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Theoretical Studies of Molecular Structure and Vibrational Spectra of 2-Ethyl-1*H*-benzo[*d*]imidazole

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> Molecular geometry and vibrational spectra of 2-ethyl-1*H*-benzo[*d*]imidazole in the ground state has been calculated using the Hartree-Fock and density functional using Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional (B3LYP) methods with 6-31G(d) basis set. The computational frequencies are in good agreement with the observed results. Comparison of the observed fundamental vibrational frequencies of 2-ethyl-1*H*benzo[*d*]imidazole and calculated by density functional B3LYP and Hartree-Fock methods indicate that B3LYP is superior to the scaled Hartree-Fock approach for molecular vibrational spectra.

> Key Words: 2-Ethyl-1*H*-benzo[*d*]imidazole, DFT, Hartree-Fock method, Infrared spectrum, Molecular calculations.

INTRODUCTION

Benzimidazoles are known to exhibit a wide variety of pharmacological properties including: antimicrobial¹, antihelmintic², antihistaminic², neuroleptic², antitumor^{3,4} and inhibition of nucleic acid synthesis⁵. Many anticancer drugs [such as Imet 3393 (cytostasan)², oncodazole⁶, Hoechst 33258 (pibenzimol)³] have a benzimidazole ring in their structures. Benzimidazoles are found in a variety of naturally occurring compounds such as vitamin B₁₂ and its derivatives, and they are structurally similar to purine bases. In addition, metal complexes of ligands which have a benzimidazole ring are more effective than free ligands as antitumoral activities⁷⁻⁹. Furthermore, benzimidazoles are also of interest as corrosion inhibitors for metals and alloys^{10,11}.

IR spectroscopy is usually considered as the most important experimental method for chemists. The experimental and theoretical vibrational spectrum assignment of free benzimidazole has been reported by several authors¹²⁻¹⁴, but there is no much report on the 2-substituted derivatives of

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benzimidazoles. In present study, the vibrational spectroscopic studies of 2-ethyl-1H-benzo[d]-imidazole which has a benzimidazole ring has been reported.

The aim of this work is to calculate the molecular geometry and vibrational spectra of 2-ethyl-1*H*-benzo[*d*]imidazole by applying the Hartree-Fock and density functional using Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional methods with 6-31G(d) basis set. The calculated vibrational frequencies were analyzed and compared with experimental results.

EXPERIMENTAL

The compound was synthesized according to the Phillips methods^{15,16}. 0.1 mol *o*-phenylendiamine and 0.1 mol propionic acid in 4.5 N HCl were refluxed gently for 3 h. The mixture was neutralized with potassium bicarbonate and the resulting precipitate was filtered off, washed with several times with cold water and finally crystallized from ethanol-water (1:1). Yield: 69 %, m.p.: $173^{\circ}C$ ($172-174^{\circ}C$)¹⁶. ¹H NMR (DMSO-d₆) δ ppm: 1.22 (3H, t, J = 7.6 Hz, CH₃), 2.73 (2H, q, J = 7.6 Hz, CH₂), 7.00 (2H, dd, J = 9.4 and 3.2 Hz, aromatic H), 7.36 (2H, m, aromatic H), 12.40 (1H, s, -NH).

The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra of the 2-ethyl-1*H*-benzo[*d*]imidazole were registered using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism (4000-525 cm⁻¹; number of scans: 250; resolution: 1 cm⁻¹).

Calculations: The molecular structures of the 2-ethyl-1*H*-benzo[*d*]imidazole in the ground state are optimized by Hartree-Fock and density functional using Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional methods with the standard 6-31G(d) basis set. The vibrational frequencies were also calculated with these methods. These calculations were carried out using Gaussian 03 W program package on a double Xeon/3.2 GHz processor with 4 GB Ram¹⁷. The frequency values computed at these levels contain known systematic errors¹⁸. We therefore, have used the scaling factor values of 0.8929 and 0.9614 for HF/6-31G (d) and B3LYP/6-31G (d), respectively¹⁹. The assignment of the calculated wavenumbers is aided by the animation option of GaussView 3.0 graphical interface for gaussian programs, which gives a visual presentation of the shape of the vibrational modes.

RESULTS AND DISCUSSION

The optimized structure parameters of 2-ethyl-1*H*-benzo[*d*]imidazole calculated at *ab initio*-HF and density functional theory-B3LYP levels with the standard 6-31G(d) basis set are listed in Table-1 in accordance with the atom numbering scheme given in Fig. 1. Here, we could not obtain a good

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crystal for X-ray single crystal diffraction analysis. Hence, we could not compare the calculation results given in Table-1 with the experimental data. FT-IR spectrum of 2-ethyl-1*H*-benzo[*d*]imidazole is given in Fig. 2. Table-2 lists the vibrational frequencies obtained using *ab initio* HF/6-31G(d) and DFT-B3LYP/6-31G(d) calculations together with the experimental frequencies and the approximate description of each normal modes. The vibrational bands' assignments have been made by using GausView molecular visualization program. To make comparison with experimental frequencies, we present correlation graphic in Fig. 3 based on calculations. As we can see from Fig. 3, experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for DFT-B3LYP than HF.



Fig. 1. Theoretical geometric structure of the 2-ethyl-1H-benzo[d]imidazole

OPTIMIZED GEOMETRIES OF THE 2-ETHYL-1H-BENZO[d]IMIDAZOLE								
Bond	Calculated (6-31G(d))		Bond angles	Calculated (6-31G(d))				
lengths (Å)	HF	B3LYP	(°)	HF	B3LYP			
C1-C2	1.394	1.416	C1-C2-C3	122.6	122.6			
C2-C3	1.388	1.395	C2-C3-C4	116.8	116.7			
C3-C4	1.380	1.393	C3-C4-C5	121.4	121.5			
C4-C5	1.401	1.409	C4-C5-C6	121.2	121.4			
C5-C6	1.379	1.392	C5-C6-C1	118.1	118.2			
C1-C6	1.391	1.400	C6-C1-N7	130.0	129.9			
C1-N7	1.385	1.390	C3-C2-N9	133.0	133.1			
N7-C8	1.285	1.312	C2-N9-C8	107.0	107.4			
C8-N9	1.367	1.384	C1-N7-C8	105.5	105.3			
C8-C15	1.498	1.498	N7-C8-N9	113.0	112.6			
C2-N9	1.378	1.385	N7-C8-C15	125.2	125.3			
C15-C16	1.534	1.540	C8-C15-C16	112.8	113.4			

 TABLE-1

 OPTIMIZED GEOMETRIES OF THE 2-ETHYL-1H-BENZO[d]IMIDAZOLE

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In all the heterocyclic compounds, v(NH) vibration occurs in the region 3500-3000 cm⁻¹. The vibration mode calculated at 3507 cm⁻¹ (DFT-B3LYP) is assigned to N-H stretching mode of vibrations. This band is calculated at 3520 cm⁻¹ by Klots *et al.*¹² for benzimidazole. Klots *et al.*¹² observed this stretching band (3509 cm⁻¹) at the argon matrix spectrum of benzimidazole. However, we could not observe this stretching vibration band in the FT-IR spectrum of title compound *via* Diamond/ZnSe ATR crystal material.

Benzimidazoles are known to be strongly associated through intermolecular hydrogen bonding. The spectrum of 2-ethyl-1*H*-benzo[*d*]imidazole show strong broad bands in 3200-2400 cm⁻¹ which indicate polymeric association through intermolecular hydrogen bonding. The CH stretching vibrations of the ring also occur in this range 3300-3050 cm⁻¹. These bands are in the same region as that expected for benzene derivatives²⁰.



Fig. 2. FT-IR spectrum of 2-ethyl-1H-benzo[d]imidazole recorded at room temperature.



Fig. 3. Correlation graphics of calculated and experimental frequencies of title compound

The ethyl group symmetric and asymmetric v(C-H) stretching vibrations are established at 2938 and 2893; 3022, 2985 and 2973 cm⁻¹, respectively. These assignments were also supported by the literature^{21,22}. The two in-plane methyl hydrogen bending modes (1483 and 1455 cm⁻¹) are Vol. 19, No. 3 (2007)

 TABLE-2

 EXPERIMENTAL AND CALCULATED VIBRATIONAL FREQUENCIES (cm⁻¹) of

 2-ETHYL-1H-BENZO[d]IMIDAZOLE*,***

Experimental Calcd. Corrected Intensity Calcd. Corrected Intensity Assignments - 3914 3495 73.39 3648 3507 40.51 NH str 307. vw 3393 3030 19.44 3217 3093 17.13 CH str, sym, ar 3044, vw 3382 3020 13.52 3194 3070 11.48 CH str, asym, ar 3052, w 3356 2997 0.15 3185 3062 0.02 CH str, asym, ar 2985, w 3229 2942 28.34 3135 3014 26.89 CH str, asym, et 2938, w 3211 2860 36.83 3040 2922 30.72 CH str, sym, CH, 2839, w 3207 2860 36.83 3040 2922 30.72 CH str, sym, ar 1541, w 1761 1484 8195 51.31 1618 11.69 CK str 1439, w 3107 12864 43.16 3053 4371 3.73 CH str, sym, cH	- HF/6-31G(d) DFT-B3LYP/6-31G(d)							
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Experimenta	1 Calcd	Corrected	Intensity	Calcd	Corrected	Intensity	 Assignments
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		3914	3495	75 39	3648	3507	40.51	NH str
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3107 vw	3393	3030	19 44	3217	3093	17.13	CH str sym ar
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3084 viv	3387	3020	35.05	3207	3083	20.43	CH str sym ar
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3065 vw	3368	3007	17.82	310/	3070	14.86	CH str asym ar
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2052 w	2256	2007	0.15	2195	3070	14.80	CH str asym, ar
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3032, w	2200	2997	20.15	2125	3002	26.80	CII str. asym. at
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	3022, w	2299	2942	20.34	2120	2007	20.89	CH su, asym, et
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2985, W	3283	2930	38.94	3128	3007	33.09	CH str, asym, et
2938, W 3211 2864 33.16 30.53 2935 31.02 CH str, sym, CH ₂ 1521, w 1833 1635 35.12 1683 1618 11.69 CC str 1589, vw 1788 1595 3.17 1642 1578 2.26 CC str 1541, w 1761 1481 5.02 1533 4137 6.94 CC str H 1497, vw 1661 1481 5.02 1533 1475 6.94 CH str, sym, CH ₃ 1438, m 1642 1464 4.25 1530 1471 3.73 CH ₃ ipb 1435, m 1642 1464 4.25 1530 1471 3.73 CC str + CH b 1442, m 1628 1452 1.76 1505 1447 2.46 CH ₃ i, sym, b 1379, w 1502 1340 24.87 1413 1358 14.87 CC str + CH b 1324, m 1466 1308 6.75 1367 1314 30.68 CH ₂ sym, b 1220, vw 1369 1221 45.35 1291 <td>2975, W</td> <td>3200</td> <td>2913</td> <td>29.54</td> <td>2052</td> <td>2990</td> <td>11.43</td> <td>CH str, asym, et</td>	2975, W	3200	2913	29.54	2052	2990	11.43	CH str, asym, et
2893, w 3207 2800 30.83 3040 2922 30.72 CR str, sym, CH2 1621, w 1833 1635 35.12 1683 1618 11.60 CC str 1589, vw 1788 1595 3.17 1642 1578 2.26 CC str 1497, vw 1661 1481 5.02 1533 4478 0.94 CC str + CH b 1483, m 1649 1471 6.53 1534 1475 6.94 CH3 ipb 1435, m 1662 1452 1.76 1505 1447 2.46 CH3 ipb 1425, m 1627 1451 50.85 1497 1439 30.71 CC str + CH b 1309, m 1563 1394 1.39 1441 1385 7.13 CH b, CH3 1379, w 1502 1340 2.487 1413 1358 14.47 CC str + CH b 1247, m 1369 1242 8.58 1303 1253 45.04 CC str + CN str 1220, w 1369 1221 45.38 128 1171	2938, W	3211	2864	33.10	3053	2935	31.02	CH str, sym, CH_3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2893, w	3207	2860	36.83	3040	2922	30.72	CH str, sym, CH_2
	1621, W	1833	1635	35.12	1683	1618	11.69	CC str
1541, w 1761 1571 84.08 1595 1533 443.90 CX str 1497, vw 1661 1481 5.02 1538 1478 0.94 CC str CH, ipb 1438, m 1649 1471 6.53 1534 1475 6.94 CH, ipb 1438, m 1628 1452 1.76 1505 1447 2.46 CH; ipb 1438, m 1627 1451 50.85 1497 1439 30.71 CC str + CH b 1407, m 1588 1416 100.70 1451 1395 49.78 CN str + CH b 1379, w 1502 1340 24.87 1413 1358 14.87 CC str + CH b 1247, m 1933 1242 8.58 1303 1253 45.04 CC str + CN str 1220, w 1369 1221 45.35 1221 124 8.23 CH; asym, b 1200, vw 1352 1206 13.83 1258 1209 2.66 CH ipb + NH ipb 1157, vw 1312 1170 7.54 1183 <td>1589, vw</td> <td>1788</td> <td>1595</td> <td>3.17</td> <td>1642</td> <td>1578</td> <td>2.26</td> <td>CC str</td>	1589, vw	1788	1595	3.17	1642	1578	2.26	CC str
1497, vw 1661 1481 5.02 1538 1478 0.94 CC str + CH b 1483, m 1642 1464 4.25 1530 1471 3.73 CH ₃ ipb 1435, m 1628 1452 1.76 1505 1447 2.46 CH ₂ ipb 1425, m 1627 1451 50.85 1497 1439 30.71 CC str + CH b 1379, w 1563 1394 1.39 1441 1385 7.13 CH b, CH ₃ 1379, w 1502 1340 2.48.7 1413 1358 14.87 CC str + CH b 1270, s 1418 1265 13.29 1344 1292 2.56 CH ipb 1247, m 1393 1242 8.58 1303 1253 45.04 CC str + CN str 1200, vw 1352 1206 13.83 1258 1209 2.66 CH ipb + NH ipb 1169, vw 1312 1170 6.38 1218 1171 4.48 NH ipb + CH ipb 1069, w 1237 103 7.54 1183 11	1541, w	1761	1571	84.08	1595	1533	43.90	CN str
1435, m 1649 1471 6.53 1534 1475 6.94 CH ₃ ipb 1435, m 1628 1452 1.76 1505 1447 2.46 CH ₂ ipb 1425, m 1627 1451 50.85 1497 1439 30.71 CC str + CH b 1407, m 1588 1416 100.70 1451 1395 49.78 CN str + CH b 1396, m 1563 1394 1.39 1441 1385 7.13 CH b, CH ₃ 1324, m 1466 1308 6.75 1367 1314 30.68 CH ₂ , sym, b 1270, s 1418 1265 13.29 1344 1292 2.56 CH ipb 1247, m 1393 1242 8.58 1303 1253 45.04 CC str + CN str 1220, vw 1352 1206 13.83 1218 1171 4.48 Hipb + CH ipb 1169, vw 1321 1170 6.38 1218 1171 4.48 NH ipb + CH ipb 1069, w 1226 1093 0.46 1143 109	1497, vw	1661	1481	5.02	1538	1478	0.94	CC str + CH b
1455, m164214644.25153014713.73CH3 ipb1438, m162814521.76150514472.46CH2 ipb1425, m1627145150.851497143930.71CC str + CH b1396, m156313941.39144113857.13CH b, CH31379, w1502134024.871413135814.87CC str + CH b1379, w1502134024.871413135814.87CC str + CH b1270, s1418126513.29134412922.56CH ipb1247, m139312428.581303125345.04CC str + CN str1200, vw1352120613.83125812092.66CH ipb + NH ipb1157, vw131211706.38121811714.48NH ipb + CH ipb109, vw123711037.54118311370.73CH ipb1042, m1195106612.60110110587.48CH ipb, et1034, w117010446.64108310418.04CH ipb, et1044, m1139936.93104010004.29CH ipb929, w10929741.769719330.06CH opb929, w10929741.769719330.06CH opb929, w10929741.769719330	1483, m	1649	1471	6.53	1534	1475	6.94	CH ₃ ipb
1438, m162814521.76150514472.46CH2ipb1425, m1627145150.851497143930.71CC str + CH b1307, m15881416100.701451139549.78CN str + NH b1379, w1502134024.871413135814.87CC str + CH b1324, m146613086.751367131430.68CH2, sym, b1270, s1418126513.29134412922.56CH ipb1247, m139312428.581303125345.04CC str + CN str1200, vw1352120613.83125812092.66CH ipb + NH ipb1157, vw131211706.38121811714.48NH ipb + CH ipb109, vw123711037.54118311370.73CH ipb, et1034, w117010446.64108310418.04CH ipb929, w10929741.	1455, m	1642	1464	4.25	1530	1471	3.73	CH ₃ ipb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1438, m	1628	1452	1.76	1505	1447	2.46	CH ₂ ipb
	1425, m	1627	1451	50.85	1497	1439	30.71	CC str + CH b
1396, m156313941.39144113857.13CH b, CH31379, w1502134024.871413135814.87CC str + CH b1324, m146613086.751367131430.68CH2, sym, b1270, s1418126513.29134412922.56CH ipb1247, m139312428.581303125345.04CC str + CN str1200, vw1352120613.83125812092.66CH ipb + NH ipb1109, vw132711037.54118311370.73CH ipb1069, w122610930.46114311970.73CH ipb, et1034, w117010446.46108310418.04CH ipb, et1004, w11139936.93104010004.29CH ipb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb793, m8998027.618418082.42Ring breating765, w8610.148008270.45CH opb793, m8998027.618418082.42Ring breating765, w8610.148606670.74CC ipb788, vs83974843.9975772841.87CH opb788, vs <td>1407, m</td> <td>1588</td> <td>1416</td> <td>100.70</td> <td>1451</td> <td>1395</td> <td>49.78</td> <td>CN str + NH b</td>	1407, m	1588	1416	100.70	1451	1395	49.78	CN str + NH b
1379, w1502134024.871413135814.87CC str + $\dot{C}H$ b1324, m146613086.751367131430.68CH2, sym, b1270, s1418126513.29134412922.56CH ipb1247, m139312428.581303125345.04CC str + CN str1220, w1369122145.35129112418.23CH asym, b1200, vw1352120613.83125812092.66CH ipb + NH ipb1109, vw123711037.54118311370.73CH ipb, et1042, m1195106612.60110110587.48CH ipb, et1034, w117010446.64108310418.04CH ipb, et1034, w117010446.64108310418.04CH ipb, et1034, w11109820.0410179780.87CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059078722.36CCC ipb879, w9718661.759078722.36CCC ipb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87	1396, m	1563	1394	1.39	1441	1385	7.13	CH b, CH ₃
1324, m146613086.751367131430.68CH2, sym, b1270, s1418126513.29134412922.56CH ipb1247, m139312428.581303125345.04CC str + CN str1220, w1369122145.35129112418.23CH2 asym, b1200, vw1352120613.83125812092.66CH ipb + NH ipb1109, vw132711037.54118311370.73CH ipb1069, w122610930.46114310991.10CH ipb1042, m1195106612.60110110587.48CH ipb, et1034, w117010446.64108310418.40CH ipb, et1044, w11139936.93104010004.29CH ipb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb879, w9658610.148608270.45CH opb747, m85376122.497767467.87C opb, fing738, vs83974843.9975772841.87CH opb748, vs83974843.9975772841.87CC ipb <trr< td=""><td>1379, w</td><td>1502</td><td>1340</td><td>24.87</td><td>1413</td><td>1358</td><td>14.87</td><td>CC str + CH b</td></trr<>	1379, w	1502	1340	24.87	1413	1358	14.87	CC str + CH b
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1324, m	1466	1308	6.75	1367	1314	30.68	CH ₂ , sym, b
1247, m 1393 1242 8.58 1303 1253 45.04 CC str + CN str 1220, w 1369 1221 45.35 1291 1241 8.23 CH2 asym, b 1200, vw 1352 1206 13.83 1258 1209 2.66 CH ipb + NH ipb 1109, vw 1327 1103 7.54 1183 1137 0.73 CH ipb 1042, m 1195 1066 12.60 1101 1058 7.48 CH ipb, et 1034, w 1170 1044 6.64 1083 1041 8.04 CH ipb, et 1004, w 1113 993 6.93 1040 1000 4.29 CH ipb 929, w 1092 974 1.76 971 933 0.06 CC ord pb 920, w 1060 945 3.04 966 929 2.07 CC str, et 903, w 1033 921 1.05 927 891 1.57 CH opb 879, w 971 866 1.75 907 872 2.36 CCC i	1270. s	1418	1265	13.29	1344	1292	2.56	CH ipb
1220, w 1369 1221 45.35 1291 1241 8.23 CH ₂ asym, b 1200, vw 1352 1206 13.83 1258 1209 2.66 CH ipb + NH ipb 1157, vw 1312 1170 6.38 1218 1171 4.48 NH ipb + CH ipb 1109, vw 1237 1103 7.54 1183 1137 0.73 CH ipb 1069, w 1226 1093 0.46 1143 1099 1.10 CH ipb 1042, m 1195 1066 12.60 1101 1058 7.48 CH ipb, et 1004, w 1113 993 6.93 1040 1000 4.29 CH ipb 929, w 1092 974 1.76 971 933 0.06 CH opb 920, w 1060 945 3.04 966 929 2.07 CS str, et 903, w 1033 921 1.05 927 891 1.57 CH opb 879, w 971 866 1.75 907 872 2.36 CC ipb <td>1247. m</td> <td>1393</td> <td>1242</td> <td>8.58</td> <td>1303</td> <td>1253</td> <td>45.04</td> <td>CC str + CN str</td>	1247. m	1393	1242	8.58	1303	1253	45.04	CC str + CN str
1200, vw1352120613.83125812092.66CH ipb + NH ipb1157, vw131211706.38121811714.48NH ipb + CH ipb1109, vw123711037.54118311370.73CH ipb1069, w122610930.46114310991.10CH ipb1042, m1195106612.60110110587.48CH ipb, et1034, w117010446.64108310418.04CH ipb, et1004, w11139936.93104010004.29CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7786050.346306060.19CCC ipb581, vw6435731.725915682.30CCC opb530, w <td< td=""><td>1220 w</td><td>1369</td><td>1221</td><td>45.35</td><td>1291</td><td>1241</td><td>8.23</td><td>CH₂ asym. b</td></td<>	1220 w	1369	1221	45.35	1291	1241	8.23	CH ₂ asym. b
1157, vw131211706.38121811714.48NH ipb + CH ipb1109, vw123711037.54118311370.73CH ipb1069, w122610930.46114310991.10CH ipb1042, m1195106612.60110110587.48CH ipb, et1034, w117010446.64108310418.04CH ipb, et1004, w11139936.93104010004.29CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb530, w555<	1200. vw	1352	1206	13.83	1258	1209	2.66	CH inb + NH inb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1157 vw	1312	1170	6 38	1218	1171	4 48	NH ipb + CH ipb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1109 vw	1237	1103	7 54	1183	1137	0.73	CH inh
1042, m112510555.46114510571.16Chipp1034, w117010446.64100110587.48CH ipb, et1004, w11139936.93104010004.29CH ipb965, w11019820.0410179780.87CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb738, w8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb530, w5554954.295205004.87CCC ipb530, w5554954.295205004.87CCC ipb-5194635.85482 </td <td>1069 w</td> <td>1226</td> <td>1093</td> <td>0.46</td> <td>11/3</td> <td>1099</td> <td>1 10</td> <td>CH ipb</td>	1069 w	1226	1093	0.46	11/3	1099	1 10	CH ipb
1034, w117010446.64108310418.04CH ipb, et1004, w11139936.93104010004.29CH ipb, et965, w11019820.0410179780.87CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CC ipb530, w5554954.295205004.87CC ipb-5194635.854824635.66CCC ipb-5194635.854824635.66CCC ipb5194635.85435 <td>1000, w 1042 m</td> <td>1105</td> <td>1055</td> <td>12.60</td> <td>1101</td> <td>1059</td> <td>7.48</td> <td>CH ipb et</td>	1000, w 1042 m	1105	1055	12.60	1101	1059	7.48	CH ipb et
1004, w11139936.93104010004.29CH ipb et965, w11019820.0410179780.87CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb581, vw6435731.725915682.30CCC opb530, w5554954.295205004.87CC ipb-44239476.1243641946.27NH opb + CH opb-49344014.1543543538.19NH opb + CH opb40436038.53<	1042, m 1034 w	1170	1044	6.64	1083	1041	8.04	CH ipb, et
1000, w11133530.5310401000 4.25 CH ipb965, w11019820.0410179780.87CH ipb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb581, vw6435731.725915682.30CCC opb530, w5554954.295205004.87CCC ipb-40344014.1545343538.19NH opb + CH opb-44239476.1243641946.27NH opb + CC opb40436038.53<	1004 w	1113	003	6.03	1005	1000	4 20	CH ipb, ct
929, w10929741.769719730.63CH µb929, w10929741.769719330.06CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb616, w6786050.346306060.19CCC ipb530, w5554954.295205004.87CCC ipb-5194635.854824635.66CCC ipb-44239476.1243641946.27NH opb + CH opb-40436038.5337736210.56CC ipb-3112771.922942831	1004, w	1101	082	0.95	1040	078	4.29	CH ipb
920, w10329741.709719330.00CH opb920, w10609453.049669292.07CC str, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb616, w6786050.346306060.19CCC ipb530, w5554954.295205004.87CCC ipb-5194635.854824635.66CCC ipb-44239476.1243641946.27NH opb + CH opb-44239476.1243641946.27NH opb + CC opb-3112771.922942831.40CCC ipb-2802501.62258248	905, w	1002	962	1.76	071	970	0.87	CH ipo
920, w100094.3 3.04 900 925 2.07 CC st, et903, w10339211.059278911.57CH opb879, w9718661.759078722.36CCC ipb823, w9658610.148608270.45CH opb793, m8998027.618418082.42Ring breating765, w86076710.337987670.74CH opb747, m85376122.497767467.87C opb, ring738, vs83974843.9975772841.87CH opb708, s8097225.497327049.10CH opb + NH opb666, w7106330.766636371.24CCC ipb616, w6786050.346306060.19CCC ipb530, w5554954.295205004.87CCC ipb-49344014.1545338.19NH opb + CH opb-49344014.1543538.19NH opb + CC opb-40436038.5337736210.56CCC ipb-3112771.922942831.40CCC ipb-2802501.622582481.95Ring t-2081860.921971890.68CC t,	929, w	1092	9/4	2.04	9/1	933	0.00	CC str. st
905, W 1053 921 1.05 927 891 1.57 CH 0pb 879, W 971 866 1.75 907 872 2.36 CCC ipb 823, W 965 861 0.14 860 827 0.45 CH opb 793, m 899 802 7.61 841 808 2.42 Ring breating 765, W 860 767 10.33 798 767 0.74 CH opb 747, m 853 761 22.49 776 746 7.87 C opb, ring 738, vs 839 748 43.99 757 728 41.87 CH opb 708, s 809 722 5.49 732 704 9.10 CH opb + NH opb 666, W 710 633 0.76 663 637 1.24 CCC ipb 616, W 678 605 0.34 630 606 0.19 CCC ipb 581, vW 643 573 1.72 591 568 2.30 CCC opb 581, vW 643 573 1.72 591 568 2.30 CCC opb 530, W 555 495 4.29 520 500 4.87 CCC ipb - 519 463 5.85 482 463 5.66 CCC ipb - 493 440 14.15 453 435 38.19 NH opb + CH opb - 442 394 76.12 436 419 46.27 NH opb + CC opb - 404 360 38.53 377 362 10.56 CCC ipb - 311 277 1.92 294 283 1.40 CCC ipb - 280 250 1.62 258 248 1.95 Ring t - 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t et	920, w	1000	943	5.04	900	929	2.07	CU su, et
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	903, W	1033	921	1.05	927	891	1.57	CH ODD
823, w 965 861 0.14 860 827 0.45 CH opb 793 , m 899 802 7.61 841 808 2.42 Ring breating 765 , w 860 767 10.33 798 767 0.74 CH opb 747 , m 853 761 22.49 776 746 7.87 C opb, ring 738 , vs 839 748 43.99 757 728 41.87 CH opb 708 , s 809 722 5.49 732 704 9.10 CH opb + NH opb 666, w 710 633 0.76 663 637 1.24 CCC ipb 616, w 678 605 0.34 630 606 0.19 CCC ipb 581, vw 643 573 1.72 591 568 2.30 CCC opb $-$ 519 463 5.85 482 463 5.66 CCC ipb $-$ 493 440 14.15 433 435 38.19 NH opb + CH opb <	879, w	9/1	800	1./5	907	872	2.36	
795, m 899 802 7.61 841 808 2.42 King breating 765 , w 860 767 10.33 798 767 0.74 $CH opb$ 747 , m 853 761 22.49 776 746 7.87 $C opb$, ring 738 , vs 839 748 43.99 757 728 41.87 $CH opb$ 708 , s 809 722 5.49 732 704 9.10 $CH opb + NH opb$ 666 , w 710 633 0.76 663 637 1.24 $CCC ipb$ 616 , w 678 605 0.34 630 606 0.19 $CCC ipb$ 530 , w 555 495 4.29 520 500 4.87 $CCC ipb$ $ 519$ 463 5.85 482 463 5.66 $CCC ipb$ $ 493$ 440 14.15 435 38.19 $NH opb + CH opb + CC opb$ $ 442$ 394 </td <td>823, W</td> <td>965</td> <td>861</td> <td>0.14</td> <td>860</td> <td>827</td> <td>0.45</td> <td>СНорр</td>	823, W	965	861	0.14	860	827	0.45	СНорр
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	793, m	899	802	/.61	841	808	2.42	Ring breating
747, m 853 761 22.49 776 746 7.87 Copb, ring 738 , vs 839 748 43.99 757 728 41.87 CH opb 708 , s 809 722 5.49 732 704 9.10 CH opb + NH opb 666 , w 710 633 0.76 663 637 1.24 CCC ipb 616 , w 678 605 0.34 630 606 0.19 CCC ipb 581 , vw 643 573 1.72 591 568 2.30 CCC opb 530 , w 555 495 4.29 520 500 4.87 CC ipb $ 519$ 463 5.85 482 463 5.66 CCC ipb $ 493$ 440 14.15 453 435 38.19 NH opb + CH opb $ 442$ 394 76.12 436 419 46.27 NH opb + CC opb $ 444$ 360 <t< td=""><td>765, w</td><td>860</td><td>767</td><td>10.33</td><td>798</td><td>767</td><td>0.74</td><td>CH opb</td></t<>	765, w	860	767	10.33	798	767	0.74	CH opb
738, vs 839 748 43.99 757 728 41.87 CH opb 708, s 809 722 5.49 732 704 9.10 CH opb + NH opb 666, w 710 633 0.76 663 637 1.24 CCC ipb 616, w 678 605 0.34 630 606 0.19 CCC ipb 581, vw 643 573 1.72 591 568 2.30 CCC opb 530, w 555 495 4.29 520 500 4.87 CCC ipb - 493 440 14.15 453 435 38.19 NH opb + CH opb - 493 440 14.15 436 419 46.27 NH opb + CC opb - 442 394 76.12 436 419 46.27 NH opb + CC opb - 404 360 38.53 377 362 10.56 CCC ipb - 311 277 1.92 294 283 1.40 CCC ipb - <td< td=""><td>747, m</td><td>853</td><td>761</td><td>22.49</td><td>776</td><td>746</td><td>7.87</td><td>C opb, ring</td></td<>	747, m	853	761	22.49	776	746	7.87	C opb, ring
708, s 809 722 5.49 732 704 9.10 CH opb + NH opb 666, w 710 633 0.76 663 637 1.24 CCC ipb 616, w 678 605 0.34 630 606 0.19 CCC ipb 581, vw 643 573 1.72 591 568 2.30 CCC opb 530, w 555 495 4.29 520 500 4.87 CCC ipb - 519 463 5.85 482 463 5.66 CCC ipb - 493 440 14.15 453 435 38.19 NH opb + CH opb - 442 394 76.12 436 419 46.27 NH opb + CC opb - 404 360 38.53 377 362 10.56 CCC ipb - 311 277 1.92 294 283 1.40 CCC ipb - 280 250 1.62 258 248 1.95 Ring t - 243 <t< td=""><td>738, vs</td><td>839</td><td>748</td><td>43.99</td><td>757</td><td>728</td><td>41.87</td><td>CH opb</td></t<>	738, vs	839	748	43.99	757	728	41.87	CH opb
666, w 710 633 0.76 663 637 1.24 CCC ipb 616, w 678 605 0.34 630 606 0.19 CCC ipb 581, vw 643 573 1.72 591 568 2.30 CCC opb 530, w 555 495 4.29 520 500 4.87 CCC ipb - 519 463 5.85 482 463 5.66 CCC ipb - 493 440 14.15 453 435 38.19 NH opb + CH opb - 442 394 76.12 436 419 46.27 NH opb + CCC opb - 404 360 38.53 377 362 10.56 CCC ipb - 311 277 1.92 294 283 1.40 CCC ipb - 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93	708, s	809	722	5.49	732	704	9.10	CH opb + NH opb
	666, w	710	633	0.76	663	637	1.24	CCC ipb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	616, w	678	605	0.34	630	606	0.19	CCC ipb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	581, vw	643	573	1.72	591	568	2.30	CCC opb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	530, w	555	495	4.29	520	500	4.87	CCC ipb
- 493 440 14.15 453 435 38.19 NH opb + CH opb - 442 394 76.12 436 419 46.27 NH opb + CCC opb - 404 360 38.53 377 362 10.56 CCC ipb - 311 277 1.92 294 283 1.40 CCC ipb - 280 250 1.62 258 248 1.95 Ring t - 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t et	_	519	463	5.85	482	463	5.66	CCC ipb
- 442 394 76.12 436 419 46.27 NH opb + CCC opb - 404 360 38.53 377 362 10.56 CCC ipb - 311 277 1.92 294 283 1.40 CCC ipb - 280 250 1.62 258 248 1.95 Ring t - 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t et	-	493	440	14.15	453	435	38.19	NH opb + CH opb
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	_	442	394	76.12	436	419	46.27	NH opb + CCC opb
- 311 277 1.92 294 283 1.40 CCC ipb - 280 250 1.62 258 248 1.95 Ring t - 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t et	_	404	360	38.53	377	362	10.56	CCC ipb
- 280 250 1.62 258 248 1.95 Ring t - 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t, et	_	311	277	1.92	294	283	1.40	CCC ipb
- 243 217 3.30 225 216 1.89 Ring t - 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t, et	_	280	250	1.62	258	248	1.95	Ring t
- 208 186 0.92 197 189 0.68 CC t, et - 104 93 2.31 98 94 1.58 Butterfly - 36 32 0.61 27 26 0.59 CC t et	_	243	217	3.30	225	216	1.89	Ring t
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	_	208	186	0.92	197	189	0.68	CC t. et
- 36 32 0.61 27 26 0.59 CC t et	_	104	93	2.31	98	94	1.58	Butterfly
	_	36	32	0.61	27	26	0.59	CC t. et

*s, strong; vs, very strong; m, medium; w, weak; vw, very weak; blank, not observed or measured, ** str, stretching; b, bending; ipb, in-plane bending; opb, out-of-plane bending; t, torsion; sym, symmetric; asym, asymmetric; et, ethyl group; ar, aromatic group.

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also well established in the spectrum. The symmetrical and asymmetrical methyl bending mode at 1324 and 1220 cm⁻¹, respectively is observed.

The v(C–C) vibrations have been observed at 1621, 1589, 1497, 1425, 1379 and 1247 cm⁻¹. The in- and out-of-plane bending vibrations of CCC group are presented in Table-2. These assignments are in good agreement with the literature^{12,13,21}. The characteristic skeletal stretching modes of carbon-carbon bonds lead to appearance of a group of eight bands in the 1630-1200 cm⁻¹ region. All observed bands are in full agreement with the literature data^{12,21}. The IR bands appearing at 1541 and 1407 cm⁻¹ are assigned to v_{CN} vibrations for the 2-ethyl-1*H*-benzo[*d*]imidazole which is in agreement with the literature data¹³. Klots *et al.*²⁰ calculated this stretching band at 1504 cm⁻¹ and observed 1500 cm⁻¹ at the argon matrix spectrum of benzimidazole.

Conclusion

In this work, we have calculated the geometric parameters and vibrational frequencies of the 2-ethyl-1*H*-benzo[*d*]imidazole by using B3LYP and HF method with the standard 6-31G(d) basis set. We have used the scaling factor values of 0.8929 and 0.9614 for HF/6-31G (d) and B3LYP/ 6-31G (d), respectively, to fit the theoretical results with experimental ones. Scaling factors results gained seemed to be in a good agreement with experimental ones. In particular, the results of DFT-B3LYP method have shown better fit to experimental ones than *ab initio* HF in evaluating vibrational frequencies.

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