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Ab initio and Density functional theory studies of vibrational spectra, and assignment of fundamental modes of Benzothiazole

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Abstract
The optimized geometry, wavenumber, polarizability and several thermodynamic properties of Benzothiazole were studied using ab initio HF/cc-pVDZ and DFT/cc-pVDZ basis set methods. The thermodynamic properties of the title compound have been computed. A complete vibrational assignment aided by the theoretical harmonic wave number analysis was proposed. From the optimized structures, HOMO–LUMO energy gap and geometrical parameters were derived.

Keywords: Density functional theory, vibrational spectra, Benzothiazole

1. Introduction
Benzothiazole is a heterocyclic compound, weak base, having varied biological activities and still of great scientific interest now a days. They are widely found in bioorganic and medicinal chemistry with application in drug discovery. Benzothiazole moites are part of compounds showing numerous biological activities such as antimicrobial [1-5] anticancer [6-8], anthelmintic [9], and anti-diabetic [10] activities. They have also found application in industry as anti-oxidants, vulkanisation accelerators. Various benzothiazoles such as 2-aryl benzothiazole received much attention due to unique structure and its uses as radioactive amyloid imagining agents [11], and anticancer agents [12]. Benzothiazoles are bicyclic ring system with multiple applications. In the 1950s, a number of 2-aminobenzothiazoles were intensively studied, as the 2-amino benzothiazole scaffold is one of privileged structure in medicinal chemistry [11, 13] and reported cytotoxic on cancer cells [13]. It must be emphasized that combination of 2- amino benzothiazoles with other heterocyclic is a well known approach to design new drug like molecules, which allows achieving new pharmacological profile, action, toxicity lowering. The 2-(4-aminophenyl) benzothiazoles are novel class of potent and selective antitumor agents and display characteristic profile of cytotoxic response across the cell lines.

In addition, benzothiazole ring is present in various marine or terrestrial natural compounds, which have useful biological properties. In last few years it was reported that benzothiazole, its Bioisostere and derivatives had antimicrobial activities against Gram-negative, Gram-positive bacterias (e.g., *Enterobacter, Pseudomonas aeruginosa, E. coli,* and *Staphylococcus epidermidis* etc.) and the yeast (e.g., *Candida albicans*). Benzothiazoles are fused membered rings, which contain the heterocycles bearing thiazole. Sulphur and nitrogen atoms constitute the core structure of thiazole and many pharmacologically and biologically active compounds. The basic structure (Fig.1) of benzothiazole consist of benzene ring fused with 4, 5 position of thiazole. The two rings together constitute the basic nucleus 1, 3-benzothiazle.

Computational details
The entire calculations conducted in the present work were performed at Hartree-Fock (HF) and B3LYP levels included in the Gaussian 09W package [14] program together with cc-pVDZ basis set function of the density functional theory (DFT) utilizing gradient geometry optimization. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree-Fock level, adopting the cc-pVDZ basis set. This geometry was reoptimized again at B3LYP level, using basis set cc-pVDZ for better description. The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima.

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At the optimized structure of the examined species, no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. By combining the results of the Gauss view program [15] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. Finally calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics.

Result and Discussion
Molecular geometry
The benzothiazole assumed as C1 point group of symmetry and the optimized geometrical parameters of the title compound are calculated according to labelling of atoms as shown in the Figure 1. The most optimized bond lengths and bond angles of this compound were calculated and shown in Table 1.
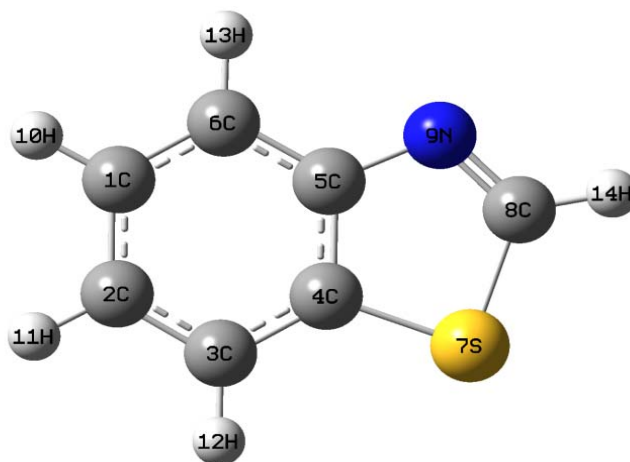

Fig 1: Geometry of the Benzothiazole optimized at the B3LYP/cc-pVDz.

From table 1, Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are on higher side than the later. According to molecular structure of benzothiazole have mainly three different bond lengths between different atom such as C-C, C-N and C-S. The bond length between C1-C2 in benzene ring is higher value for comparing to other C-C bonds in benzene ring. The C5-N9

bond length is 1.3893 and 1.3897 for HF and DFT methods respectively and C4-S7 bond length is 1.7516 and 1.7710 for HF and DFT methods respectively. The bond angles are almost same for all atoms between, but (C4, S7, and C8) are smaller than other bond angles (88.0744 and 88.0308 HF and DFT), because of hetero atom S is present.

Table 1. Optimized parameters of Benzothiazole

Bond type	Bond lengths in A⁰		Bond angle type	Bond angle in A⁰	
	HF	**DFT**		**HF**	**DFT**
C1-C2	1.4012	1.4089	(C2,C1,C6)	120.8408	120.8602
C1-C6	1.3790	1.3908	(C2,C1,H10)	119.4255	119.4281
C1-H10	1.0815	1.0919	(C6,C1,H10)	119.7337	119.7117
C2-C3	1.3805	1.3937	(C1,C2,C3)	120.9236	121.1020
C2-H11	1.0817	1.0921	(C1,C2,H11)	119.5883	119.5776
C3-C4	1.3930	1.4005	(C3,C2,H11)	119.4881	119.3204
C3-H12	1.0809	1.0912	(C2,C3,C4)	118.0351	118.0020
C4-C5	1.3951	1.4184	(C2,C3,H12)	120.8499	120.8256
C4-S7	1.7497	1.7572	(C4,C3,H12)	121.1150	121.1724
C5-C6	1.3955	1.4053	(C3,C4,C5)	121.4962	121.4856
C5-N9	1.3893	1.3897	(C3,C4,S7)	129.6227	129.3878
C6-H13	1.0805	1.0912	(C5,C4,S7)	108.8811	109.1266
S7-C8	1.7516	1.7710	(C4,C5,C6)	119.8523	119.5096
C8-N9	1.2675	1.2923	(C4,C5,N9)	115.3744	115.4610
C8-H14	1.0814	1.0920	(C6,C5,N9)	124.7733	125.0294
			(C1,C6,C5)	118.8521	119.0406
			(C1,C6,H13)	121.7019	121.8866
			(C5,C6,H13)	119.4460	119.0727
			(C4,S7,C8)	88.0744	88.0308
			(S7,C8,N9)	117.0902	116.9530
			(S7,C8,H14)	119.7430	119.3129
			(N9,C8,H14)	123.1668	123.7341
			(C5,N9,C8)	110.5799	110.4286

Vibrational analysis and theoretical prediction of spectra
Benzothiazole is a planar molecule and possesses C1 point group symmetry. The molecule has 14 atoms and 36 normal modes of fundamental vibrations. All the 35 vibrations are

active in IR and one of the vibration mode is not active (32 vibration number in table). The harmonic vibrational frequencies calculated at HF and B3LYP level using cc-pVDZ basis set have been collected in Table 2. Comparison of the

frequencies calculated at B3LYP with HF method assignments (present in Table 2) reveals the overestimation of the HF vibrational modes due to the neglect of electron correlation contributions which are especially important in systems contacting extensive electron conjugation and /or electron lone pairs in the real system.

Table 2: Calculated vibrational frequencies of Benzothiazole at HF/cc-pVDZ and DFT/cc-pVDZ level.

S. No	HF/cc-pVDZ		DFT/cc-pVDZ		Assignments
	Wave number	Intensity	Wave number	Intensity	
1	3380.02	10.2187	3210.40	8.79	C-H stretch
2	3378.60	2.3318	3207.36	0.91	C-H stretch
3	3371.07	17.1484	3203.27	13.20	C-H stretch
4	3358.15	8.9699	3192.48	6.71	C-H stretch
5	3343.61	1.5706	3179.84	1.28	C-H stretch
6	1796.00	3.7034	1646.33	2.70	C=C stretch
7	1759.10	20.1567	1605.55	3.35	C=C stretch
8	1721.98	63.8601	1538.29	56.22	C=N stretch
9	1606.26	17.0927	1486.25	5.83	C-H in plane bend
10	1591.59	31.747	1458.25	23.90	C-H in plane bend
11	1435.46	16.4621	1365.02	10.48	C-C stretch
12	1387.48	0.5821	1315.85	8.03	C-N stretch
13	1346.45	6.7126	1278.86	1.88	C-H in plane bend
14	1313.45	2.5634	1216.93	1.68	C-H in plane bend
15	1242.09	5.0463	1170.73	1.30	C-H in plane bend
16	1208.81	0.4538	1136.40	2.67	C-H in plane bend
17	1159.42	8.5003	1071.18	9.09	C-C stretch
18	1107.78	5.0576	1037.58	4.27	C-H out plane bend
19	1102.34	0.0612	1002.21	0.03	C-H out plane bend
20	1068.04	2.8629	963.98	1.81	C-H out plane bend
21	981.58	12.8561	882.62	2.89	C-H out plane bend
22	956.88	3.1298	877.97	26.30	C-H out plane bend
23	954.98	37.3229	830.51	16.68	C-S strech
24	862.57	23.4633	797.12	24.78	C-H out plane bend
25	852.83	43.0351	779.27	19.14	C-H out plane bend
26	817.78	21.3711	749.11	22.54	Benzene ring vibration
27	766.23	4.4102	712.94	3.43	C-S strech
28	720.30	3.7399	662.92	5.99	C-N bend strech
29	646.98	0.2367	600.91	0.04	-------------
30	577.43	0.3553	535.21	0.66	-------------
31	543.31	0.7154	507.45	0.41	------------
32	535.95	0.0000	497.75	0.00	-------------
33	468.28	8.8575	432.66	5.67	Rings vibration
34	380.07	2.8783	354.84	2.38	Rings vibration
35	231.23	2.8914	214.47	1.63	Rings vibration
36	211.98	1.9968	196.36	1.63	Rings vibration

Vibrational assignments
C-H vibrations
The hetero cyclic aromatic compounds and its derivatives are structurally very close to benzene. The C-H stretching frequency of such compounds falls very nearly in the region of 3100- 2900 cm^{-1} for asymmetric stretching and 2980 - 2900cm^{-1} for symmetric stretching modes of vibration. This permits the ready identification of the structure. Further in this region, the bands are not much affected by the nature and position of the substitutions [16]. Hetero cyclic compound C-H vibration absorption bands are usually week; in many cases it is too week for detection. In general, the aromatic C-H stretching vibrations calculated theoretically in the region 3210 – 3179 cm^{-1} for B3LYP and 3380 - 3343cm^{-1} for HF predicts the CH stretching bands, which supports the literature values [17,18].

The bands due to C-H in-plane bending vibration interact somewhat with C-C stretching vibrations, are observed as number of bands in the region 1300–1000 cm^{-1} .The C-H out-of-plane bending vibrations occur [19] in the region 900–667 cm^{-1}. In the present investigation, the bands observed at 1606, 1591,1346,1313,1242, and 1208 cm^{-1} and 1486,1458,1278,1216,1170, and 1025 cm^{-1} are assigned to C-H in plane bending vibration for HF and DFT methods respectively. The C-H out of plane bending modes was also assigned at 1107, 1102, 1068, 981, 956, 862 and 852 cm^{-1} and 1278, 1216, 1170, 1136, 1037, 1002, 963,882, 877, 797 and 779 cm^{-1}for HF and DFT methods respectively.

C-C vibrations
Generally the C-C stretching vibrations in aromatic compounds form [20] the band in the region of 1430 to 1650 cm-1. In the present case investigation the bands are observed at 1640,1595,1580,1505, 1440, 1325 and 1310 cm-1. The last two bands lie below the expected range; this may be due to the substitution of heavy elements oxygen and methyl group in the present case. The in-plane bending C-C vibrations generally occur at higher frequencies than of out-of-plane bending28. In the present study the bands observed at 760, 720, 580, 500, 465 and 430 are assigned to C-C in plane bending modes. The out of plane bending modes of frequencies are attributed to 554, 460 and 420 cm-1 in Raman and 175, 140 and 85 cm-1 in IR.

C=N, C–N vibrations

The identification of C–N vibrations is a difficult task, since the mixing of vibrations is possible in this region. However, with the help of the animation option of gauss view 5.0 graphical interfaces for Gaussian programs the C–N vibrations identified. Silverstein [21] assigned C–N stretching absorption in the region 1382–1266 cm^{-1} for aromatic amines. The IR bands appearing at 1721 and 1538 cm^{-1} are assigned to νC=N vibrations and 1387 and 1315 cm^{-1} are assigned to νC–N vibrations with the δCH for the title compound for HF and DFT methods respectively. The 954 and 830 cm^{-1} assigned to C-S bond at HF and DFT level of theory.

Other calculated properties

Theoretically computed energies (a.u.), enthalpies, entropies rotational constants (GHz) heat capacity, dipole moment (μ) and molecular Polarizabilities ($<\alpha>$) are presented in Table 3.

Table 3: Theoretically computed energies (a.u.), rotational constants (GHz) entropies (cal mol^{-1}K^{-1}), heat capacity (Kcal mol^{-1}K^{-1}), dipole moment (μ) and molecular Polarizabilities ($<\alpha>$)

	HF	**DFT**
energy	-719.994809022	-722.739450013
Enthalpy	-719.878228	-722.629870
Free energy	-719.915686	-722.668045
Entropy	78.836	80.345
CV	23.383	25.574
μ	1.1342	1.1547
$<\alpha>$	84.777	90.743
HOMO	-0.32234	-0.24132
LUMO	-0.10179	-0.0426
Rotational constants (GHZ):	3.21266 1.34336 0.94726	3.14530 1.32588 0.93271

One of the objectives of this investigation is to study the effect of the basis set on molecular polarizability of benzothiazole using Gaussian 09W. In this study the computation of molecular polarizability of benzothiazole with HF and DFT are reported. Here, α is a second rank tensor property called the dipole polarizability and mean polarizability (α) are evaluated using Eq. (1) [22].

$$<\alpha> = 1/3(\alpha_{xx} + \alpha_{YY} + \alpha_{ZZ}) \qquad (1)$$

The calculated polarizabilities using two methods for benzothiazole molecule are summarized in Table 4.

Table 4. Calculated polarizabilities for Benzothiazole

Method	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$<\alpha>$
HF/cc-pVDZ	124.857	1.210	93.728	0.0000	-0.001	35.746	84.777
DFT/cc-pVDZ	232.410	4.780	195.411	-0.004	0.000	59.992	90.743

Frontier molecular orbital analysis

The frontier molecular orbitals play an important role in the electric and optical properties, as well as in UV-vis spectra and chemical reactions [59]. The HOMO–LUMO energies were also calculated and the values and figures are listed in Table 3 and Figure 3 respectively. In the present study, the HOMO LUMO gap values of the molecule are at -0.32234, -0.10179 and -0.24132 and-0.0426 a.u for HF/cc-pVZD and, DFT /cc-pVZD methods, respectively, as seen in Table 3.
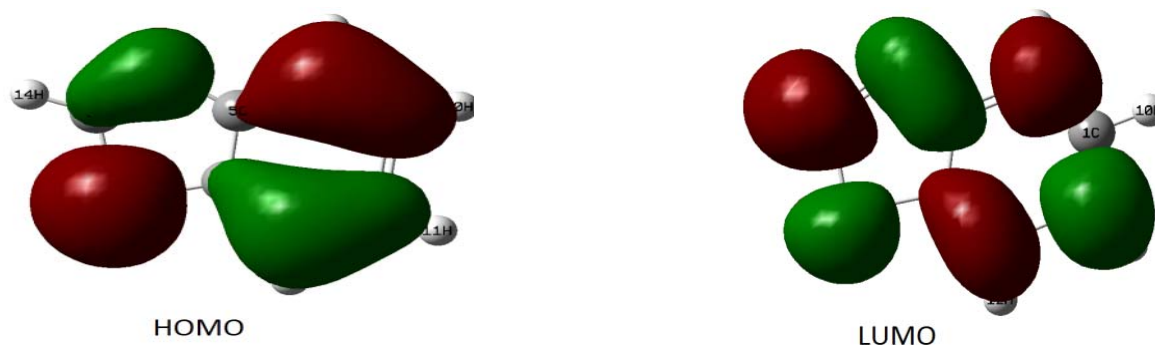

Fig. 3. HOMO–LUMO plots of benzothiazole.

Conclusion

A complete vibrational analysis of benzothiazole was performed on the basis of HF and DFT functional calculations at B3LYP/cc-pVDZ basis level. On the basis of calculated results, assignments of the entire fundamental vibrational Frequencies have been made. The optimized geometry parameters calculated at B3LYP/cc-pVDZ are slightly larger than those calculated at HF/cc-pVDZ level. The calculated first hyperpolarizability is comparable with the reported values of similar structures, which makes this compound an attractive object for future studies of nonlinear optics.

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