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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: antimicrobial[1], antihelmintic[2], antihistaminic[2], neuroleptic[2], antitumor[3,4] and inhibition of nucleic acid synthesis[5]. Many anticancer drugs [such as Imet 3393 (cytostasan)[2], oncodazole[6], Hoechst 33258 (pibenzimol)[3]] have a benzimidazole ring in their structures. Benzimidazoles are found in a variety of naturally occurring compounds such as vitamin B_{12} 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 activities[7-9]. 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 authors[12-14], 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-1*H*-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°C (172-174°C)[16]. ^1H NMR (DMSO-d_6) δ ppm: 1.22 (3H, t, J = 7.6 Hz, CH_3), 2.73 (2H, q, J = 7.6 Hz, CH_2), 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 Ram[17]. The frequency values computed at these levels contain known systematic errors[18]. We therefore, have used the scaling factor values of 0.8929 and 0.9614 for HF/6-31G (d) and B3LYP/6-31G (d), respectively[19]. 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 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.

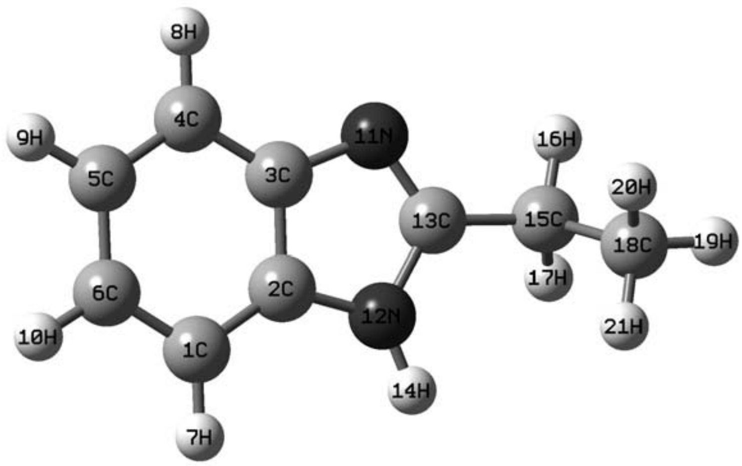

Fig. 1. Theoretical geometric structure of the 2-ethyl-1*H*-benzo[*d*]imidazole

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

Bond lengths (Å)	Calculated (6-31G(d))		Bond angles (°)	Calculated (6-31G(d))	
	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

In all the heterocyclic compounds, ν(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 derivatives[20].

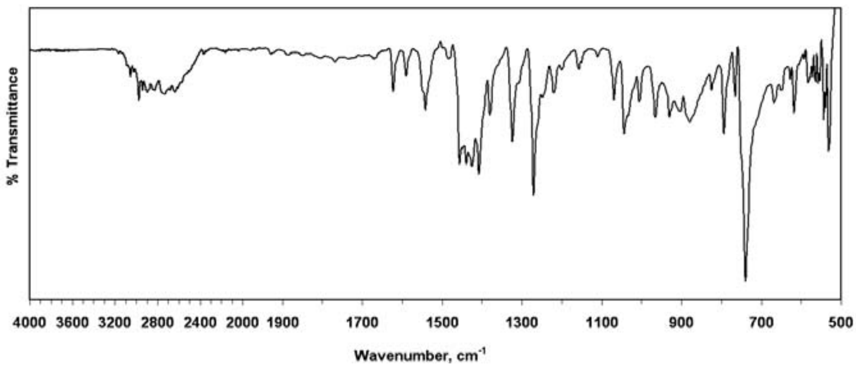

Fig. 2. FT-IR spectrum of 2-ethyl-1*H*-benzo[*d*]imidazole recorded at room temperature.

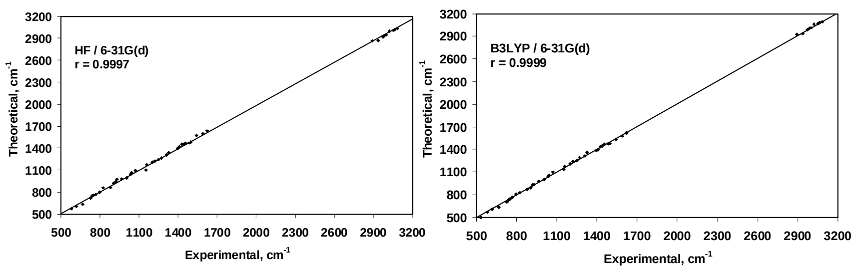

Fig. 3. Correlation graphics of calculated and experimental frequencies of title compound

The ethyl group symmetric and asymmetric ν(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

TABLE-2
EXPERIMENTAL AND CALCULATED VIBRATIONAL FREQUENCIES (cm^{-1}) of 2-ETHYL-1*H*-BENZO[*d*]IMIDAZOLE*,**

Experimental	HF / 6-31G(d)			DFT-B3LYP / 6-31G(d)			Assignments
	Calcd.	Corrected	Intensity	Calcd.	Corrected	Intensity	
–	3914	3495	75.39	3648	3507	40.51	NH str
3107, vw	3393	3030	19.44	3217	3093	17.13	CH str, sym, ar
3084, vw	3382	3020	35.95	3207	3083	29.43	CH str, sym, ar
3065, vw	3368	3007	17.82	3194	3070	14.86	CH str, asym, ar
3052, w	3356	2997	0.15	3185	3062	0.02	CH str, asym, ar
3022, w	3299	2942	28.34	3135	3014	26.89	CH str, asym, et
2985, w	3285	2930	38.94	3128	3007	33.09	CH str, asym, et
2973, w	3266	2913	29.34	3110	2990	11.43	CH str, asym, et
2938, w	3211	2864	33.16	3053	2935	31.02	CH str, sym, CH_3
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
1589, vw	1788	1595	3.17	1642	1578	2.26	CC str
1541, w	1761	1571	84.08	1595	1533	43.90	CN str
1497, vw	1661	1481	5.02	1538	1478	0.94	CC str + CH b
1483, m	1649	1471	6.53	1534	1475	6.94	CH_3 ipb
1455, m	1642	1464	4.25	1530	1471	3.73	CH_3 ipb
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
1407, m	1588	1416	100.70	1451	1395	49.78	CN str + NH b
1396, m	1563	1394	1.39	1441	1385	7.13	CH b, CH_3
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
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, 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
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
965, w	1101	982	0.04	1017	978	0.87	CH ipb
929, w	1092	974	1.76	971	933	0.06	CH opb
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 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
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
–	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

*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.

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

The ν(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 ν_{CN} vibrations for the 2-ethyl-1*H*-benzo[*d*]imidazole which is in agreement with the literature data[13]. 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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