SAKARYA ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ DERGİSİ
SAKARYA UNIVERSITY JOURNAL OF SCIENCE

e-ISSN: 2147-835X
Dergi sayfası: http://dergipark.gov.tr/saufenbilder

Geliş/Received
13.07.2016
Kabul/Accepted
16.02.2017

Doi
10.16984/saufenbilder.296818

5-bromo-1h benzimidazolun ft-raman, ft-ir, nmr ölçümleri ve dft hesaplamalari

Emine Babur Şaş[1*], Mustafa Kurt[2]

ÖZ

Bu makalede 5-bromo-1h benzimidazolun (5Br1HB) spektroskopik özellikleri FT-Raman ve FT-IR spektral teknikleriyle incelendi. Optimize yapının titreşim spektrumlarının, Mulliken ve NMR analizinin tablosunu oluşturmak için Yoğunluk Fonksiyoneli Teorisi (YFT) hesaplamaları B3LYP/6-311+G(d,p) metoduyla hesaplandı. Başlıktaki molekül için elektronik yapı özellikleri (HOMO-LUMO ve moleküler elektrostatik potansiyel yüzey (MEP)) TD-DFT/B3LYP/6-311+G(d,p) metodu kullanılarak gerçekleştirildi. Deneysel değerlerle teorik değerler çok iyi uyum gösterdi.

Anahtar Kelimeler: 5-bromo-1h benzimidazol, FT-Raman, FT–IR.

Ft-raman, ft-ir, nmr and dft calculations of 5-bromo-1h benzimidazole

ABSTRACT

This paper were investigated spectroscopic studies of 5-bromo-1h benzimidazole (5Br1HB) with FT-Raman and FT-IR spectral techniques. To produce a tables of vibrational spectra, Mulliken and NMR analysis, density functional theory (DFT) calculations with B3LYP/6-311+G(d,p) level of theory were calculated for optimized structure. Features of the electronic structure (HOMO-LUMO and molecular electrostatic potential surface (MEP)) of 5Br1HB were performed using TD-DFT/B3LYP/6-311+G(d,p) method. The theoretical values with the experimental values showed very good agreement.

Keywords: 5-bromo-1h benzimidazol, FT-Raman, FT–IR.

1. GİRİŞ (INTRODUCTION)

Which plays an important role for the development of new antimicrobial agents, benzimidazole is bicyclic heteroatomic molecules [1]. Benzimidazole is reported to the applications in the treatment of some diseases like diabetes, epilepsy and antifertility [2, 3]. Its several variants have effective against biological activities as antitumor, antiviral [4], antimicrobial, antihistaminic, [5, 6] and antihelminthic [7] agents. Applications in different areas of the benzimidazole and some of its derivatives has affected many theorist and experimentalist to examine properties [8-11].

In this study, 5Br1HB molecule was analyzed using FT-Raman, FT-IR and ^{1}H and ^{13}C NMR spectra. Structural optimizations are performed, vibrational wavenumber and ^{1}H and ^{13}C chemical shift values 5Br1HB molecule are calculated by DFT/B3LYP method and the results are compared with similar molecules, x-ray data and experimental values. These values showed good agreement. Moreover, in order to understand the electronic structure HOMO-LUMO, MEP and Mulliken analysis have been also examined.

2. DENEYSEL (EXPERIMENTAL)

The infrared spectrum was recorded using a Bruker IFS 66/S spectrometer with a scanning speed of 10 cm^{-1} min^{-1} and the spectral resolution of 4.0 cm^{-1}in the range of 4000–400 cm^{-1}. Thermo Scientific Nicolet 6700 FT-IR / NXR FT-Raman Modül instrument using 1064 nm excitation from an Nd:YAG laser was used and recorded between 4000–400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were observed in Bruker Superconducting FT.NMR Spectrometer Avance TM. The results were presented in ppm relative to tetramethylsilane in DMSO solvent. ^{1}H and ^{13}C chemical shift values were recorded at the base frequency of 300 MHz for ^{13}C and ^{1}H nuclei.

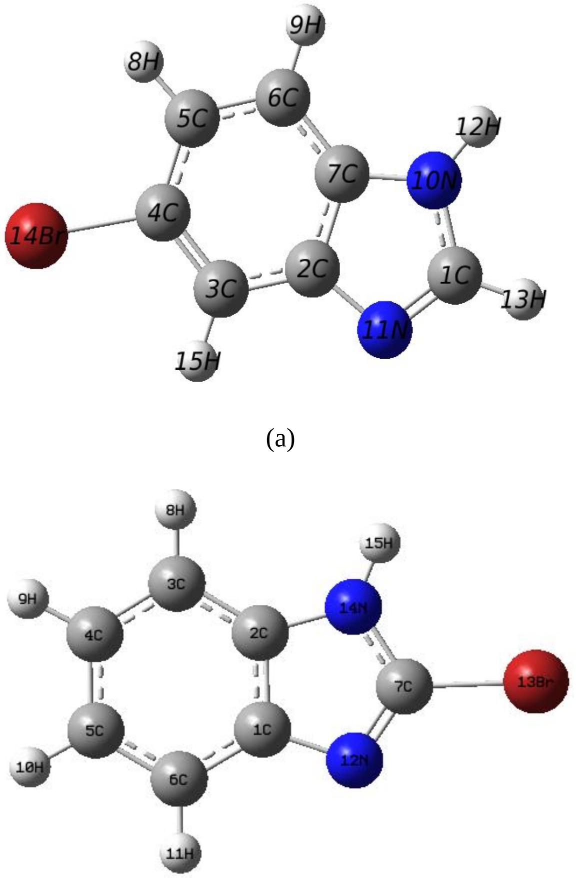
3. HESAPLAMALAR (COMPUTATIONAL DETAILS)

The molecular geometry of 5Br1HB was fully optimized and vibrational wavenumbers were computed with DFT/B3LYP/6-311G+(d,p) method. Theoretical vibrational modes were scaled using the scale factor 0.9688 [12]. The Raman activities (S_{Ra}) were converted to relative Raman intensities (I_{Ra}) and vibration modes are assigned on the basis of TED calculated by using SQM program [13, 14]. The electronic structure properties of 5Br1HB were calculated by TD-DFT [15]. NMR spectra used GIAO approach [16] were calculated at the B3LYP/6-311+G(d,p) level.

4. SONUÇLAR VE TARTIŞMA (CONCLUSIONS AND DISCUSSION)

4.1. Moleküler geometri (Molecular Geometry)

The optimized structure of 5-bromo-1h benzimidazole were computed with DFT/B3LYP/6-311+G(d,p) level is shown in Fig. 1. Geometrical parameters are compared a similar molecule with 2-bromo 1-h benzimidazole molecule [17] and X-ray data of 2-[4-(1H-1,2,4-Triazol-1-yl)phenyl]-1H-benzimidazole (1H4TPHB) molecule [18] and given in Table 1. In the title compound, the bond length C2-C7 and C4-C5 (1.41 Å) are greater than the other C–C bonds (1.39, 1.40) in the ring. C-C bond length in 2-bromo 1-h benzimidazole molecule were computed in between of 1.414-1.391 [17] and were recorded in the range of 1.400-1.368 in X-ray data of 1H4TPHB molecule [18].



(a)

(b)

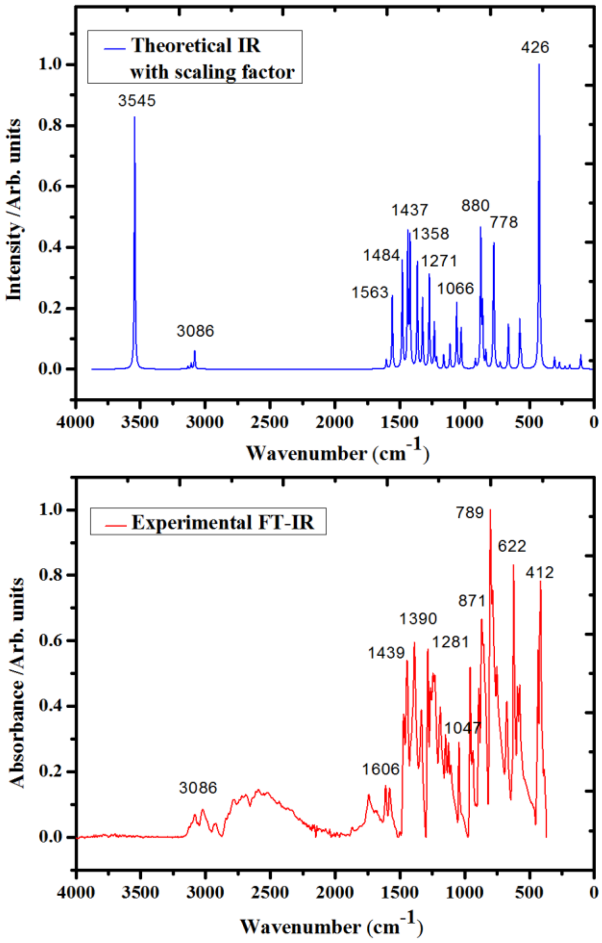
Şekil 1. a) 5Br1HB ve b) 2Br1HB ün optimize yapısı (The geometric structures of the 5Br1HB and 2Br1HB)

Which some internal bond angles of 5Br1HB as C2-C3-C4 and C5-C6-C7 (117°) are smaller than bond angle of a hexagon, bond angles as C3-C4-C5 and C2-C7-C6 (122°) are greater than the normal bond angle.

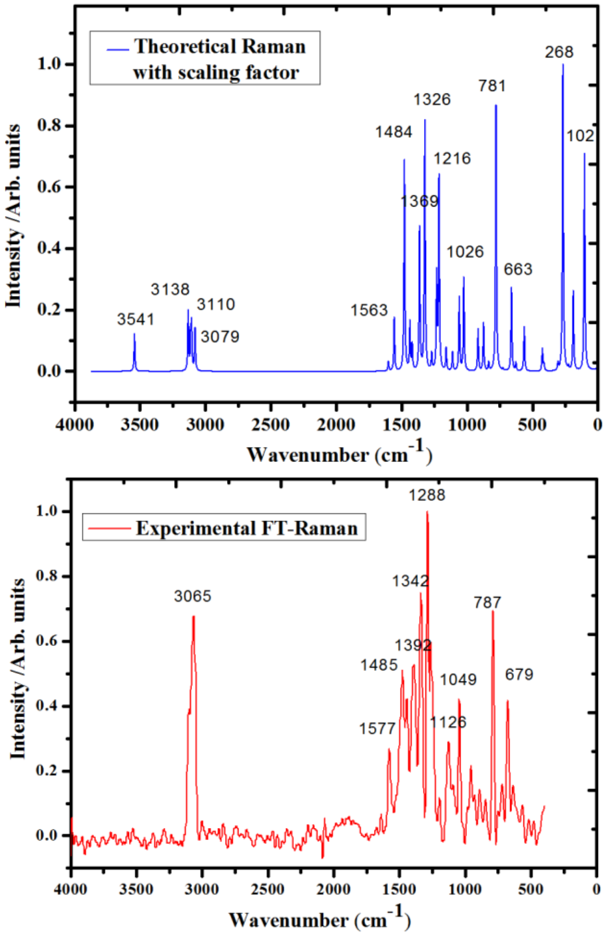
Tablo 1. 5Br1HB ve 2Br1HB hesaplanan optimize parametreleri (Calculated optimized parameter values of the 5Br1HB and 2Br1HB)

Bond Length	**5Br 1HB**	**2Br 1HB**	**Bond Length**	**5Br 1HB**	**2Br 1HB**	**Bond Length**	**5Br 1HB**	**2Br 1HB**
C1-N10	1.38	1.37	C2-N11	1.39	1.39	C5-C6	1.39	1.39
C1-N11	1.31	1.29	C3-C4	1.39	1.39	C5-H8	1.08	1.08
C1-H13	1.08	-	C3-H15	1.08	1.08	C6-C7	1.39	1.39
C2-C3	1.40	1.40	C4-C5	1.41	1.41	C6-H9	1.08	1.08
C2-C7	1.41	1.41	C4-Br14	1.92	1.89	C7-N10	1.38	1.39
						N10-H12	1.01	1.01
Bond Angle						**Bond Angle**		
N10-C1-N11	113.5	114.7	C3-C4-C5	122.8	121.5	C2-C7-N10	104.5	104.5
N10-C1-H13	121.3	-	C3-C4-Br14	119.0	-	C6-C7-N10	133.3	132.9
N11-C1-H13	125.2	-	C5-C4-Br14	118.2	-	C1-N10-C7	106.8	106.1
C3-C2-C7	120.2	119.9	C4-C5-C6	120.5	121.58	C1-N10-H12	126.3	126.0
C3-C2-N11	129.4	129.7	C4-C5-H8	119.6	119.27	C7-N10-H12	126.9	127.9
C7-C2-N11	110.4	110.4	C6-C5-H8	119.9	119.15	C1-N11-C2	104.9	104.4
C2-C3-C4	117.0	117.8	C5-C6-C7	117.2	116.57	C2-C7-C6	122.3	122.6
C2-C3-H15	120.8	120.4	C5-C6-H9	120.5	121.28	C7-C6-H9	122.3	122.1
C4-C3-H15	122.2	121.8						

This may be because of attached bromo atom in phenyl groups. Similar deviations are observed in the 2-bromo 1-h benzimidazole molecule and XRD ring also [17,18].



Şekil 2. 5Br1HB deneysel ve teorik IR spektrumu (The experimentaland calculated IR spectrum of the 5Br1HB)



Şekil 3. 5Br1HB deneysel ve teorik Raman spektrumu (The experimental and calculated Raman spectrum of the 5Br1HB)

The C-H bond lengths in phenyl ring are three constant, at 1.08 Å by DFT/B3LYP method. This value by XRD were observed as 0.930 Å and C-H bond length in 2Br1HB were calculated at 1.08 Å [18,17].

The N10-H12 bond length of the 5Br1HB was calculated as 1.01 Å. This bond length were calculated as 1.01 Å in 2-bromo 1-h benzimidazole [17], 5-benzimidazole carboxylic acid [19] and 2-(4-Bromophenyl)-1H-benzimidazole [20] molecules also. The N-H bond length in x-ray data of 1H4TPHB molecule were observed as 0.86 Å [18].

4.2. Titreşim spectrum Analizi (Vibrational spectral analysis)

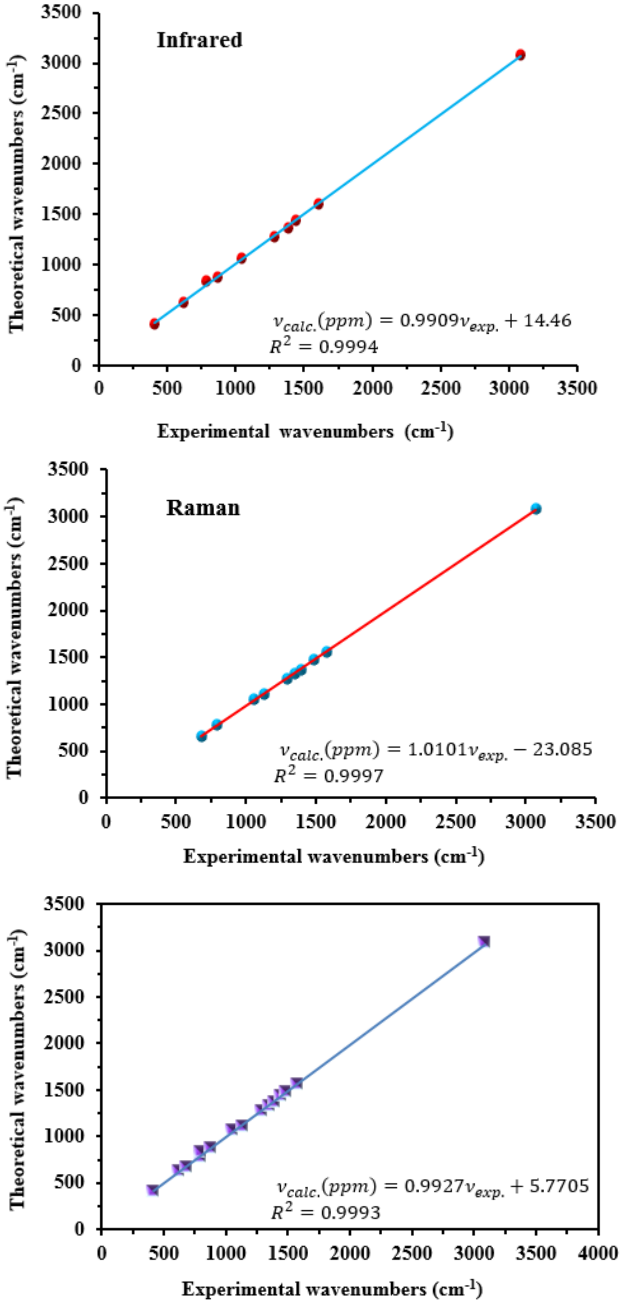
IR and Raman spectrum of the studied compound obtained using 6-311+G(d,p) basis set by DFT method. The theoretical and experimental Raman and IR spectrum shown in Fig. 2. All band assignments are presented in Table 2. 5Br1HB has 15 atoms and 39 vibrational modes. Vibrational bands were studied with TED (Total Energy Distribution). In this study, the scaling factor is 0.9688 for B3LYP/6–311G+(d,p) basis set. The correlation graphic of the theoretical and experimental bands for the compound was drawn and was shown in Fig 4.

4.2.1. N-H Titreşimleri (N-H vibrations)

N-H stretching modes show between 3500–3000 $\mathrm{cm^{-1}}$ in heterocyclic compounds [21]. This band were calculated as 3546 $\mathrm{cm^{-1}}$ in 2Br1HB [17], as 3513 $\mathrm{cm^{-1}}$ in 2-arylaminomethyl-1H-benzimidazole [22], 3509 $\mathrm{cm^{-1}}$ in 2-chloromethyl-1H-benzimidazole hydrochloride [23], as 3502 $\mathrm{cm^{-1}}$ in 2-(4-Bromophenyl)-1H-benzimidazole [20], 3206 $\mathrm{cm^{-1}}$ in 5-benzimidazole carboxylic acid [19]. N-H stretching vibration for 5Br1HB molecule were computed at 3543 $\mathrm{cm^{-1}}$. The N-H in-plane and out of plane bending vibrations are obtained at 1364 $\mathrm{cm^{-1}}$ with a TED of 22% and 425 $\mathrm{cm^{-1}}$ with a TED of 55%. This band in FT-Raman and FT-IR were observed as1392 and 1390 $\mathrm{cm^{-1}}$, respectively.

4.2.2. C-H Titreşimleri (C-H vibrations)

C-H stretching modes occurs in interval 3000-3100 $\mathrm{cm^{-1}}$ in hetero aromatic rings [21, 24-26]. This vibrations were computed in the region between 3081-3133 $\mathrm{cm^{-1}}$ by DFT/B3LYP/6–311G+(d,p) method were recorded at 3065 and 3085 $\mathrm{cm^{-1}}$ in FT–Raman and FT-IR. The C–H in–plane bending and out plane bending vibrations occurs in the ranges 1000–1300 $\mathrm{cm^{-1}}$ and 800-950 $\mathrm{cm^{-1}}$ for aromatic rings, respectively [27,28]. These vibrations for 5Br1HB molecule were calculated in the range of 1113-1234 $\mathrm{cm^{-1}}$ with significant TED (>20%) and at 916, 862 $\mathrm{cm^{-1}}$ with significant TED (>30%) were observed at 1126 $\mathrm{cm^{-1}}$ in FT-Raman. İn similar molecules also calculated and observed in the ranges same band [17, 19-20, 22-23].



Şekil 4. 5Br1HB hesaplanan ve deneysel korelasyon grafikleri (Correlation graphic of calculated and experimental frequencies for 5Br1HB)

4.2.3. Halka Titreşimleri (Ring vibrations)

The bands at 1480 and 1650 $\mathrm{cm^{-1}}$ are reported to C-C stretching vibrational [29]. In this study, the C-C stretching vibrations were observed at 1577, 1485, 1392, 1342, 1288, 1126 $\mathrm{cm^{-1}}$ and 1606, 1439, 1390, 1281 $\mathrm{cm^{-1}}$

in the FT-Raman and FT-IR, respectively. The same band were obtained in the ranges 1603-1113 and 1026-917 cm^{-1} with DFT method. The main C–C stretching mode were obtained at 1558 cm^{-1} with the TED contribution 70%. The out of plane and in-plane and bending vibrations are consistent with literature [30].

Tablo 2. 5Br1HB molekülünün deneysel ve thesaplanan titreşim spektrumlarının karşılaştırılması (Comparison of the calculated and experimental vibrational spectra and proposal assignments of 5Br1HB molecule)

	Experimental wavenumber			**Theoretical wavenumber**			**TED (10%)**
No	FT-IR	FT-Raman	Scaled^b	I_{IR}	S_{Ra}	I_{Ra}	Assignments
1			104	4.60	1.79	1.00	τCCCN(24)+τCCCBr(40)+ τCCHBr(15)
2			189	1.36	1.27	0.25	δCCBr(78)
3			226	0.94	0.06	0.01	τCCCC(15)+τCCCN(52)
4			269	2.24	7.39	0.81	υCBr(57)+ δCCC(14)
5			306	3.75	0.20	0.02	τCCCN(39)+ τCCCBr(24)
6	412		413	7.44	0.28	0.02	τCCCC(46)+τCCCH(20)+ τCCCN(18)
7			425	93.56	0.84	0.05	τCCHN(55)+τCHHN(17)+ τCHNN(17)
8			429	6.37	0.19	0.01	δCCC(25)+ δCCN(40)
9			564	4.49	2.73	0.10	υCC(13)+ υCN(11)+ δCCC(34)
10			575	15.47	0.10	0.00	τCCCC(37)+τCCCH(22)+ τCCCN(18)
11	622		628	0.09	0.56	0.02	τCCCN(15)+τCCHN(12)+ τCCNN(36)+ τCHNN(12)
12		679	662	14.45	6.41	0.18	υCC(13)+ υCBr(14)+ δCCC(19)+ δCCN(32)
13			726	1.93	0.18	0.00	τCCCC(24)+τCCCH(22)+ τCCCN(18)+ τCCNN(15)
14			775	37.88	0.17	0.00	τCCCH(52)+ τCCHN(22)+ τCCCBr(15)
15		787	780	8.30	26.19	0.58	υCC(40)+ υCN(18)+ δCCN(11)
16	789		837	5.24	0.92	0.02	τCCHN(55)+ τCHHN(28)
17			862	19.35	0.02	0.00	τCCCH (31)+ τCCHN(28)+ τCCHBr(23)
18	871		875	44.28	5.62	0.11	υCN(17)+ δCCC(38)+ δCCH(13)
19			916	0.69	0.22	0.00	τCCCH (30)+ τCCHH(41)+ τCCHBr(11)
20			917	2.27	5.11	0.09	υCC(19)+ δCCN(24)+ δCNN(25)+ δCHN(22)
21			1026	13.27	14.39	0.21	υCC(52)+ δCCH(29)
22	1047	1049	1061	21.20	11.90	0.17	υCN(52)+ δCHN(37)
23		1126	1113	7.95	3.32	0.04	υCC(18)+ δCCH(47)
24			1161	4.60	4.30	0.05	υCN(23)+ δCCH(20)+ δCHN(18)
25			1216	3.10	39.76	0.45	υCC(18)+ υCN(31)+ δCCH(38)
26			1234	14.79	20.02	0.22	υCC(12)+ υCN(17)+ δCCH(41)+ δCHN(21)
27	1281	1288	1272	30.19	3.72	0.04	υCC(44)+ υCN(27)+ δCHN(14)
28		1342	1327	22.42	60.85	0.00	υCC(34)+ υCN(20)+ δCHN(21)
29	1390	1392	1365	34.32	37.42	0.35	υCC(28)+ υCN(20)+ δCCH(19)+ δCHN(22)
30			1421	41.41	7.05	0.06	υCC(21)+ υCN(11)+ δCCH(37)+ δCHN(11)
31	1439		1438	42.85	13.90	0.12	υCC(40)+ δCCH(20)
32		1485	1480	34.42	64.51	0.53	υCC(11)+ υCN(51)+ δCHN(22)
33		1577	1558	23.49	18.21	0.14	υCC(70)
34	1606		1603	2.98	3.57	0.03	υCC(56)+ υCN(11)
35	3086	3065	3081	5.96	99.38	0.16	υCH(100)
36			3108	1.77	102.20	0.16	υCH(99)
37			3114	0.12	78.17	0.12	υCH(99)
38			3133	0.89	147.28	0.22	υCH(99)
39			3543	81.59	156.07	0.16	υNH(100)

4.2.4. C-Br Titreşimleri (C–Br vibrations)

C–Br stretching vibrations absorbs strongly in interval 650–395 cm^{-1} in most aromatic bromo compounds [31]. This stretching mode for 5Br1HB were assigned 662 and 269 cm^{-1} with a TED of 14% and 57% and observed as 679 cm^{-1} in FT-Raman. This stretching vibrations in 2Br1HB were predicted as 569 and 287 cm^{-1} and recorded as 577 cm^{-1} in FT-Raman [17]. C–Br in-plane bending mode was computed as 189 cm^{-1} and the out of plane bending vibration is as 104 cm^{-1}.

4.2.5. C-N Titreşimleri (C-N vibrations)

The C–N stretching mode assigned as 1368 cm^{-1} in benzamide by Pinchas et al. [32]. The stretching vibration of the C=N band identified as 1617 cm^{-1} in salicylic aldoxime by Kahovec and Kohlreusch [33]. For 5Br1HB molecule the observed bands at 1606, 1390, 1281 and 1047 cm^{-1} in FT-IR and 1577, 1485, 1392, 1342, 1288, 1049 cm^{-1} in FT-Raman and this band in 1047 cm^{-1} and 1049 cm^{-1} have TED of 52%. The theoretically value C-N stretching vibration computed between 1603-1161, 1061 cm^{-1}. In according to TED, this band looks coupled with C–C vibration.

4.3. NBO analizi (NBO analysis)

NBO (natural bond orbital) analysis usually makes to understand the contribution of atomic orbitals. NBO orbitals are specified as bonding orbital, lone pair and core. The foremost interactions in NBO analysis between Lewis-type NBOs and non-Lewis NBOs. The hyperconjugative interactions in molecules can be identified by finding the increase in electron density (ED) in anti-bonding orbital. Electron density at the two conjugated σ bond (~1.98 e) and σ* bond (~0.02 e) the strong delocalization in 5Br1HB and tabulated in Table 3. Our compound by stabilization energy ~89 kJ/mol strong delocalization is seen of π-electron in ring.

Tablo 3. 5Br1HB için NBO bazında Fock matrisinin ikinci mertebeden pertürbasyon teorisi analizi (Second order perturbation theory analysis of Fock matrix in NBO basis for 5Br1HB)

Donor (i)	Type	ED/e	Acceptor(j)	Type	ED/e	$E^{(2)a}$(KJ mol^{-1})	E(j)-E(i)^{b} (a.u)	F(i.j)^{c} (a.u)
C1-N10	σ	1.99	C6-C7	σ*	0.02	4.83	1.39	0.07
C1-N11	σ	1.98	C2-C3	σ*	0.02	5.36	1.42	0.08
C1-N11	π	1.88	C2-C7	π*	0.47	18.4	0.34	0.08
C2-C3	σ	1.97	C4-Br14	σ*	0.03	5.69	0.80	0.06
C2-C7	σ	1.97	C2-C3	σ*	0.02	3.43	1.25	0.06
			C6-C7	σ*	0.02	4.72	1.24	0.07
C2-C7	π	1.59	C1-N11	π*	0.32	14.3	0.26	0.06
			C3-C4	π*	0.36	20.0	0.28	0.07
			C5-C6	π*	0.33	19.2	0.28	0.07
C3-C4	σ	1.98	C2-C3	σ*	0.02	3.16	1.30	0.06
			C4-C5	σ*	0.03	3.02	1.28	0.06
C3-C4	π	1.73	C2-C7	π*	0.47	16.5	0.29	0.07
			C5-C6	π*	0.33	19.1	0.29	0.07
C4-Br14	σ	1.98	C2-C3	σ*	0.02	2.67	1.20	0.05
			C5-C6	σ*	0.02	2.93	1.21	0.05
C5-C6	σ	1.97	C4-C5	σ*	0.03	3.62	1.26	0.06
			C7-N10	σ*	0.03	6.46	1.14	0.08
C5-C6	π	1.73	C2-C7	π*	0.47	19.1	0.28	0.07
			C3-C4	π*	0.36	17.6	0.28	0.06
N10	LP(1)	1.62	C1-N11	π*	0.32	44.9	0.28	0.10
			C2-C7	π*	0.47	31.9	0.30	0.09
N11	LP(1)	1.92	C2-C7	σ*	0.04	5.99	0.90	0.07
C1-N11	π*	0.32	C2-C7	π*	0.47	89.3	0.02	0.06

In 5Br1HB intramolecular hyperconjugative interactions of the π (C2–C7) distributed to antibonding orbital of π^* (C3–C4), (C5–C6) which leads to strong delocalization of 20.00, 19.20 kJ/mol. These have enhanced further to conjugate of the σ(C2–C7) distributed to σ^*(C2–C3), (C6–C7) leads to less stabilization of 3.43, 4.72 kJ/mol. This stabilization energy also are seen σ(C4-Br14) conjugation with σ^*(C2-C3) and σ^*(C5-C6) leads to less stabilization energy of 2.67 and 2.93 kJ/mol. The σ(C4-Br14) bond do not have the equilibration to cause any change in 5Br1HB and are tabulated in Table 3.

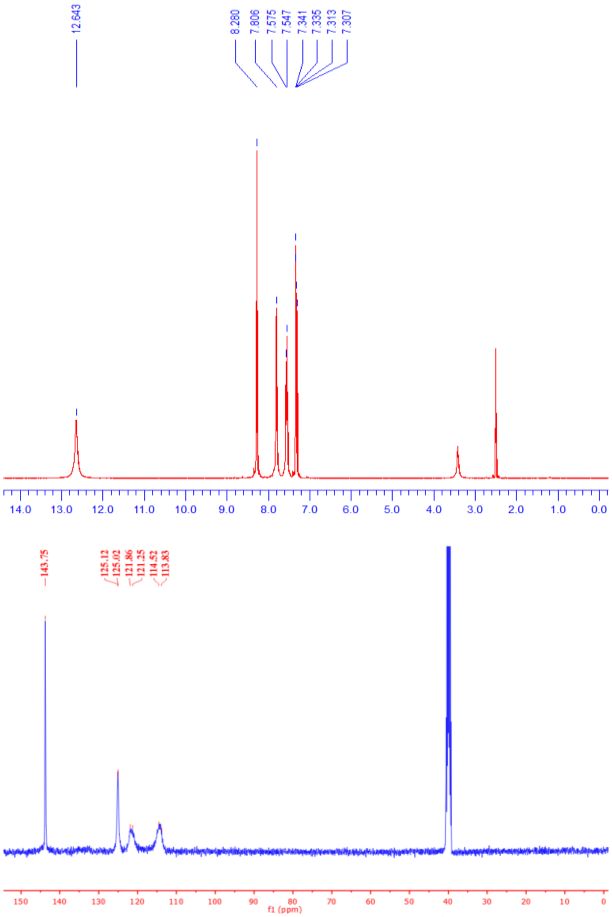
4.4. NMR Analizi (NMR analysis)

^{13}C and ^{1}H NMR values calculated by GIAO method were presented in Table 4 [34, 35]. Carbons in the ring give signals in between of 100–200 ppm [36, 37]. The experimental shift values of ring carbons of 5Br1HB observed between 114.53–143.80 ppm and they theoretically predicted in the range of 115.83–150.22 ppm in DMSO. The carbon atom C1 is slightly higher due to effect of nitrogen in the ring, thus its NMR value is found in the downfield at 143.80 ppm.

Tablo 4. 5Br1HB deneysel ve hesaplanan kimyasal kaymaları (Experimental and calculated chemical shifts (ppm) of 5Br1HB.

Atom	Calculated				Experimental
	DMSO	Water	Gas	Ethanol	DMSO
C2	150.22	150.21	150.77	150.25	125.12
C1	147.48	147.55	143.29	147.34	143.75
C7	138.09	138.11	136.53	138.03	125.02
C4	137.10	137.07	139.75	137.19	-
C5	130.92	130.92	131.10	130.92	121.86
C3	127.38	127.33	129.60	127.48	121.25
C6	115.83	115.89	112.61	115.69	113.83
H12	8.85	8.86	7.94	8.81	12.64
H13	8.12	8.12	7.81	8.11	8.28
H15	7.99	7.99	8.07	8.00	7.80
H9	7.67	7.68	7.27	7.66	7.57
H8	7.45	7.45	7.34	7.44	7.34

Complete ^{13}C and ^{1}H NMR chemical shift values are tabulated in Table 4. In this study, ^{1}H chemical shifts were computed in interval 7.45-8.85 ppm, whereas the experimental shifts are recorded in the range of 8.34-7.34 ppm in DMSO solution.



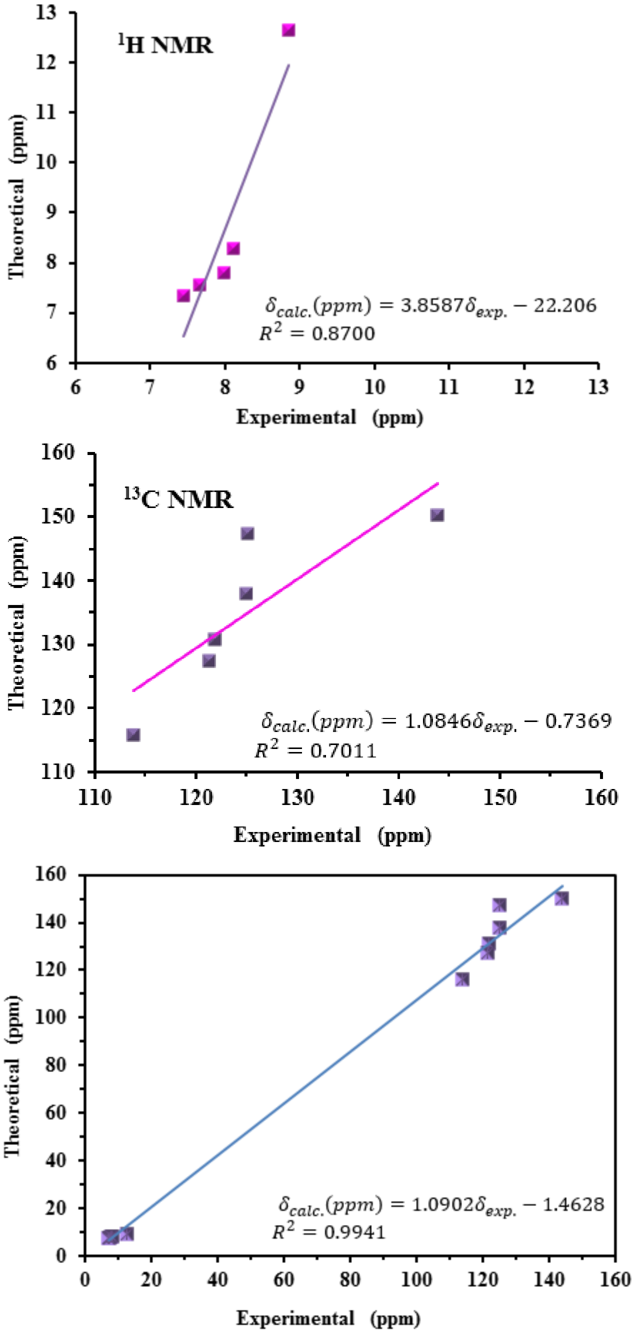
Şekil 5. 5Br1HB nin DMSO çözeltisindeki ^{1}H and ^{13}C NMR spektraları (^{1}H and ^{13}C NMR spectra of 5Br1HB in DMSO solution)

The measured ^{13}C and the ^{1}H NMR spectra are given in Fig. 5. Correlation graphics between the theoretical and experimental NMR values were plotted in Fig. 6.

4.5. Sınır Molekül Orbitalleri (Frontier Molecular Orbitals)

The energy values HOMO and LUMO orbitals play a characteristic role in the optical and electrical attributes. [38, 39]. These values are presented by TD-DFT method for 5Br1HB and are given in Fig. 7 for gas phase. The HOMO orbitals is localized in the whole of molecule and LUMO orbitals is localized in the whole of molecule except bromo atom. The energy gap of HOMO and LUMO is found to be 5.30 eV (in DMSO) for 5Br1HB.

The values chemical harness, chemical potential, electrophilicity index and electronegativity for 5Br1HB were also calculated and are given Table 5.



Şekil 6. 5Br1HB hesaplanan ve deneysel kimyasal kayma korelasyon grafikleri (Correlation graphic of calculated and experimental chemical shifts of the 5Br1HB.)

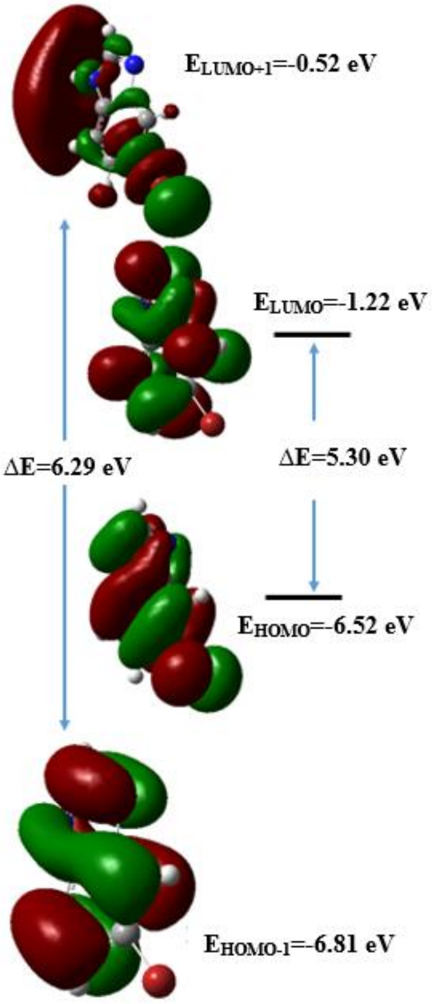
4.6. Moleküler Elektrostatik Ptansiyel Yüzeyi (Molecular electrostatic potential surface)

2D contour map provide predicting the interaction of different geometries [40-46]. 2D contour map and 3D molecular electrostatic potential surface for 5Br1HB were drawn and given in Fig. 8. The negative (red) regions and positive (blue) regions shows electrophilic reactivity and nucleophilic reactivity, respectively.

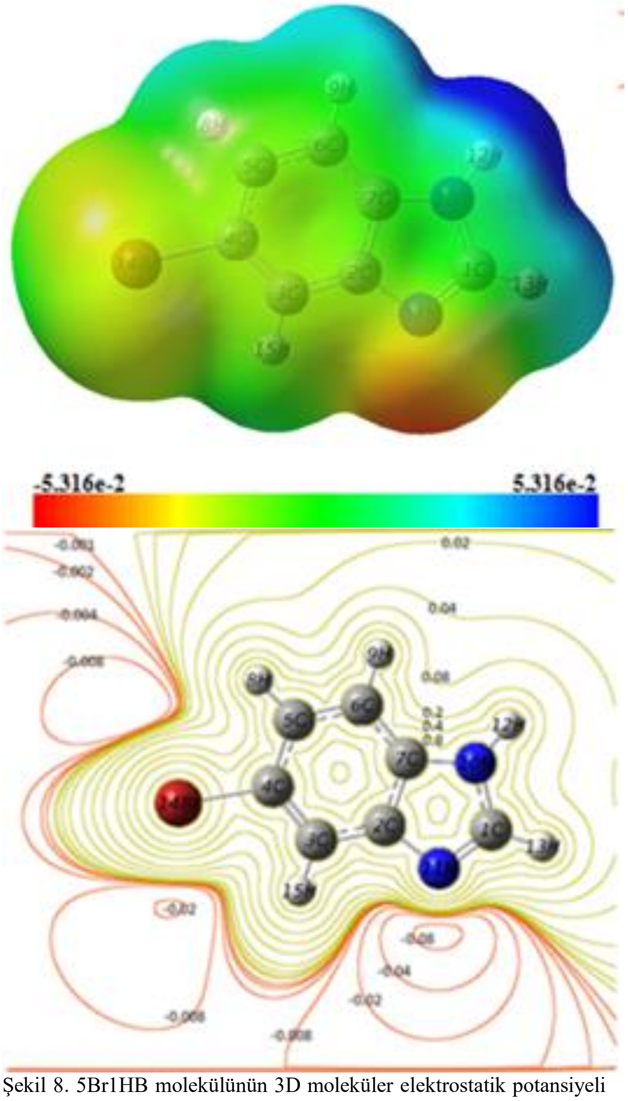
Tablo 5. 5Br1HB ün hesaplanan enerji değerleri (The calculated energies values of 5Br1HB)

5Br1HB	**Gas**	**DMSO**	**Water**	**Ethanol**
E_{total} (Hartree)	-2953.50895880	-2953.52132809	-2953.52132809	-2953.52072353
E_{HOMO} (eV)	-6.52	-6.71	-6.60	-6.60
E_{LUMO} (eV)	-1.22	-1.22	-1.22	-1.22
E_{HOMO-1} (eV)	-6.81	-6.85	-6.85	-6.57
E_{LUMO+1} (eV)	-0.52	-0.56	-0.56	-0.55
$E_{HOMO-1-LUMO+1\ gap}$ (eV)	**-6.29**	**-6.29**	**-6.29**	**-6.02**
$E_{HOMO-LUMO\ gap}$ (eV)	**-5.30**	**-5.49**	**-5.38**	**-5.38**
Chemical hardness (h)	-2.65	-2.74	-2.69	-2.69
Electronegativity (χ)	3.87	3.96	3.91	3.91
Chemical potential (μ)	-3.87	-3.96	-3.91	-3.91
Electrophilicity index(ω)	-2.83	-2.86	-2.84	-2.84

The color code maps for the title compound were predicted in between of –0.05316 (deepest red) and 0.05316 a.u. (deepest blue). Fig. 8 indicates that the region around the nitrogen atom (N11) linked with carbon through the double bond is the most electrophilic reactivity (red) and the hydrogen atom linked with nitrogen (N10) is the most of nucleophilic reactivity (blue).



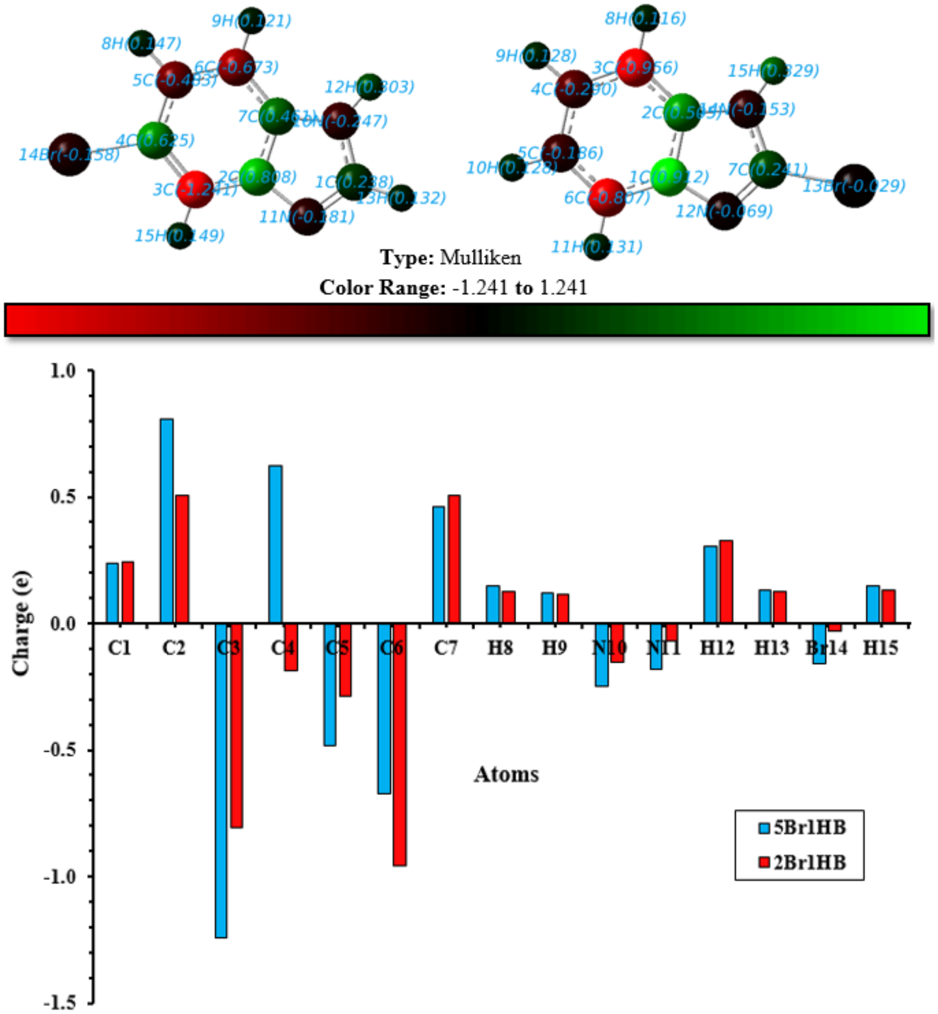
Şekil 7. Gaz fazı için 5Br1HB ün sınır molekül orbitalleri (The frontier molecular orbitals of the 5Br1HB for gas phase)



Şekil 8. 5Br1HB molekülünün 3D moleküler elektrostatik potansiyeli ve 2D kontör haritası (Molecular electrostatic potential (MEPs) 3D map and 2D contour map for 5Br1HB molecule)

4.7. Mulliken atomic Yükleri (Mulliken atomic charges)

In this study, Mulliken atomic charges of 5Br1HB were calculated using B3LYP method and with 2-bromo 1-h benzimidazole [17] were tabulated in Table 6.



Şekil 9. 5Br1HB ve 2Br1HB için Mulliken yük dağılımı (The Mulliken charge distribution for 5Br1HB and 2Br1HB)

Tablo 6. 5Br1HB ve 2Br1HB için Mulliken yük dağılımı (The Mulliken charge distribution for 5Br1HB and 2Br1HB molecule.

Atoms	5Br1HB	2Br1HB
C1	0.238	0.241
C2	0.808	0.912
C3	-1.241	-0.807
C4	0.625	-0.186
C5	-0.483	-0.290
C6	-0.673	-0.956
C7	0.461	0.505
H8	0.147	0.128
H9	0.121	0.116
N10	-0.247	-0.153
N11	-0.181	-0.069
H12	0.303	0.329
H13	0.132	0.128
Br14	-0.158	-0.029
H15	0.149	0.131

The comparison of the Mulliken charge distribution of molecules were shown in Fig. 9. In these two compounds among the ring carbon atoms C1/C2/C7 have positive charges 0.238e/0.808e/0.461e for 5Br1HB and 0.241e/0.912e/0.505e for 2Br1HB while others have negative charges, however, the charge of C4 of 5Br1HB molecule gives a different charge with each other, is positive.

5. SONUÇLAR (CONCLUSION)

In the present study, we have examined the molecular structure and vibrational wavenumbers of 5Br1HB using DFT/B3LYP/6-311+G(d,p) level. Bond angles bond lengths and of 5Br1HB compared with X-ray data and similar structures. FT-IR spectra and chemical shifts of molecule were compared with the experimental values, showing a very good agreement. MEPs contour/surface, HOMO-LUMO and Mulliken charge graphics were drawn to the understanding of attributes and dynamics of the molecule. The correlations between the thermodynamic parameters and temperature were drawn.

Acknowledgements

This work was supported by Ahi Evran University Scientific Project Unit (BAP) with, Project No: PYO–FEN.4003–12.009.

KAYNAKÇA (REFERENCES)

[1] Charansingh, G., Ganesh, J., Mohammad, S., Rajesh, K., Anant, G., Deepak, N., Mahendra, S.," Clubbed [1, 2, 3] triazoles by fluorine benzimidazole: A novel approach to H37Rv inhibitors as a potential treatment for tuberculosis", Bioorg. Med. Chem. Lett. 2008, 18, 6244.

[2] Orjales, A.; Mosquera, R.; Labeaga, L.; Rodes, R. "New 2-piperazinylbenzimidazole derivatives as 5-HT3 antagonists. Synthesis and pharmacological evaluation", J. Med. Chem. 1997, 40, 586.

[3] Grimmett, M. R., Katritzky, A. R., Rees, C. W., Scriven, "Comprehensive Heterocyclic Chemistry II", E. F. V., Eds.; Pergamon Press: Oxford, 1996. Vol. 3, pp. 77–220

[4] (a) J. Mann, A. Baron, Y. Opoku-Boahen, E. Johansson, G. Parkinson, L.R. Kelland, S. Neidle, "A new class of symmetric bisbenzimidazole-based DNA minor groove-binding agents showing antitumor activity", J. Med. Chem. 44 (2001) 138–144

(b) N.T. Abdel-Ghani, A.M. Mansour, "Novel palladium (II) and platinum (II) complexes with 1H-benzimidazol-2-ylmethyl-N-(4-bromo-phenyl)-amine: structural studies and anticancer activity", Eur. J. Med. Chem. 47 (2012) 399–411.

[5] N.M. Goudgaon, V. Dhondiba, A. Vijayalaxmi, "Synthesis and antimicrobial activity of N-1 substituted benzimidazoles", Indian J. Heterocycl. Chem. 13 (2004) 271–272

[6] N.T. Abdel-Ghani, A.M. Mansour, "Molecular structures of 2-arylaminomethyl-1H-benzimidazole: Spectral, electrochemical, DFT and biological studies", Spectrochim. Acta A 91 (2012) 272–284.

[7] P.N. Preston, "Synthesis, reactions, and spectroscopic properties of benzimidazoles", Chem. Rev. 74 (1974) 279–314.

[8] S. Mohan, "FTIR and Raman studies on benzimidazole", Spectrochim. Acta, A 47 (1991) 1111.

[9] T.D. Klots, P. Devlin, W.B. Collier, "Heteroatom derivatives of indene: V. Vibrational spectra of benzimidazole1Contribution number 368 from the Bartlesville Thermodynamics Group. 1", Spectrochim. Acta, A 53 (1997) 2445.

[10] M.A. Morsy, M.A. Al-Khadi, A. Suwaiyan, "Normal Vibrational Mode Analysis and Assignment of Benzimidazole by ab Initio and Density Functional Calculations and Polarized Infrared and Raman Spectroscopy", J. Phys. Chem. A 106 (2002) 9196.

[11] S. Yurdakul, C. Yilmaz, "Vibrational spectroscopic investigations of M (benzimidazole) 2 Ni (CN) 4 and Cd (benzimidazole) Cl 2 complexes", Vibrational Spectrosc. 21 (1999) 127.

[12] http://cccbdb.nist.gov/vsfx.asp.

[13] J. Baker, A.A. Jarzecki, P. Pulay, "Direct scaling of primitive valence force constants: an alternative approach to scaled quantum mechanical force fields", J. Phys. Chem. A102 (1998) 1412–1424.

[14] P. Pulay, J. Baker, K. Wolinski, 2013 Green AcresRoad, Suite A, Fayettevile, AR72703, USA.

[15] M.E. Casida, J.M. Seminario (Eds.), Recent Developments and Applications of Modern Density Functional Theory, Theoretical and Computational Chemistry, vol. 4, Elsevier, Amsterdam, 1996, p. 391.

[16] R.Ditchfield, Chem. Phys.76(1972)5688–5691.

[17] E.B. Sas, M. Kurt, M. Karabacak, A. Poiyamozhi, N. Sundaraganesan, "FT-IR, FT-Raman, dispersive Raman, NMR spectroscopic studies and NBO analysis of 2-Bromo-1H-Benzimidazol by density functional method", Journal of Molecular Structure 1081 (2015) 506–518.

[18] Long-Huai Cheng, Zheng Zheng, Zhi-Li Han, Zhi-Chao Wu, Hong-Ping Zhou, "2-[4-(1*H*-1,2,4-Triazol-1-yl)phenyl]-1*H*-benzimidazole", Acta Cryst. E68 (2012) o2890. ISSN 1600.

[19] V. Arjunan, A. Raj, C.V. Mythili, S. Mohan, "Vibrational, electronic and quantum chemical studies of 5-benzimidazole carboxylic acid", Journal of Molecular Structure 1036 (2013) 326–340

[20] T.S. Xavier, N. Rashid, I. H. Joe, "Vibrational spectra and DFT study of anticancer active molecule 2-(4-Bromophenyl)-1H-benzimidazole by normal coordinate analysis", Spectrochimica Acta Part A 78 (2011) 319–326

[21] N. Puviarasan, V. Arjunan, S. Mohan, "FT-IR and FT-Raman studies on 3-aminophthalhydrazide and N-aminophthalimide", Turk.*J. Chem*.,2002, 26, 323.

[22] N. T. A. Ghani, A. M. Mansour, "Molecular structures of 2-arylaminomethyl-1H-benzimidazole: Spectral, electrochemical, DFT and biological studies", Spectrochimica Acta Part A, 91 (2012) 272–284

[23] N. T. A. Ghani, A. M. Mansour, "Molecular structure of 2-chloromethyl-1H-benzimidazole hydrochloride: Single crystal, spectral, biological studies, and DFT calculations", Spectrochimica Acta Part A, 86 (2012) 605–613

[24] G. Varsanyi, Vibrational Spectra of Benzene Derivatives, Academic Press: New York, 1969.

[25] V. Krishnakumar, V. Balachandran, T. Chithambarathanu, "Density functional theory study of the FT-IR spectra of phthalimide and N-bromophthalimide", *Spectrochim. Acta*,2005, 62A, 918.

[26] V. Krishnakumar, R. John Xavier, "Normal coordinate analysis of 2-mercapto and 4, 6-dihydroxy-2-mercapto pyrimidines", *Indian J. Pure Appl. Phys*.,2003, 41, 597.

[27] V. Krishnakumar, V.N. Prabavathi,"Simulation of IR and Raman spectral based on scaled DFT force fields: A case study of 2-amino 4-hydroxy 6-trifluoromethylpyrimidine, with emphasis on band assignment", *Spectrochim. Acta*, 2008, Part A 71, 449.

[28] F. Weinhold, C. R. Landıs, ,"Natural bond orbitals and extensions of localized bonding concepts", *Chemistry Education Research and Practice in Europe*, 2001, 2, 2, 91–104

[29] D.N. Sathyanarayana, Vibrational Spectroscopy – Theory and Applications, second ed., New Age International (P) Limited Publishers, New Delhi, 2004.

[30] V. KrishnaKumar, R. John Xavier, "Normal coordinate analysis of 2-mercapto and 4, 6-dihydroxy-2-mercapto pyrimidines", Ind. J. Pure Appl. Phys. 41 (2003) 95.

[31] G. Varsanyi, Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives, vol. 1, Adam Hilger, London, 1974.

[32] S. Pinchas, D. Samuel, M. Weiss-Broday, "329. The infrared absorption of 18 O-labelled benzamide", J. Chem. Soc. 1688. (1961).

[33] L. Kahovec, K.W.F. Kohlreusch, "Studien zum Raman-Effekt", Monatsh. Chem. 74 (1941) 333.

[34] R. Ditchfield, *J. Chem. Phys*.,1972, 56 ,5688–5691.

[35] K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc*.,1990, 112, 8251–8260.

[36] H.O. Kalinowski, S. Berger, S. Braun, "Carbon–13 NMR spectroscopy", John Wiley and Sons, Chichester, 1988

[37] K. Pihlaja, E. Kleinpeter (Eds.), "Carbon–13 chemical shifts in Structural and Sterochemical Analysis", VCH Publishers, Deerfield Beach, 1994

[38] I. Fleming, Frontier Orbitals and Organic Chemical Reactions, Wiley, London, 1976.

[39] K. Fukui, "Role of frontier orbitals in chemical reactions", Science 218, 1982, 747-754.

[40] E. Scrocco, J. Tomasi, "Electronic molecular structure, reactivity and intermolecular forces: aneuristic interpretation by means of electrostatic molecular potentials", Adv. Quantum Chem. 11 (1978) 115–121.

[41] C. Muñoz-Caro, A. Niño, M.L. Sement, J.M. Leal, S. Ibeas," Modeling of protonation processes in acetohydroxamic acid", J. Org. Chem. 65 (2000) 405–410.

[42] P. Politzer, K.C. Daiker, The Force Concept in Chemistry, Van Nostrand Reinhold Co., 1981.

[43] P. Politzer, P.R. Laurence, K. Jayasuriya, in: J. McKinney, Structure Activity Correlation in Mechanism Studies and Predictive Toxicology, Special Issue of Environ. Health Perspect., vol. 61, 1985, p. 191.

[44] P. Politzer, J.S. Murray, in: D.L. Protein, R. Beveridge, R. Lavery (Eds.), Theoretical Biochemistry and Molecular Biophysics: A Comprehensive Survey, vol. 2, Adenine Press, Schenectady, NY, 1991, pp. 165–191.

[45] E. Scrocco, J. Tomasi, Topics in Current Chemistry, vol. 42, Springer Verlag, Berlin, 1973.

[46] P. Politzer, D.G. Truhlar (Eds.), Chemical Applications of Atomic and Molecular Electrostatic Potentials, Plenum Press, NY, 1981.