N13	1.383	1.383	1.383	1.339	C7–N12	1.377	1.377	1.376	1.377
C7–N14	1.311	1.311	1.308	1.335	C7–N13	1.308	1.308	1.305	1.307
C7–C15	1.494	1.493	1.492		C4–C14	1.083	1.083	1.081	1.511
H12–N13	1.009	1.008	1.007		H11–N12	1.009	1.008	1.007	1.007
C15–H16	1.091	1.090	1.089		C14–H15	1.095	1.093	1.092	1.092
C15–H17	1.097	1.096	1.095		C14–H16	1.098	1.096	1.095	1.097
C15–H18	1.097	1.096	1.095		C14–H17	1.098	1.096	1.095	1.097

2-Methylbenzimidazole					5-Methylbenzimidazole				
Bond angles (°)	6-31G(d)	6-31G(d,p)	6-311++G(d,p)	2-MB [1]	Bond angles (°)	6-31G(d)	6-31G(d,p)	6-311++G(d,p)	5,6-DMB [14]
C2–C1–C6	122.6	122.6	122.5	122.5	C2–C1–C6	122.1	122.1	122.0	122.2
C2–C1–N13	104.3	104.3	104.4	104.3	C2–C1–N12	104.5	104.5	104.6	104.5
C6–C1–N13	133.1	133.1	133.1		C6–C1–N12	133.4	133.4	133.4	133.4
C1–C2–C3	119.7	119.7	119.8	119.8	C1–C2–C3	119.8	119.9	120.0	122.2
C1–C2–N14	110.4	110.4	110.2	110.1	C1–C2–N13	110.5	110.5	110.3	
C3–C2–N14	129.9	129.9	130.0		C3–C2–N13	129.7	129.7	129.8	
C2–C3–C4	118.1	118.1	118.1	118.1	C2–C3–C4	119.1	119.1	119.1	119.5
C2–C3–H8	120.2	120.2	120.3	120.2	C2–C3–H8	119.7	119.8	119.7	119.7
C4–C3–H8	121.7	121.7	121.7		C4–C3–H8	121.1	121.1	121.2	
C3–C4–C5	121.4	121.4	121.4	121.3	C3–C4–C5	119.6	119.6	119.6	120.3
C3–C4–H9	119.5	119.5	119.6	119.6	C3–C4–C14	120.9	120.9	120.9	119.7
C5–C4–H9	119.1	119.1	119.1		C5–C4–C14	119.5	119.5	119.5	
C4–C5–C6	121.5	121.5	121.5	121.4	C4–C5–C6	122.6	122.6	122.5	
C4–C5–H10	119.3	119.3	119.3	119.3	C4–C5–H9	118.6	118.6	118.7	
C6–C5–H10	119.2	119.2	119.2		C6–C5–H9	118.8	118.8	118.8	
C1–C6–C5	116.7	116.7	116.8	116.7	C1–C6–C5	116.8	116.8	116.9	
C1–C6–H11	122.0	122.0	122.1	122.1	C1–C6–H10	122.1	122.1	122.1	121.6
C5–C6–H11	121.3	121.3	121.2		C5–C6–H10	121.1	121.1	121.0	
N13–C7–N14	112.7	112.7	112.4	112.4	N12–C7–N13	113.7	113.7	113.5	113.7
N13–C7–C15	122.0	122.0	122.0	122.0	N12–C7–H18	121.2	121.2	121.3	121.1
N14–C7–C15	125.4	125.4	125.6		N13–C7–H18	125.2	125.2	125.2	
C1–N13–C7	107.4	107.3	107.4	107.3	C1–N12–C7	106.7	106.7	106.7	106.7
C1–N13–H12	126.6	126.6	126.6	126.5	C1–N12–H11	126.9	126.9	127.0	127.0
C7–N13–H12	126.1	126.1	126.0		C7–N12–H11	126.4	126.4	126.3	
C2–N14–C7	105.3	105.3	105.6	105.6	C2–N13–C7	104.6	104.6	104.9	
C7–C15–H16	108.7	108.7	108.8	108.8	C4–C14–H15	111.3	111.3	111.2	110.9
C7–C15–H17	111.6	111.6	111.4	111.4	C4–C14–H16	111.5	111.5	111.3	111.9
C7–C15–H18	111.6	111.6	111.4		C4–C14–H17	111.5	111.5	111.3	111.9
H16–C15–H17	108.6	108.6	108.6		H15–C14–H16	107.7	107.7	107.8	
H16–C15–H18	108.6	108.6	108.6		H15–C14–H17	107.7	107.7	107.8	
H17–C15–H18	107.6	107.7	107.9		H16–C14–H17	107.0	107.0	107.2	

in-plane stretch (i.e., in-plane hydrogen stretching modes); CH<sub>3</sub> ipb: in-plane-bending (i.e., hydrogen deformation modes); CH<sub>3</sub> sb: symmetric bending; CH<sub>3</sub> ipr: in-plane rocking; CH<sub>3</sub> opr: out-of-plane rocking and tCH<sub>3</sub>: twisting hydrogen bending modes. In addition to that, CH<sub>3</sub> ops: out-of-plane stretch and CH<sub>3</sub> opb: out-of-plane bending modes of the CH<sub>3</sub> group would be expected to be depolarized for A'' symmetry species. The stretching in CH<sub>3</sub> occurs at lower frequencies than those of aromatic ring (3000–3100 cm<sup>-1</sup>). The asymmetric C–H stretching mode of CH<sub>3</sub> group is expected around 2980 cm<sup>-1</sup> and symmetric one [21,22] is expected in the region 2870 cm<sup>-1</sup>. For 2-MB molecule, the CH<sub>3</sub>, stretching around 2900–3000 cm<sup>-1</sup>, the in-plane deformations around 1370–1450 cm<sup>-1</sup> and the rocking around 990–1040 cm<sup>-1</sup> [23]. The calculated and observed wavenumbers of asymmetric vibrations of CH<sub>3</sub> group for both molecules are listed in Tables 2 and 3.

For the methyl substituted benzene derivatives the asymmetric and symmetric deformation vibrations of methyl groups normally appear in the region 1440–1465 cm<sup>-1</sup> and 1370–1390 cm<sup>-1</sup>, respectively [23,24]. The wavenumbers of these modes involving the CH<sub>3</sub> deformation agree with commonly accepted regions of these vibrations [25,26]. The work carried by Long et al. [27] on 4-methylpyridine, the frequency of 974 and 1041 cm<sup>-1</sup> in FT-Raman are assignment to the rocking modes of CH<sub>3</sub>. The rocking vibrations of the CH<sub>3</sub> group in 2- and 5-MB appear as independent vibrations. These modes usually appear [28] in the region 1010–1070 cm<sup>-1</sup>. The theoretically calculated value by B3LYP/6-311++G(d,p) method for 2-MB at 1151 cm<sup>-1</sup> show excellent agreement with literature data [28]. The same vibration observed in 5-MB as a weak band in FT-IR at 1208 and 1219 cm<sup>-1</sup> in FT-Raman. The calculated value at 1201 cm<sup>-1</sup> also coincides with experimental observation. As



**Table 2**  
Comparison of the calculated and experimental (FT-IR and FT-Raman) vibrational spectra and related assignments of 2-MB.

No	Sym.	6-31G(d,p)			6-311++G(d,p)			Exp.		Characterization of normal modes with TED(%)
		Freq <sup>a</sup>	IR Int.	Raman	Freq <sup>b</sup>	IR Int.	Raman	Ir	Raman	
1	A'	3671	48.47	105.62	3655	55.91	113.14			$\nu_{\text{NH}}(100)$
2	A'	3212	14.39	224.69	3195	11.12	256.07		3076s	$\nu_{\text{CH}}(97)$
3	A'	3202	25.88	120.22	3186	19.31	105.29		3065s	$\nu_{\text{CH}}(100)$
4	A'	3190	13.48	113.87	3174	10.87	114.05	3181w		$\nu_{\text{CH}}(99)$
5	A'	3180	0.01	48.60	3164	0.03	47.00			$\nu_{\text{CH}}(97)$
6	A'	3167	3.35	69.93	3142	3.26	68.93	3146vw	2970w	$\text{M}\nu_{\text{CH}}(100)$
7	A''	3096	16.18	117.50	3074	14.18	118.10	3064w	2920m	$\text{M}\nu_{\text{CH}}(100)$
8	A'	3043	30.89	288.51	3027	31.17	375.27			$\text{M}\nu_{\text{CH}}(100)$
9	A'	1681	14.87	5.16	1664	18.80	6.07	1624m		$\nu_{\text{CC}}(53) + \nu_{\text{CN}}(12)$
10	A'	1639	1.78	19.84	1623	2.35	25.14		1589s	$\nu_{\text{CC}}(67)$
11	A'	1596	51.50	115.81	1583	55.56	135.25	1556s	1544s	$\nu_{\text{CN}}(40) + \nu_{\text{CC}}(25)$
12	A'	1533	0.96	1.81	1519	0.80	2.08			$\delta_{\text{HCC}}(34) + \nu_{\text{CC}}(27)$
13	A'	1504	2.58	34.17	1490	0.42	27.40			$\text{M}\delta_{\text{CH}_2}(41)$
14	A''	1497	7.93	21.41	1483	9.09	10.41	1489w	1484vw	$\text{M}\delta_{\text{CH}_2}(57) + \Gamma_{\text{CCCN}}(20) + \delta_{\text{CCH}}(12)$
15	A'	1487	35.25	54.92	1473	43.81	51.09	1450vs	1451s	$\delta_{\text{CCH}}(35) + \nu_{\text{CC}}(20)$
16	A'	1437	52.46	7.73	1423	54.76	5.99			$\delta_{\text{CNH}}(22) + \nu_{\text{CN}}(25) + \nu_{\text{CC}}(15) + \delta_{\text{CCH}}(15)$
17	A'	1427	14.56	10.92	1416	16.67	4.84	1417s	1419w	$\text{M}\delta_{\text{CH}_2}(41) + \delta_{\text{CCH}}(36)$
18	A'	1393	34.14	8.57	1378	31.39	7.07	1387vs	1362w	$\nu_{\text{CC}}(34) + \nu_{\text{CN}}(12) + \text{M}\delta_{\text{CH}_2}(14)$
19	A'	1337	3.95	0.58	1327	1.67	1.27		1320w	$\delta_{\text{CCH}}(44) + \nu_{\text{CN}}(18)$
20	A'	1300	47.72	85.48	1286	59.74	98.57	1270vs	1272vs	$\nu_{\text{CN}}(40) + \nu_{\text{CC}}(24) + \delta_{\text{CCH}}(12)$
21	A'	1255	3.01	16.09	1248	3.13	25.35		1221w	$\delta_{\text{CCH}}(27) + \nu_{\text{CN}}(22) + \nu_{\text{CC}}(13)$
22	A'	1212	5.17	2.28	1207	5.81	2.14			$\delta_{\text{CNH}}(38) + \nu_{\text{CN}}(19) + \nu_{\text{CC}}(11)$
23	A'	1177	0.74	4.90	1171	1.28	7.34			$\delta_{\text{CCH}}(88)$
24	A'	1139	1.11	8.48	1133	1.89	6.42	1120m	1119w	$\delta_{\text{CCH}}(50) + \nu_{\text{CC}}(30)$
25	A''	1064	1.98	0.41	1060	1.10	0.06		1041vw	$\delta_{\text{CCH}}(68) + \Gamma_{\text{NCCH}}(25)$
26	A'	1044	1.81	27.99	1040	2.99	33.08	1044w	1029s	$\nu_{\text{CC}}(28) + \nu_{\text{CN}}(13)$
27	A'	1026	3.17	2.06	1020	4.88	6.04	1027s	1003w	$\nu_{\text{CC}}(45) + \delta_{\text{CCH}}(14)$
28	A'	986	0.97	2.95	982	2.34	1.56			$\nu_{\text{CN}}(33) + \delta_{\text{CCH}}(30)$
29	A''	975	0.06	0.13	968	0.05	0.08			$\Gamma_{\text{HCCH}}(53) + \Gamma_{\text{CCCH}}(32)$
30	A''	933	1.73	0.78	935	2.19	0.10	926w		$\Gamma_{\text{HCCH}}(45) + \Gamma_{\text{CCCH}}(29)$
31	A'	902	2.58	0.17	903	2.16	0.57	896w		$\delta_{\text{CCC}}(37) + \delta_{\text{CCH}}(14)$
32	A''	861	0.44	4.21	850	0.66	0.14			$\Gamma_{\text{CCCH}}(45) + \Gamma_{\text{HCCH}}(28) + \Gamma_{\text{HCCH}}(17) + \Gamma_{\text{CCCH}}(17)$
33	A'	849	3.94	14.11	845	3.54	18.23	835w	838m	$\nu_{\text{CC}}(55)$
34	A''	776	8.92	2.03	761	38.79	0.56	767w		$\Gamma_{\text{CCCH}}(34) + \Gamma_{\text{CCCC}}(28)$
35	A''	757	44.76	2.20	743	43.42	0.11	735vs		$\Gamma_{\text{CCCH}}(57) + \Gamma_{\text{HCCH}}(13)$
36	A'	679	0.95	8.74	679	0.83	10.99		675m	$\nu_{\text{CC}}(25) + \delta_{\text{CCC}}(20) + \delta_{\text{CCN}}(13)$
37	A''	674	4.62	1.74	669	8.04	0.44			$\Gamma_{\text{CNCH}}(32) + \Gamma_{\text{HCCH}}(19) + \Gamma_{\text{CCCN}}(12) + \Gamma_{\text{HCCH}}(10)$
38	A'	630	0.18	7.80	631	0.29	8.49		626m	$\delta_{\text{CCN}}(32) + \delta_{\text{CCC}}(32) + \nu_{\text{CC}}(19)$
39	A''	591	3.34	0.12	582	2.98	0.06			$\Gamma_{\text{CCCC}}(40) + \Gamma_{\text{CCCN}}(21) + \Gamma_{\text{CCCH}}(13)$
40	A'	504	0.28	9.57	503	0.20	10.06		498m	$\delta_{\text{CCC}}(19) + \nu_{\text{CC}}(23) + \nu_{\text{CN}}(16)$
41	A'	478	6.07	0.88	481	6.35	1.16			$\delta_{\text{CCN}}(61) + \delta_{\text{CCC}}(20) + \nu_{\text{CC}}(13)$
42	A''	441	18.75	0.63	434	25.14	0.29	435m		$\Gamma_{\text{CCCC}}(35) + \Gamma_{\text{CCCH}}(15) + \Gamma_{\text{CCNH}}(13) + \Gamma_{\text{CCNC}}(11)$
43	A''	435	76.52	1.63	417	61.20	0.27		423vw	$\Gamma_{\text{CCNH}}(86)$
44	A''	320	0.43	0.39	313	0.24	0.01		317vw	$\Gamma_{\text{CCCN}}(35) + \Gamma_{\text{CCNH}}(11)$
45	A'	264	1.96	0.50	265	2.43	0.39		259vw	$\delta_{\text{CCN}}(68)$
46	A''	258	2.36	0.82	252	3.02	0.20			$\Gamma_{\text{CCCN}}(40) + \Gamma_{\text{CCCC}}(27)$
47	A''	138	3.76	2.18	134	5.05	1.20		122vs	$\Gamma_{\text{CCCN}}(58) + \Gamma_{\text{HCCH}}(15)$
48	A''	93	0.20	0.43	78	0.09	0.56			$\Gamma_{\text{HCCH}}(95)$

M: methyl group; vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sym: symmetry species; exp: experimental; freq: frequencies.

<sup>a</sup> Scaling factor: 0.961.

<sup>b</sup> Scaling factor: 0.968.

expected the  $\text{CH}_3$  torsional mode is expected below  $400\text{ cm}^{-1}$ , the computed bands at  $77$  in 2-MB and  $54\text{ cm}^{-1}$  in 5-MB are assigned to this mode, for the same vibration no spectral measurements were possible in this region due to instrumental limits.

#### 4.2.4. C=N and C–N vibrations

The identification of C–N stretching frequency in the side chain is a rather difficult task since there are problems in identifying this frequency from other vibrations due to mixing. Pinchas et al. [29] assigned the C–N stretching band at  $1368\text{ cm}^{-1}$  in benzamide. Kahovec and Kohlreusch [30] identified the stretching frequency of the C=N band in salicylic aldoxime at  $1617\text{ cm}^{-1}$ . Sundaraganesan et al. assigned the band at  $1689\text{ cm}^{-1}$  and  $1302\text{ cm}^{-1}$  to C=N and C–N stretching vibration, respectively [2]. Referring to the above workers, the band at  $1556\text{ cm}^{-1}$  is a strong band in FT-IR and  $1272\text{ cm}^{-1}$  is also a very strong band in FT-Raman is assigned to C=N and C–N stretching vibration respectively in 2-MB. The the-

oretically scaled values at  $1556$  and  $1264\text{ cm}^{-1}$  exactly correlates with experimental observation. The same vibration observed as a strong band in 5-MB at  $1543\text{ cm}^{-1}$  and in FT-Raman at  $1250\text{ cm}^{-1}$  as also a very strong band in FT-IR. The theoretically scaled values for 5-MB also exactly correlates well with experimental observation as shown in Table 3. The TED of these vibrations for both the molecules is mixed modes as evident from Tables 2 and 3.

#### 4.2.5. C=C vibrations

The C=C vibration are more interesting if the double bonds are in conjugation with the ring. The actual positions are determined not so much by the nature of substituents but by the form of the substitution around the ring [31]. The two doubly degenerate  $e_{2g}$  modes corresponding to C–C stretching in benzene are assigned to the bands at  $1387$ ,  $1556$ ,  $1589$  and  $1624\text{ cm}^{-1}$  in 2-MB. The same vibrations in 5-MB are at  $1340$ ,  $1479$ ,  $1590$  and  $1626\text{ cm}^{-1}$ . The theoretically scaled values for both the molecules also show exact

**Table 3**

Comparison of the calculated and experimental (FT-IR and FT-Raman) vibrational spectra and related assignments of 5-MB.

No	Sym.	6-31G(d,p)			6-311++G(d,p)			Exp.		Characterization of normal modes with TED(%)
		Freq <sup>a</sup>	IR Int.	Raman	Freq <sup>b</sup>	IR Int.	Raman	IR	Raman	
1	A'	3676	61.38	145.15	3662	70.74	150.94	3447vw		$\nu_{\text{NH}}(100)$
2	A'	3248	3.52	147.23	3231	1.50	137.43	3073m		$\nu_{\text{CH}}(99)$
3	A'	3199	3.52	156.39	3181	2.02	198.77			$\nu_{\text{CH}}(100)$
4	A'	3195	24.79	86.44	3179	21.32	65.82			$\nu_{\text{CH}}(99)$
5	A'	3175	8.57	69.75	3159	7.43	70.86	3017m	3075m	$\nu_{\text{CH}}(100)$
6	A'	3125	16.51	59.93	3102	17.21	63.83	2986m	2967vw	$\nu_{\text{CH}}(100)$
7	A''	3089	23.56	106.31	3068	19.50	102.89	2917vw	2917v	$\nu_{\text{CH}}(100)$
8	A'	3036	39.44	211.95	3022	40.75	280.78	2804vs		$\nu_{\text{CH}}(100)$
9	A'	1683	0.90	5.90	1665	2.35	4.62	1626m	1621vw	$\nu_{\text{CC}}(61)$
10	A'	1637	9.99	19.04	1622	11.97	20.41	1590w	1588m	$\nu_{\text{CC}}(67)$
11	A'	1547	34.79	46.07	1528	36.22	69.06		1543s	$\nu_{\text{CN}}(50) + \delta_{\text{CNC}}(22)$
12	A'	1535	10.87	11.78	1522	8.72	6.69	1479vs		$\nu_{\text{CC}}(33) + \text{M}\delta_{\text{CH}_2}(16)$
13	A'	1506	16.06	2.71	1492	19.25	0.79	1445vs		$\text{M}\delta_{\text{CH}_2}(26) + \delta_{\text{CCH}}(22) + \Gamma_{\text{CCCH}}(14)$
14	A''	1499	4.85	21.52	1487	7.07	10.32			$\text{M}\delta_{\text{CH}_2}(58) + \Gamma_{\text{CCCH}}(20)$
15	A'	1482	15.84	5.32	1467	23.03	4.93	1420w	1451m	$\nu_{\text{CC}}(17) + \delta_{\text{CCH}}(14) + \delta_{\text{CNH}}(10)$
16	A'	1429	22.39	35.83	1415	5.02	35.67			$\text{M}\delta_{\text{CH}_2}(44) + \delta_{\text{CCH}}(43)$
17	A'	1427	0.87	22.76	1414	20.54	13.71		1418m	$\nu_{\text{CC}}(26) + \delta_{\text{CNC}}(22) + \delta_{\text{CCH}}(17)$
18	A'	1382	33.80	58.60	1369	24.29	69.65	1342s	1360w	$\nu_{\text{CC}}(32) + \nu_{\text{CN}}(17) + \delta_{\text{CNH}}(15)$
19	A'	1333	18.65	1.75	1320	20.91	2.01	1291vs		$\nu_{\text{CC}}(30) + \nu_{\text{CN}}(26)$
20	A'	1299	10.74	35.82	1288	11.66	38.54			$\nu_{\text{CC}}(30) + \delta_{\text{CCH}}(27)$
21	A'	1284	14.25	8.11	1274	16.57	34.35	1250vs	1278vs	$\nu_{\text{CN}}(25) + \delta_{\text{CCH}}(20) + \delta_{\text{CNH}}(19) + \nu_{\text{CC}}(17)$
22	A'	1228	2.69	5.86	1222	3.68	6.66	1208w	1219w	$\delta_{\text{CCH}}(28) + \delta_{\text{CNH}}(16) + \nu_{\text{NH}}(12)$
23	A'	1165	3.66	3.82	1158	4.23	3.46	1162s	1152w	$\delta_{\text{CCH}}(57) + \nu_{\text{CC}}(27)$
24	A'	1147	3.25	3.85	1139	3.26	3.26	1123m	1117vs	$\delta_{\text{CCH}}(25) + \nu_{\text{CC}}(23) + \nu_{\text{CN}}(23)$
25	A''	1102	15.32	10.63	1095	20.19	11.81			$\nu_{\text{CN}}(51) + \delta_{\text{CNH}}(37)$
26	A'	1066	3.86	0.55	1061	2.78	0.06	1040w		$\text{M}\delta_{\text{CCH}}(62) + \Gamma_{\text{CCCH}}(33)$
27	A'	1026	10.57	2.34	1021	10.40	1.22	1003w	1029s	$\delta_{\text{CCH}}(54) + \Gamma_{\text{CCCH}}(34) + \nu_{\text{CC}}(12)$
28	A'	953	3.49	6.69	951	4.51	10.69	953vs		$\nu_{\text{CC}}(24) + \delta_{\text{NCC}}(12) + \delta_{\text{CCN}}(11)$
29	A''	945	2.16	2.58	945	1.77	1.94			$\nu_{\text{CC}}(23) + \delta_{\text{NCC}}(16) + \delta_{\text{CNH}}(13)$
30	A''	938	0.43	0.74	939	0.74	0.14			$\Gamma_{\text{CCCH}}(48) + \Gamma_{\text{HCCH}}(40)$
31	A'	902	7.66	2.82	889	11.31	0.03	865s		$\Gamma_{\text{CCCH}}(78)$
32	A''	854	4.78	1.25	849	8.23	0.63			$\Gamma_{\text{CNCH}}(57) + \Gamma_{\text{HNCH}}(28)$
33	A'	821	3.47	10.69	820	3.77	13.69	806vs	838m	$\nu_{\text{CC}}(27) + \nu_{\text{CN}}(17) + \delta_{\text{CCN}}(18) + \delta_{\text{CCC}}(17)$
34	A''	806	27.23	2.60	798	39.56	0.10			$\Gamma_{\text{CCCH}}(88)$
35	A''	774	0.80	1.58	759	0.46	18.79	748w		$\Gamma_{\text{CCCC}}(26) + \Gamma_{\text{CCCH}}(17) + \Gamma_{\text{CCCN}}(14) + \Gamma_{\text{CNCH}}(14)$
36	A'	760	0.57	15.84	753	0.06	0.15			$\nu_{\text{CC}}(43) + \delta_{\text{CCN}}(12)$
37	A''	657	0.34	1.80	651	0.88	0.91	633s	674m	$\Gamma_{\text{CNCH}}(35) + \Gamma_{\text{CCCN}}(14) + \Gamma_{\text{HNCH}}(12) + \Gamma_{\text{CNCH}}(11)$
38	A'	616	0.00	5.54	616	0.05	4.91	606s	626m	$\delta_{\text{CCC}}(34) + \nu_{\text{CC}}(22) + \delta_{\text{CCN}}(14)$
39	A''	605	12.05	0.43	599	16.81	0.03			$\Gamma_{\text{CCCC}}(24) + \Gamma_{\text{CCCH}}(16)$
40	A'	485	1.04	8.22	485	1.17	8.81	482vw	497s	$\delta_{\text{CCC}}(30) + \nu_{\text{CC}}(25)$
41	A'	440	43.12	0.55	438	4.37	2.06	427vs		$\delta_{\text{CCC}}(41) + \delta_{\text{CCN}}(27)$
42	A''	437	4.01	1.49	427	14.84	0.49			$\Gamma_{\text{CCCC}}(40) + \Gamma_{\text{CCCH}}(20) + \Gamma_{\text{CCCN}}(14)$
43	A''	432	65.58	2.57	422	85.14	0.46			$\Gamma_{\text{CNCH}}(58) + \Gamma_{\text{CNCH}}(16) + \Gamma_{\text{CNCH}}(16)$
44	A''	337	1.11	0.67	330	1.22	0.62			$\Gamma_{\text{CCCN}}(33) + \Gamma_{\text{CCCC}}(21) + \Gamma_{\text{CCCH}}(19)$
45	A'	292	3.84	0.05	292	4.47	0.12			$\delta_{\text{CCC}}(65) + \delta_{\text{CCN}}(12)$
46	A''	238	0.29	0.38	230	0.39	0.09			$\Gamma_{\text{CCCN}}(44) + \Gamma_{\text{CCCC}}(20)$
47	A''	148	7.15	1.39	143	9.33	1.08		123vs	$\Gamma_{\text{CCCC}}(35) + \Gamma_{\text{CCCN}}(32)$
48	A''	65	0.20	0.22	55	0.16	0.41			$\Gamma_{\text{CCCH}}(95)$

M: methyl group; vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sym: symmetry species; exp: experimental; freq: frequencies.

<sup>a</sup> Scaling factor: 0.961.<sup>b</sup> Scaling factor: 0.968.

correlation with our measured experimental data as well as literature data [32]. The TED of these vibrations for both the molecules is mixed modes as it is shown in Tables 2 and 3. The C–C ring breathing and C–C–C trigonal bending modes are assigned to the bands at 835 and 1027 cm<sup>-1</sup> in 2-MB. The ring breathing mode predicted at 831 cm<sup>-1</sup> by B3LYP/6-311++G(d,p) method exactly correlate with FT-Raman value at 838 cm<sup>-1</sup> for 2-MB. The theoretically computed value of C–C–C trigonal bending vibrational mode of 5-MB at 1003 cm<sup>-1</sup> exactly matches with experimental observation at 1003 cm<sup>-1</sup> in FT-Raman spectrum. As it is evident from TED (Tables 2 and 3) for both the molecules, the ring breathing mode is a pure mode where as C–C–C trigonal bending mode is a mixed mode. In addition, there are several C–C–C in-plane and out-of-plane bending vibrations of the benzimidazole ring carbons. The C–C–C in-plane and out-of-plane bending vibrations is in agreement with both experimental and theoretical spectra. Small changes in frequency observed for these modes are due to the change in force

constants, reduced mass ratio resulting mainly due to the extent of mixing between ring and substituent groups.

#### 4.3. Conclusions

Attempts have been made in the present work for the molecular parameters and frequency assignments for the compounds 2- and 5-MB molecules from FT-IR and FT-Raman spectra. The equilibrium geometries, harmonic frequencies of 2- and 5-MB were determined and analyzed at DFT level of theory using 6-31G(p,d) and 6-31++G(d,p) basis sets. The DFT level using 6-311++G(d,p) as higher basis set results exactly correlates with experimental data when compared with other 6-31G(d,p) lower basis set. The difference between observed and theoretical values of most the fundamental is very small. Any discrepancy noted between the observed and the calculated wavenumbers may be due to the fact that the calculations have been done on single molecule in the

gaseous state is contrary to the experimental value recorded in the presence of inter molecular interactions. Therefore, the assignments made at DFT level of theory using 6-311++G(d,p) as higher basis set with only reasonable deviations from the experimental values seem to be correct. The theoretically constructed FT-IR and FT-Raman spectrum exactly coincides with experimental spectra.

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### References

- [1] R.I. Castillo, L.A.R. Montalvo, S.P.H. Rivera, *J. Mol. Struct.* 877 (2008) 10.
- [2] N. Sundaraganesan, S. Ilakiamani, P. Subramanian, B.D. Joshua, *Spectrochim. Acta* 67A (2007) 628.
- [3] V. Krishnakumar, S. Seshadri, S. Muthunatsen, *Spectrochim. Acta* 68A (2007) 811.
- [4] B.B. Ivanova, L.I. Pindeva, *J. Mol. Struct.* 79 (2007) 144.
- [5] V. Klimesova, J. Koci, K. Waisser, J. Kaustova, *I.L. Farmaco* 57 (2002) 259.
- [6] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [7] A.P. Scott, L. Radom, *J. Phys. Chem.* 16502 (1996) 100.
- [8] J. Baker, A.A. Jarzeczki, P. Pulay, *J. Phys. Chem.* 102A (1998) 1412.
- [9] G. Rauhut, P. Pulay, *J. Phys. Chem.* 99 (1995) 3093.
- [10] A. Frisch, A. B. Nielsen, A. J. Holder, *Gauss-View Users Manual*, Gaussian Inc., Carnegie Office Park, Building 6, Pittsburg, PA 15106, USA, 2000.
- [11] Gaussian 03 Program, Gaussian Inc., Wallingford, CT, 2004.
- [12] G. Keresztury, S. Holly, J. Varga, G. Besenyi, A.Y. Wang, J.R. Durig, *Spectrochim. Acta* 49A (1993) 2007.
- [13] G. Keresztury, J.M. Chalmers, P.R. Griffith (Eds.), *Raman Spectroscopy; Theory, Hand book of Vibrational Spectroscopy*, vol. 1, John Wiley and Sons Ltd., New York, 2002.
- [14] A.E. Obodovskaya, Z.A. Starikova, S.N. Belous, I.E. Pokrovskaya, *J. Struct. Chem.* 32 (1991) 421.
- [15] B.Y.J. Lee, W.R. Schmidt, *Acta Crystallogr.* 42C (1986) 1652.
- [16] L.E. Sutton, *Tables of Interatomic Distance*, Chem. Soc., London, 1958.
- [17] D. Habibollahzadeh, J.S. Murray, P.C. Redfern, P. Politzer, *J. Phys. Chem.* 95 (1991) 7702.
- [18] G. Socrates, *Infrared and Raman Characteristic Group Frequencies, Table and Charts*, 3rd ed., Wiley, Chichester, 2001.
- [19] M. Tsuboi, *Spectrochim. Acta* 16A (1960) 505.
- [20] G. Varsanyi, *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*, vols. 1 and 2, Academia Kiado, Budapest, 1973.
- [21] D.A. Kleinman, *Phys. Rev.* 126 (1977) 1962.
- [22] B. Smith, *Infrared Spectral Interpretation, A Systematic Approach*, CRC Press, Washington, DC, 1999.
- [23] N.B. Colthup, L.H. Daly, S.E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1990.
- [24] G. Socrates, *Infrared Characteristic Frequencies*, Wiley-Inter Science Publication, New York, 1990.
- [25] D.L. Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Boston, 1991.
- [26] M. Diem, *Introduction to Modern Vibrational Spectroscopy*, Wiley, New York, 1993.
- [27] D.A. Long, W.O. George, *Spectrochim. Acta* 19 (1963) 1777.
- [28] M. Silverstein, G. Clayton Basseler, C. Morill, *Spectrometric Identification of Organic Compound*, Wiley, New York, 1981.
- [29] S. Pinchas, D. Samuel, M.W. Broday, *J. Chem. Soc.* (1961) 1688.
- [30] L. Kavovec, K.W.F. Kohlreusch, *Monatsch. Chem.* 74 (1941) 333.
- [31] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley, New York, 1959.
- [32] N.B. Colthup, L.H. Daly, S.E. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964, p. 74.