Structure and Vibrational Studies of ± 1 -(1H-Benzoimidazol-2-YL) Ethanol, Using DFT Method

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In this study, conformational analysis and quantum chemical calculations of ± 1 -(1H-Benzoimidazol-2-YL) Ethanol were carried out. The geometric structure, infrared intensities, UV-VIS spectrum, HOMO-LUMO energies, ^1H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts were calculated by using the density functional method (DFT/B3LYP) with 6-311++G(d,p) basis set. The vibrational studies were interpreted in terms of potential energy distribution (PED). Finally, calculated values were compared with the experimental ones.

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1. Introduction

Benzimidazole derivatives are important heteroaromatic compounds, which have attracted considerable attention because of their useful biological and pharmaceutical properties [1–3], such as anticancer, antimicrobial, antifungal, antitumor, etc. activities [1, 4, 5]. There are many reports in the literature, dealing with benzimidazole derivatives [1, 2, 6–8]. However till now, a detailed analysis of vibrational frequencies, IR and Raman spectra of title compound has not been reported. In this study, experimental and theoretical investigation of the vibrational frequencies, ^1H and ^{13}C NMR chemical shifts and excitation energies of this molecule were studied. The results obtained from theoretical calculations and experiment were compared.

2. Experimental details

The ± 1 -(1H-Benzoimidazol-2-YL) Ethanol compound in solid form was purchased from Sigma-Aldrich chemical Company (U.S.A.), with a stated purity of greater than 98%. It was used as such, without further purification. The FT-IR spectrum was recorded using KBr pellets on a Perkin Elmer Spectrum BX FTIR spectrophotometer in the region 4000–400 cm^{-1} . The FT-Raman spectrum was obtained on a DXR-Raman Microscope in the region 3500–12 cm^{-1} . The ^1H and ^{13}C NMR were taken in DMSO solutions on a Bruker Ultrashield 400 Plus NMR spectrometer. Proton and carbon signals were referenced to TMS. UV-visible analyses were carried out with a Perkin Elmer Lambda 20 spectrophotometer. All spectra were measured at room temperature.

3. Computational details

Gaussian 09 [9] software package was used for the theoretical calculations. The quantum chemical calculations were performed by applying the DFT method, with

the B3LYP functional and the 6-311G++(d,p) basis set. Since B3LYP vibrational wavenumbers are known to be higher than the experimental wavenumbers, due to neglect of anharmonicity effects, they were scaled down by a uniform scaling factor of 0.983, for wavenumbers up to 1700 cm^{-1} and 0.958 for wavenumbers greater than 1700 cm^{-1} [10]. The scaled wavenumbers in general show good agreement with experimental ones.

The geometry optimizations were followed by frequency calculations using the same basis set. Also, the same basis set and functional were used for the ^1H and ^{13}C NMR shielding constants calculations, by applying the GIAO method. UV-Vis spectra and electronic properties such as HOMO and LUMO energies were determined by time-dependent DFT (TD-DFT). The results were visualized using Gauss View program [11]. Total energy distribution (TED) corresponding to the observed frequencies was calculated using VEDA 4 program [12].

4. Results and discussion

4.1. Conformer analysis

The structure of the molecule, with numbering scheme for the atoms and torsion angles, is presented in Fig. 1. We performed (PES) analysis on the rotations regarding N12-C1-C14-O16 and C1-C14-O16-H20 torsion angles, scanning from -180° to 180° in steps of 5° . PES scan studies have been carried out by DFT calculations with 6-311++G(d,p) basis set (Fig. 2). The most stable conformer is obtained with the energy -533.8574 (-14527.005 eV), and with the torsion angles of 151.85° and -75° , respectively.

4.2. Vibrational frequencies

Experimental and theoretical FT-IR and FT-Raman spectra of title compound were recorded. Very good correlation was observed between experimental and calculated IR and Raman spectra (Figs. 3, 4). Characteristic bands of aromatic compounds can be found in five regions of IR spectrum. These are 3100–3000 cm^{-1} (CH stretching), 2000–1700 cm^{-1} (overtone and combinations),

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Fig. 1. The optimized molecular structure of ± 1 -(1H-Benzimidazol-2-yl) Ethanol.

Fig. 2. PES spectrum of ± 1 -(1H-Benzimidazol-2-yl) Ethanol.

1650–1430 cm^{-1} (C=C stretching), 1275–1000 cm^{-1} (in-plane CH deformation) and 900–690 cm^{-1} (out of plane CH deformation) [13]. The title molecule stretching vibrational bands were observed at 3055, 3166, 3132, 3103 and 3055 cm^{-1} for IR spectrum and 3060 cm^{-1} for Raman spectrum.

The observed symmetric and asymmetric stretching bands for CH_3 group in the interval of 2898–3100 cm^{-1} were calculated to be in the interval of 2934–3015 cm^{-1} . Rani et al. [14] identified the C–N stretching bands in the region of 1328–1266 cm^{-1} . In our title molecule C–N stretching band is observed at 1272 cm^{-1} for IR spectrum, and at 1260 cm^{-1} for Raman spectrum.

Generally the C–C ring stretching gives rise to several peaks in the region 1600 to 1400 cm^{-1} [15]. The C–C stretching band of title molecule is found in the IR spectrum between 1664 and 1485 cm^{-1} , and at 1599 and 1443 cm^{-1} in the Raman spectrum. Stretching, bending, torsion vibrational modes of title compound, and combination of these, are summarized in Table I.

4.3. NMR Analysis

NMR spectroscopy continues to be the most valuable tool for structure elucidation in solutions. By far, the most common nuclei studied in the NMR of organic and bio-organic molecules are the ^1H and ^{13}C .

TABLE I

Fundamental band assignments of ± 1 -(1H-Benzimidazol-2-yl) Ethanol.

Mo- de	calc.		exp.		Assignment
	unsc.	scaled	IR	RS*	
1	3853	3787			ν_{OH} (100)
2	3655	3593			ν_{NH} (100)
3	3195	3141	3166		ν_{CH} (94)
4	3186	3132	3132		ν_{CH} (93)
5	3175	3121			ν_{CH} (98)
6	3162	3108	3103		ν_{CH} (88)
7	3124	3071	3055	3060	ν_{CH} (96)
8	3099	3046	3010		ν_{CH} (96)
9	3030	2978	2974	2977	ν_{CH} (100)
10	2986	2935	2898	2917	ν_{CH} (99)
11	1661	1591	1664	1599	ν_{CC} (54)
12	1621	1553	1566	1543	ν_{CC} (23) + δ_{CNC} (22) + δ_{CCC} (13)
13	1578	1512	1534	1493	ν_{NC} (32) + ν_{CC} (17) + δ_{HNC} (10)
14	1517	1453	1485	1443	ν_{CC} (46) + δ_{HCC} (27)
15	1493	1430	1440		δ_{HCH} (65) + τ_{HCCC} (10)
16	1486	1424			δ_{HCH} (71) + τ_{HCCC} (13)
17	1473	1411			δ_{CNC} (12) + δ_{HCC} (43)
18	1446	1385			ν_{NC} (21) + δ_{HNC} (12)
19	1412	1353	1370	1358	ν_{CC} (14) + δ_{HOC} (12)
20	1405	1346			δ_{HCH} (89)
21	1376	1318	1318	1319	ν_{CC} (23) + δ_{HCO} (28)
22	1353	1296			δ_{HCO} (34) + τ_{HCOH} (35)
23	1326	1270	1272	1260	ν_{NC} (10) + δ_{HCC} (46) + τ_{HCOH} (10)
24	1288	1234			ν_{CC} (24) + ν_{NC} (28) + δ_{CNC} (10) + δ_{HCC} (10)
25	1250	1198	1215		ν_{NC} (11) + δ_{HNC} (16) + δ_{HCC} (28)
26	1234	1182	1190		δ_{HOC} (24) + δ_{HCO} (13) + τ_{HCOH} (15)
27	1173	1124	1121	1157	δ_{HCC} (55)
28	1161	1112	1112		ν_{NC} (11) + δ_{HOC} (25) + δ_{HNC} (24) + δ_{HCC} (10)
29	1135	1087	1087		δ_{CCC} (16) + δ_{HCC} (36)
30	1119	1072			ν_{OC} (18) + τ_{HCCC} (28)
31	1106	1060	1041		ν_{CC} (32) + ν_{OC} (14) + τ_{HCCC} (23)
32	1048	1004	1006	1014	ν_{NC} (10) + ν_{CC} (13) + ν_{OC} (11)
33	1027	984	989		δ_{HCC} (14) + δ_{CCC} (12) + δ_{CCN} (15)
34	998	956			ν_{NC} (16) + δ_{CNC} (17) + τ_{HCCC} (16)
35	972	931		906	τ_{HCCC} (83)
36	938	899	893		τ_{HCCC} (73) + τ_{CCCC} (10)
37	907	869	852		δ_{CCC} (43)
38	894	856			ν_{CC} (19) + ν_{OC} (28) + τ_{HCCC} (12)
39	851	815	812	815	τ_{HCCC} (75) + γ_{CCNC} (12)
40	828	793			ν_{CC} (25) + δ_{NCN} (18)
41	766	734	744	730	τ_{HCCC} (11) + τ_{CCCC} (15) + τ_{CCNC} (36)
42	748	717			τ_{HCCC} (40) + τ_{CCNC} (18) + γ_{CCNC} (11)
43	739	708	692		τ_{HCCC} (41) + γ_{CCNC} (14)
44	656	628	623	622	ν_{CC} (15) + δ_{CCC} (12) + δ_{CNC} (13)
45	634	607	599		ν_{CC} (32) + δ_{CCC} (23) + δ_{CNC} (23)
46	591	566	585		τ_{CCCC} (40) + τ_{CCNC} (11) + γ_{CCNC} (25)
47	575	551			δ_{CCN} (14) + τ_{HCC} (12) + γ_{OCCC} (23)
48	543	520			τ_{HCC} (56)
49	512	490	495		δ_{CCC} (20) + δ_{CCN} (10) + τ_{HCC} (16)
50	467	447	470	462	δ_{OCC} (35)
51	429	411	426		τ_{HCCC} (11) + τ_{CCCC} (23) + γ_{CCNC} (47)
52	365	350			δ_{CCN} (13) + δ_{CCC} (25) + γ_{OCCC} (16)
53	333	319		330	ν_{CC} (12) + δ_{OCC} (33) + τ_{CCCC} (16)
54	258	247			δ_{CCC} (11) + τ_{HCCC} (19) + τ_{CCCC} (13)
55	253	242			τ_{CCCC} (19) + τ_{CCNC} (30) + γ_{CCNC} (33)
56	230	220			δ_{CCC} (10) + τ_{HCCC} (37) + τ_{CCCC} (15)
57	194	186			τ_{HOC} (91)
58	157	150			δ_{CCN} (54) + δ_{CCC} (15)
59	92	88			τ_{CCCC} (11) + γ_{CCNC} (44) + γ_{CCNC} (16)
60	32	31			τ_{CCCC} (88)

* Raman spectroscopy

Fig. 3. (a) Experimental, (b) theoretical IR spectrum of ± 1 -(1H-Benzoimidazol-2-YL) Ethanol.

Fig. 4. (a) Experimental, (b) theoretical Raman spectrum of ± 1 -(1H-Benzoimidazol-2-YL) Ethanol.

The wide array of available techniques yield a wealth of information, not only in the form of just chemical shifts and coupling constants of the involved nuclei, but also as through-bond and through-space connectivity between them [16]. Therefore a full geometry optimization of title molecule was performed by using B3LYP/6-311++G(d,p). Then, gauge-including atomic orbital (GIAO) ^1H and ^{13}C chemical shift calculations of the compound have been made by the same method.

The experimental and calculated values for ^{13}C and ^1H NMR are shown in Table II. Considering that the range of ^{13}C NMR chemical shift for analogous organic molecules is usually greater than 100 ppm [14, 17], this ensures reliable interpretation of spectroscopic parameters. Also in this study, ^{13}C NMR chemical shifts in the ring for the title molecule are greater than 100 ppm. Because the nitrogen atoms are more electronegative, the chemical shift of carbon atoms (C1, C2, C7), next to nitrogen, falls in the region of higher ppm values, than those of other carbon atoms. As is shown in Table II, the chemical shift values of C1, C2 and C7 have been observed to be 159.20, 154.95, and 131.90 ppm, respectively. In addition, four carbon peaks in the ring are observed at 123.01, 127.85, 129.27, 118.39 ppm. The corresponding calculated values are at 130.7, 133.77, 135.55 and 123 ppm.

The signals of aromatic proton were observed at 7.72–7.48 ppm. ^1H NMR lines of H17, H18, H19 atoms were observed at 3.41, 4.95 and 2.42 ppm, respectively. Between the experimental and theoretical chemical shifts in ^{13}C and ^1H NMR spectra, there is a very good agreement.

TABLE II

Experimental and theoretical chemical shifts (^{13}C , ^1H) of ± 1 -(1H-Benzoimidazol-2-YL) Ethanol by B3LYP/6-311G(d,p) method [$\delta(\text{ppm})$].

Atom	Exp.	B3LYP	Atom	Exp.	B3LYP
C(1)	159.20	170.64	H(8)	7.72	9.15
C(2)	154.95	159.8	H(9)	7.12	8.8
C(3)	123.01	130.7	H(10)	7.13	8.88
C(4)	127.85	133.77	H(11)	7.48	9.08
C(5)	129.27	135.55	H(17)	3.41	3
C(6)	118.39	123	H(18)	4.95	3.31
C(7)	131.90	147.21	H(19)	2.42	2.55
C(14)	63.67	81.51	H(20)	4.93	3.29
C(15)	22.96	33.67	H(21)	12.26	10.68
			H(22)	5.78	6.68

4.4. UV-VIS Analysis

The TD-DFT/B3LYP/6-311++G(d,p) calculations have been used to determine the low-lying excited states of title molecule. The calculated results, involving the vertical excitation energies, oscillator strength (f) and wavelengths, are compared with measured experimental wavelengths in Table III. Calculation of molecular orbital geometry shows that the visible maximum absorption of this molecule corresponds to the electron transition between frontier orbitals such as HOMO and LUMO.

The HOMO energy characterizes the ability of giving an electron, LUMO characterizes the ability of electron accepting. The calculation predicts three sharp peaks at

254, 250 and 236 nm, which is in good agreement with the measured experimental data ($\lambda_{\text{exp.}} = 266$ and 194 nm).

TABLE III

The experimental and calculated UV-Vis excitation energies (ΔE) and oscillator strength (f) for ± 1 -(1H-Benzoimidazol-2-YL) Ethanol.

Excitation	C1 expansion coefficient	Excitation energy [eV]	λ_{exp}	λ_{calc} B3LYP/6-311++G(d,p)	f	
1		4.8740	266	254	0.1449	
42→44	0.42984					HOMO-1→LUMO (37%)
42→45	0.10373					HOMO-1→LUMO+1 (2%)
43→48	-0.14021					HOMO→LUMO+4 (4%)
43→44	0.47042					HOMO →LUMO(44%)
43→48	0.20462					HOMO → LUMO+4 (8%)
2		4.9573		250	0.0357	
42→44	-0.42096					HOMO-1→LUMO (35%)
43→44	0.48481					HOMO →LUMO (47%)
43→45	-0.19974					HOMO → LUMO+1 (8%)
43→48	-0.16204					HOMO → LUMO+4 (5%)
3		5.2635	194	236	0.0197	
42→44	-0.25035					HOMO-1→ LUMO (13%)
42→45	0.22985					HOMO-1→ LUMO+1(11%)
42→48	-0.15649					HOMO-1→ LUMO+4 (5%)
43→45	0.57031					HOMO → LUMO+1 (65%)

5. Conclusions

The FT-IR and FT-Raman spectra have been recorded and the detailed vibrational assignment is presented for the title molecule. The harmonic vibrational wavenumbers, NMR shifts, IR and Raman spectra of title compound are determined and analyzed by DFT/B3LYP/6-311++G(d,p) method. The predicted NMR shifts are also in good agreement with experimental results. Some discrepancy between theoretically predicted and experimental proton and carbon chemical shifts was observed. This was explained by the fact that the non-specific solute-solvent interactions were neglected in the calculations. UV analysis of title compound has been carried out using TD-DFT/B3LYP/6-311++G(d,p) basis set. All theoretical results were compared with the experiment and found to be in good agreement.

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