Structures and vibrational Frequencies of Imidazole,benzimidazole and its 2-alkyl Derivatives determined by DFT Calculations

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Abstract

The molecular structures of imidazole, benzimidazole and its 2-alkylderivatives as well as their vibrational frequencies have been determined by DFT method using B3LYP theory level at 6-311G (d,p) basis set. Some physical properties such as total energy, HOMO, LUMO energies and dipole moments of studied molecules were calculated also determined. 2-ethyl derivative posses the lowest energy -458 hartree compare with imidazole -226.27 hartree whereas the smallest energy gap between HOMO and LUMO is in 2-methyl derivative it is the most chemically reactive. Imidazole and benzimidazole are planar molecules and have dipole moments 3.7285 and 3.5528 D respectively. C4 atom carries the highest negative charge compare with the C2 atom in imidazole. In all studied molecules N1 carries higher negative charge than N3, but N1 and N3 atoms show the highest negative charge in 2-ethyl derivative. The hydrogen atom of N-H group is coplanar in all studied molecules.

Vibration frequencies and simulated spectra have been discussed and compared with the measured spectra.

Keywords: DFT calculations, molecular structures, vibrational frequencies, imidazole, benzimidazole and its 2-alkyl derivatives.

Introduction

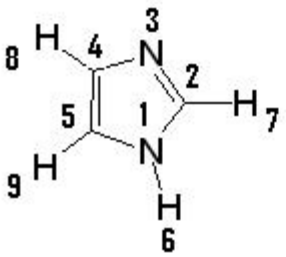
Imidazole and benzimidazole are aromatic hetro cyclic compounds occur widely as essential constituent in the most versatile binding sites in protein. Their derivatives are present in antibacterial, antifungal, antiprotozoal and antihelminthic medications (Katritzky et al. 2000)(DeLuca 2006) , metal ion complexes containing imidazole rings are used as metal corrosion inhibitors(Otacic and

Stupinisck-Lisca 2003) and potential anticancer agent(Zhoo and Lin 2005). Imidazole and benzimidazole are expected to function as aromatic **π** ligand or simple **σ** ligand in binding with aromatic or molecular species (Sundberg and Martin 1974). For metal complexes, binding energies of a series of metal ions of univalent have been measured by collision-induced dissociation(Rannulu and Rodgers 2005). The metal ions in these complexes have been predicated to be **σ** –bound to N3 group of imidazole(Alcami and Janez 1992). Metal complexes of heterocyclic compounds have been studied by zero electron kinetic energy spectroscopy(Wang et al. 2006). Structure of imidazole and Al-imidazole, Cu-imidazole have been determined by MP2/6-311+G(d,p) calculations(Xu Wang et al. 2006) .

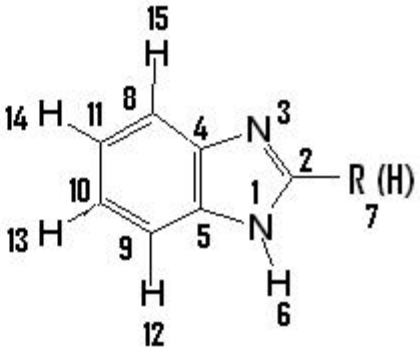
The aim of the present study is to investigate the molecular structures and vibrational frequencies of imidazole, benzimidazole and 2-alkylbenzimidazole derivatives.

Experimental and computational method

The studied molecules are represented with atoms numbering by the following Figure. They were prepared by general method from condensation of o-phenelene diamine with corresponding aliphatic carboxylic acids. The compounds were characterized by melting points and IR spectra(Seka and Müller 1931)(Pool et al. 1977). Imidazole was obtained from Fluka Company and used without further purification.



Imidazole



Benzimidazole derivatives where R=H,CH_3 and C_2H_3

These compounds have been to liberate from acidic solution by addition of ammonia which indicates that these heterocyclic aromatic compounds are basic. Experimental tests showed that they are also acidic (p^{Ka} =5.4**)** and stable to the hydrolytic action of alkalis, as well as that of acids(Fisser and Willimson 1975)**.**

IR measured by SHIMADZU FTIR as KBr disc in the range 4000-500 cm^{-1}.The theoretical calculations were carried out by personal computer type Pentium-4 with CPU 3.4 GHz and ram 512 Mbit. Software package G03W program has been used which involves ab initio, DFT and semi empirical calculations.DFT molecular orbital calculations have been performed using B3LYP theory level at 6-311G (d,p) basis set. The geometry optimization was performed before the calculations of vibrational frequencies, then simulated IR spectra were obtained.

Results and discussion

Some of the calculated physical properties of studied molecules such as total energy, HOMO and LUMO orbital energies and dipole moments are shown in Table (1), whereas Mulliken charges on the atoms are listed in Table (2).

Table (1): Some physical properties of studies molecules determined by DFT method using B3LYP/6-311G (d,p) theory level-basis set.

Molecules	Total energy	HOMO energy	LUMO Energy	ΔE	Dipole moment
Imidazole	-226.226	-0.234	0.021	0.255	3.7285
Benzimidazole	-379.960	-0.232	0.012	0.244	3.4799
2-methylbenzimidazol	-419.294	-0.018	0.015	0.033	3.4177
2-ethylbenzimidazole	-458.618	-0.228	0.014	0.242	3.5528

Dipole moment in Debye unit (D), Energy in hartree unit.

It's clear from Table (1) that 2-ethylbenzimidazole has the lowest total energy which suggests it is relatively more thermally stable than the other molecules. However the energy difference between HOMO and LUMO energies shows the lowest value in 2-methylbenzimidazole which reflects its relatively high chemical reactivity compared with other studied molecules. On the other hand, the results of dipole moment showed only two components which indicate the planarity of the molecules.

However, imidazole showed a higher dipole moment value than benzimidazole which is in agreement with the high melting point that can be explained in terms of presence of strong intermolecular interactions and hydrogen bonding. On the other hand, substitution at 2-position affects the dipole moment.

The theoretically calculated Mulliken charges on the atoms are shown in Table (2). It is clear from Table (2) that the carbon atom C4 carries the highest negative charge which suggests the electrophonic attack is more likely to occur at this such as chlorination, nitration and sulphonation in imidazole. However, nitrogen atom N1 carries the largest negative charge in all studies molecule (see Table 2). It has -0.461 in 2-ethylbenzimidazole compare with -0.328 in imidazole. In addition N1 always shows a higher negative charge than that on N3.

Table (2): Mulliken charges on some atoms determined by DFT using B3LYP theory level at 6-311G(d, p) basis set

Molecules / Atom No.	Imidazole	Benz-imidazole	2-Methylbenz-imidazole	2-Ethylbenzi-midazole
N1	-0.328	-0.423	-0.454	-0.461
C2	0.152	0.1177	0.245	0.310
N3	-0.298	-0.316	-0.332	-0.345
C4	-0.073	-0.015	-0.012	-0.011
C5	0.000	0.178	0.186	-0.189
H6	0.227	0.230	0.227	0.226
H7	0.111	0.111	------	-----
C8	-----	-0.053	-0.064	-0.056
C9	------	-0.045	-0.053	-0.054
C10	--------	-0.011	-0.112	-0.112

Some of the geometrical parameters, bond lengths and bond angles, calculated by DFT method at B3LYP/6-311G (d,p) theory level / bases set are listed in Tables (3) and (4).

From Table (3), the two bonds, C2-N1 and C5-N1,are quite different in imidazole molecule whereas they are similar in bezimidazole,2-methylbenzimidazole molecules. The calculated bond lengths in imidazole are in good agreement with previously reported values in the literature (Hus and Craven 1974) (Wang et al. 2006) (Kok et al. 1975). On the other hand, these bonds become longer in benzimidazole and the substituted benzimidazole. These facts can be interpreted in term of inductive effect of

the methyl and ethyl groups or the fused aromatic ring. In addition the N-H bond is unaffected by the substituent at 2-position but C3-N3 bond becomes slightly shorter while C4-N3 bond get longer than in imidazole.

From Table (4), the aromatic hydrogen atoms and N-H atom are coplanar in all studied molecules. The calculated bond angles are in agreement with previously reported values determined by X-ray diffraction measurements (Makino et al.1999) and that calculated by MP2/6-311G + (d, p) in imidazole(Lide and Frederikse 1997).

The vibrational frequencies and their relative intensities of the studied molecules have been determined by DFT molecular orbital calculations. These molecules show 3N-6 normal modes of vibrations, the numbers of normal moods are 21, 39, 48 and 57 for imidazole, benzimidazole, 2-methylbenzimidazole and 2-ethylbenzeimidazole respectively.

Table (3): Some bond lengths (A°) of studied molecules determined by DFT method at B3LYP/ 6-311G (d,p) bases set.

molecule / Bond	Imidazole	Benzimidazole	2-Methylbenzimid-azole	2-ethylbenzimidazo-le
C2-N1	1.366	1.377	1.383	1.383
C5-N1	1.379	1.383	1.384	1.384
N1-H6	1.007	1.007	1.007	1.007
C2-N3	1.312	1.304	1.308	1.307
C2-H7	--------	1.081	---------	----------
C2-C7	----------	--------	1.492	1.500
C4-N3	1.377	1.389	1.388	1.389
C4-H8	1.079	--------	--------	--------
C4-C8	------	1.398	1.397	1.397
C5-H9	1.077	--------	--------	----------
C5-C9	--------	1.395	1.393	1.397
C9-C10	---------	1.390	1.391	1.391
C9-C11	------	1.084	1.084	1.084
C10-C11	-------	1.408	1.406	1.406

The vibrational frequencies between 3656 and 3724 cm^{-1} is assigned to N-H stretching (Table 5) as also shown in simulated spectra Figs (1) and (2).This band appears very broad in the solid state (KBr disk)due to strong hydrogen bonding. The vibrational frequencies at 3270 cm^{-1} in imidazole and at 3228 cm^{-1} in benzimidazole are arised from stretching vibration of the hydrogen at 2-position (Table 5) and Fig 1.The other frequencies 3241 and 3237 cm^{-1} are attributed to C-H stretching of the hetroaromatic ring. However the four frequencies at 3196, 3186, 3175 and 3165 cm^{-1} are assigned to the stretching vibration of the aromatic hydrogen's, symmetric and antisymmetric. In addition the four frequencies at 3204, 3188, 3173 and 3163 cm^{-1} are attributed to the C-H Stretching of the aromatic hydrogen in 2-methylbenzimidazole and 2-ethylbenzimidazle respectively.

Table (4): Some of the calculated bond angles in studied molecules (Angles°) determined by DFT method using B3LYP /6-311G (d,p)theory bases set.

Molecule / Angle	Imidazole	Benzimidazole	2-Methylbenzi-midazole	2-ethylbenzim-idazole
N1-C5-H9	123.3	------	--------	---------
C4-C5-C9	------	133.1	133.2	133.2
C2-N3-C4	105.4(105.2)[a]	104.8	105.5	105.6
N3-C2-H7	125.9	125.2	------	------
C2-N1-C5	107.2	106.8	107.4	107.4
N3-C4-C5	110.7(110.1)[a]	110.4	110.3	110.2
N3-C4-H8	121.4	-------	-------	-------
N3-C4-C8	--------	129.9	130	130
C4-C4-H8	127.9	------	--------	--------
C5-C4-C8	-------	119.7	119.7	119.7
C4-C5-H9	132.6	-----	--------	---------
C4-C8-C11	------	118.1	118.1	118.1
C4-C8-H15	--------	120.1	120.1	120.1
C5-C9-C10	--------	116.7	116.8	116.8
C5-C9-H12	--------	122.1	122.1	122.0
C2-N1-H6	126.6	126.4	126.1	126.1
N1-C2-N3	111.7(111.4)[a]	113.6	112.5	112.4
N1-C2-H7	122.4	121.3	---------	-------
N1-C2-C7	-------	122.0	121.5	-------
C5-N1-H6	126.2	126.8	126.5	126.5
C4-C5-N1	105.1(106.3)[a]	104.4	104.3	104.3
C5-N1-C2	107.2(107.6)[a]	107.2	107.2	107.3

a) Ref, K. Makino, H. S. Kim and Y. K. urasawa, J. Hetrocycl. Chem, 35, 489, (1999).

b) Ref, D. R. Lide, H. P. R. Frederiks, Handbook of Chemistry and Physics, 78 th ed.(1997).

From comparison of the data of benzimidazole and 2-methyl derivative it is clear that the frequencies at 3308, 3302, 3228 cm^{-1}, and 3132, 3113, 3096, 3035, 3033 cm^{-1} in 2-methylbenzimidazole and 2-ethylbenzimidazole respectively are attributed to the C-H aliphatic asymmetric and symmetric stretching vibrational frequencies (Figs (1) and (2)). The other frequencies between 1558-1434 cm^{-1} and 1664-1496 cm^{-1} and 1775-1445 cm^{-1} and 1661-1496 cm^{-1}in imidazole, benzimidazole, 2-methylbenzeimidazole and 2-ethylbenzimidazole respectively are assigned to C=N and C=C in the aromatic rings, Table (5). These are in agreement with the experimentally measured spectra.

On the other hand, the frequencies between 1455-1384 cm^{-1} and 1477-1370 cm^{-1} in 2-methyl and 2-ethylbenzimidazole respectively are attributed to C-H bending deformation of the aliphatic groups.

From the theoretical data and the simulated spectra Figs 1 and 2, the strong frequencies at 816 and 730 cm^{-1} in imidazole, and 754 cm^{-1} benzimidazole, and 726,673 cm^{-1} in 2-ethyl, and 749,725 cm^{-1} in 2-ethylbezimidazole could be raised from C-H out of plane bending of the aromatic hydrogen atoms whereas the frequencies between 1100-1019 cm^{-1} region may be attributed to C-H bending in plane for all the studied molecules.

From comparison of the data in Table 5, it is clear that lower frequencies at 132 and 124 cm^{-1} in 2-methylbenzeimidazole are raised from torsional motions of the methyl group whereas the frequencies at 211, 181, 98 and 39 cm-1 are attributed to torsional motion of the ethyl group, as shown in the simulated spectra Fig (2). The corresponding peaks have not been observed in the measured spectra in the solid state since the instrument range is limited down to 500 cm^{-1}.

Table (5): Some of the theoretically calculated vibrational frequencies of the studied molecules by DFT method using B3LYP theory level at 6-311G (d,p) basis set.

Imidazole freq./intensity%		**Benzimidazole freq./intensity%**		**2-Methylbenzimidazole freq./intensity%**		**2-Ethylbenzimidazole freq./intensity%**	
3656	50.01	3660	63.22	3724	14.82	3645	45.92
3270	1.95	3228	2.32	3328	8.96	3204	12.18
3241	0.46	3196	11.18	3326	6.39	3118	23.59
3237	0.95	3186	22.23	3322	14.11	3173	13.68
1558	21.69	3175	12.79	3316	10.11	3164	1.97
1500	17.14	3165	0.07	3308	3.18	3132	16.69
1434	14.02	1664	6.54	3302	0.22	3113	28.47
1363	6.33	1623	3.63	3228	15.01	3096	28.93
1281	0.37	1534	25.65	1755	8.51	3035	29.74
1162	4.73	1521	4.65	1596	2.59	3033	27.52
1145	2.68	1477	25.15	1524	59.35	1661	5.66
Imidazole freq./intensity%		**Benzimidazole freq./intensity%**		**2-Methylbenzimidazole freq./intensity%**		**2-Ethylbenzimidazole freq./intensity%**	
1092	20.36	1421	30.48	1455	9.89	1694	0.56
1074	38.84	1378	29.46	1443	17.14	1566	65.41
964	2.05	1334	9.21	1384	11.14	1561	0.22
909	8.88	1286	30.24	1332	6.92	1501	10.32
870	4.26	1274	1.84	1326	2.97	1496	4.15
816	33.82	1203	1.04	1310	1.59	1477	3.16
730	36.18	1170	1.72	1260	44.63	1773	31.88
683	5.07	1130	2.39	1184	1.61	1443	44.95
646	11.39	1095	18.01	1138	8.95	1407	3.67
528	95.13	1028	5.36	1117	4.37	1400	29.90
		985	0.12	1086	4.29	1370	24.58
		947	1.64	1032	12.41	1332	13.04
		945	2.62	990	2.84	1293	12.04

		891	3.25	972	6.88	1272	7.97
		870	8.08	807	6.14	1229	10.02
		856	3.08	856	3.9	1215	4.86
		790	4.63	830	1.24	1167	2.66
		786	4.34	779	5.80	1146	1.01
		7.54	70.93	773	7.08	1091	3.43
		651	2.53	726	0.82	1062	8.08
		630	0.11	699	41.79	1019	0.87
		591	4.59	673	23.06	1062	8.07
		552	0.19	629	20.54	1019	0.87
		457	86.83	619	7.61	992	2.55
		431	13.75	573	7.80	980	0.08
		418	7.93	442	100.6	950	3.59
		256	3.41	428	20.02	945	1.01
		222	7.93	418	18.02	909	2.41
				295	1.94	854	0.95
				275	19.48	826	3.72
				222	5.48	793	2.46
				132	5.81	780	5.47
				124	0.12	749	52.91
						725	15.58
						660	2.44
						627	0.09
						584	2.75

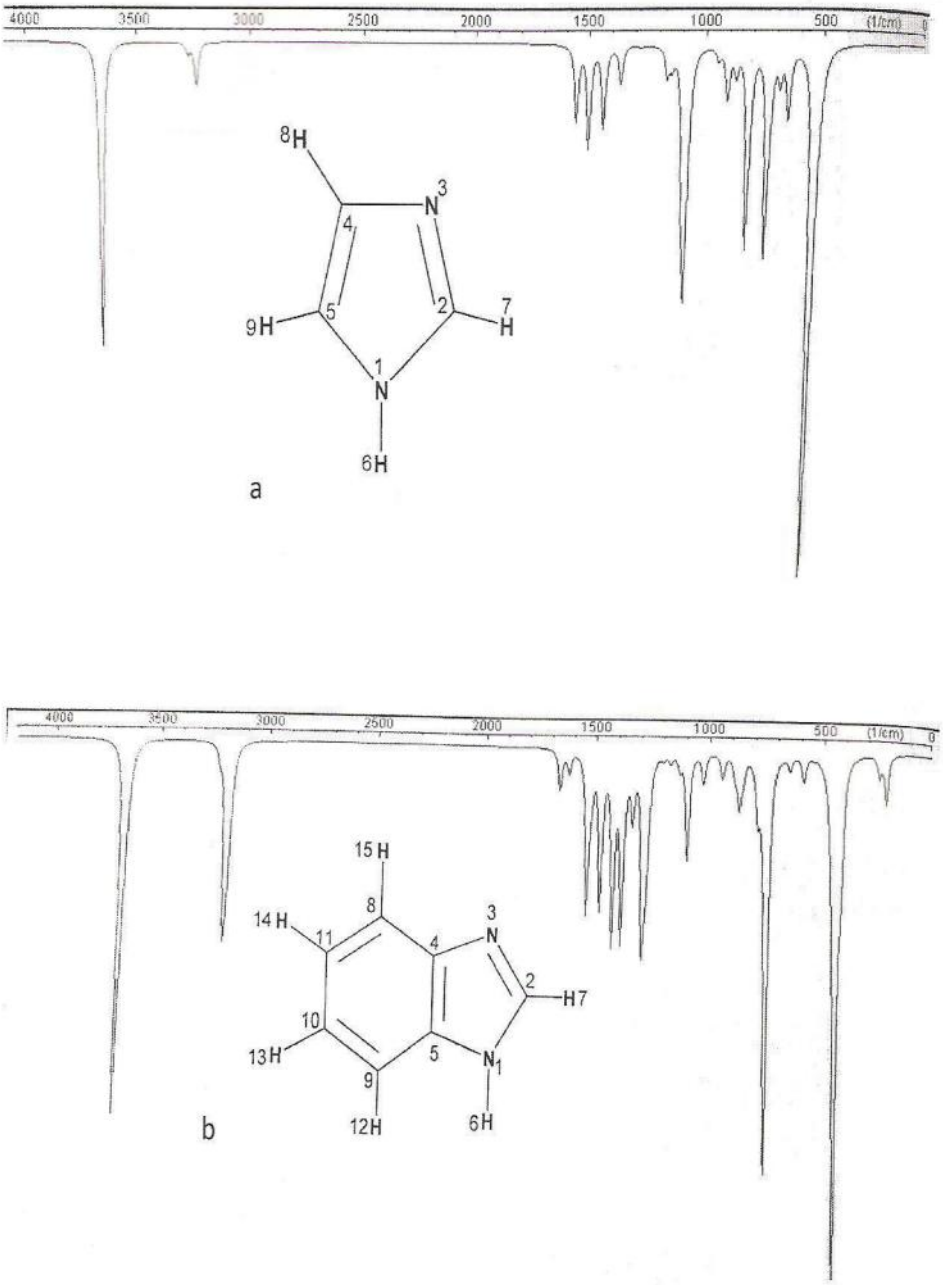


Figure 1.

Simulated spectra calculated by DFT using B3LYP/6-311G(d,p) basis set

a-Imidazole b- benzimadazole

(1)

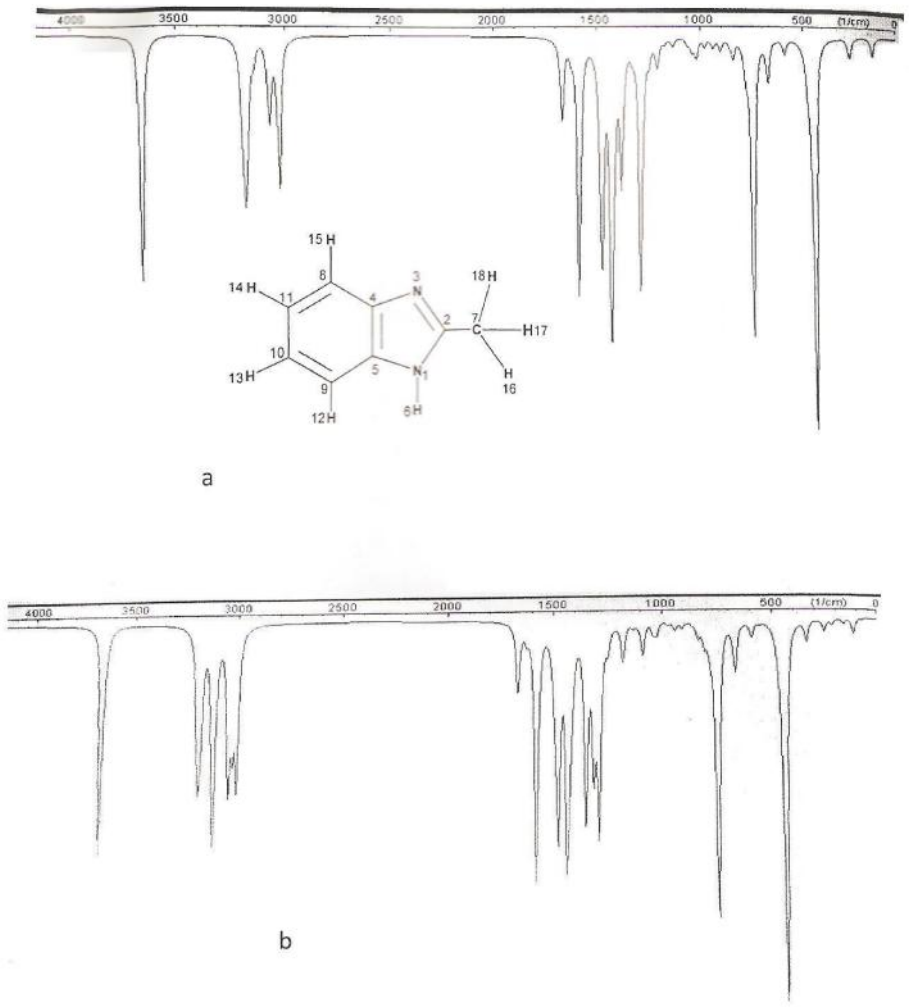


Figure (2)

Simulated spectra calculated by DFT using B3YLP/6-311G(d,p) basis set

a- 2-methylbenzimidazole b- 2- ethylbenzimidazole

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التركيب والترددات التذبذبية لأيميدازول و بنزايميدازول و مشتقة 2-الكيل محسوبة بطريقة نظرية دالة الكثافة (DFT)

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الخلاصة

التراكيب الجزيئية للاميدازول وبنزايميدازول ومشتقاته الالكيلية بالموقع -2 و كذلك ترددااتها التذبذبية عينت بطريقة نظرية دالة الكثافة و بأستخدام المستوى النظري B3LYP عند مجموعة دالة 6-31G(d,p) . بعض الخواص الفيزيائية مثل الطاقة الكلية و طاقة اعلى مستوى مشغول و اوطأ مستوى فارغ كذلك عينت . مشتقة 2- الكيل تمتلك اوطأ طاقة -458 هارتري بالمقارنة مع بنزايميدازول -226.27 هارتري بينما اقل فرق طاقة بين HOMO و LUMO يكون في مشتقة 2- مثيل و كذلك هي اكثر فعالية كيميائية. ايميدازول و بنزايميدازول جزيئات مستوية و لها عزم ثنائي قطب 3.7285 و3.5528 ديباي على التوالي. C4 تحمل اكبر شحنة سالبة بالمقارنة مع C2 و C4 في الايميدازول. في جميع الجزيئات الدروسة N1 تحمل اكبر شحنة سالبة من N3 و لكن ذرتي النتروجين N1 و N3 تظهران اكبر شحنة سالبة في مشتقة 2-اثيل. ذرة الهيدروجين لمجموعة N-H مستوية في جميع الجزيئات. الترددات التذبذبية المحسوبة نوقشت و قورنت مع الاطياف المقاسة و المستحصلة نظرياً