

Full Research Paper

## Synthesis and Ab Initio/DFT Studies on 2-(4-methoxyphenyl)benzo[d]thiazole

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**Abstract:** 2-aminothiophenol and 4-methoxybenzaldehyde were cyclized under microwave irradiation and solvent free conditions to synthesize 2-(4-methoxyphenyl)benzo[d]thiazole. The molecular structure and vibrational frequencies of the title compound in the ground state have been investigated with ab initio (HF) and density functional theory methods (BLYP, B3LYP, B3PW91 and mPW1PW91) implementing the standard 6-311G(d,p) basis set. Comparison of the observed fundamental vibrational frequencies of title compound and calculated results by HF and DFT methods indicate that B3LYP is superior to the scaled HF approach for molecular problems.

**Keywords:** Benzothiazole; Ab initio calculations; Density functional calculations; FT-IR.

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### 1. Introduction

The synthesis of benzothiazoles and their derivatives has been of considerable interest to organic and medicinal chemists for many years as indicated by large number of drugs including this group [1-4]. This heterocyclic nucleus is a very important group because of its potent antitumor activity [5-8] and other important pharmaceutical utilities, such as treatment of inflammatory diseases, epilepsy, analgesia, viral infections, cancer, and tuberculosis [9-15]. Particularly, there is significant interest in

the synthesis of 2-substituted benzothiazoles in recent years [16,17]. The benzothiazoyl-moiety is a structure element of compounds with potent and selective antitumor activity. For instance, 2-(4-aminophenyl)benzothiazoles exhibit nanomolar inhibitory activity against a range of human breast, ovarian, colon, and renal cell lines in vitro [18,19]. Structure-activity relationships derived using these cell types has revealed that activity follows the heterocyclic sequence benzothiazole>benzoxazole>benzimidazole and the 2-(4-amino-3-methylphenyl)benzothiazole derivative is found as the most potent compound in this series with its activity extending to ovarian, lung and renal cell lines. Our earlier work led to the development of new antitumor active compounds with a benzothiazole skeleton.

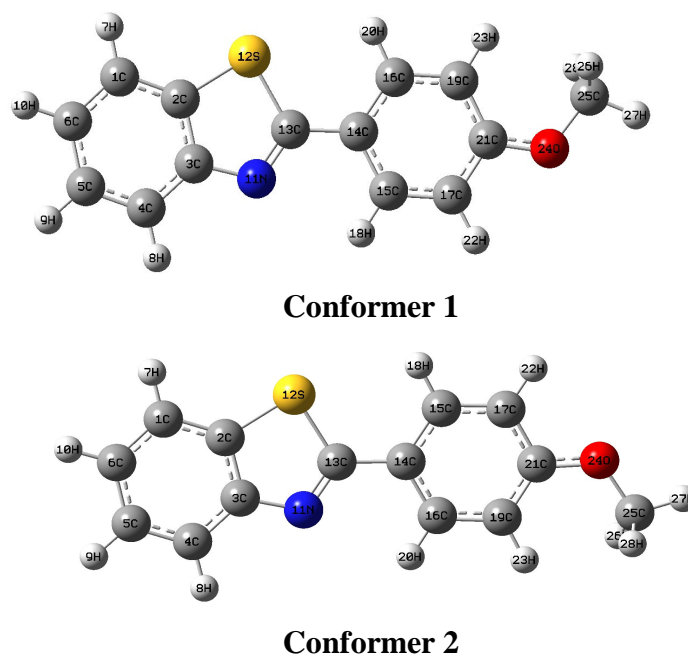
IR spectroscopy is usually considered as an important experimental method for chemists. The experimental and theoretical vibrational spectrum assignments of free benzothiazole have not been published so far. In the present work, we have synthesized and calculated the geometric parameters and vibrational frequencies of the title compound in the ground state to distinguish the fundamental from the experimental vibrational frequencies using the Hartree-Fock (HF) [20], density functional by employing Becke's three-parameter hybrid method [21] with the Lee, Yang, and Parr correlation functional methods [22] (B3LYP), Becke's exchange functional in combination with the Lee, Yang and Parr correlation functional methods (BLYP) [22,23], the Barone and Adamo's Becke-style one-parameter functional using the modified Perdew–Wang exchange and Perdew–Wang 91 correlation method, (mPW1PW91) [24,25], Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991 (B3PW91) [23,26], and 6-311G(d,p) basis set. Furthermore, we interpreted the calculated spectra in terms of potential energy distributions (PEDs) and made the assignment of all experimental bands based on PED analysis results.

## 2. Results and Discussion

The simplest route to substitute 2-phenylbenzothiazoles involves various reactions between *o*-aminothiophenols and substituted benzoic acid derivatives (e.g., in polyphosphoric acid) [27]. In recent years, the use of microwave irradiation to simplify and improve classical organic reactions has become a very popular method [28] because it often leads to high yields, clean reactions, and shorter reaction times. We have carried out the reaction of aromatic aldehydes with *o*-aminothiophenol in the presence of silica gel under microwave irradiation and solvent free conditions. It has been found that the 2-(4-methoxyphenyl)benzo[d]thiazole was obtained in good yield. The optimum conditions employed are that a molar ratio of aldehyde and *o*-aminothiophenol is 1:2 and irradiation time and power levels of microwave set-up are 6 min and 300 W.

### 2.1. Conformational stability

To establish the most stable conformation as the initial point for further calculations, the molecule was submitted to a rigorous conformation analysis around the free rotation bonds. This study was performed with the software Spartan 06 [29]. The structure of the title compound shown in Figure 1 has two conformations. Energetics, gathered in Table 1, show that the Conformer 1 is the most stable. Therefore, further in this paper, we focus on this particular form of the title compound.



**Figure 1.** Two stable conformers of the title compound calculated at HF/6-311G(d,p) level.

**Table 1.** Energies of the different conformations of the title compound calculated at the HF/6-311G(d,p) level<sup>a</sup>.

Conformer	<i>E</i> (Hartree)	$\Delta E$ (kcal/mol)	Dipole moment (D)
1	-1063.40977	0.0000	2.2783
2	-1063.40973	0.0249	1.3747

<sup>a</sup> Total energies, *E* (with the zero-point vibrational energy correction).

## 2.2. Molecular geometry

In this work, we performed full geometry optimization of the title compound. The optimized structure parameters of the title compound calculated by ab initio and DFT methods listed in Table 2 are in accordance with atom numbering scheme given in Figure 1. To the best of our knowledge, crystal data of the 2-(4-methoxyphenyl)benzo[d]thiazole are not available in the literature. Therefore, the optimized structure can only be compared with crystal structure of other similar systems [30-32]. We have noticed that the DFT calculations are consistent with the results of X-ray data. From Table 2, it was found that the bond angles calculated by DFT methods are consistent with those by HF method. However the bond lengths calculated by HF method are little shorter than those obtained by DFT method.

**Table 2.** Optimized and experimental geometries of the title compound in the ground state.

Parameters	Calculated				Experimental	
	HF	DFT				
		BLYP	B3LYP	B3PW91		mPW1PW91
<b>Bond lengths (Å)</b>						
R(1,2)	1.388	1.403	1.394	1.392	1.391	1.394(2) <sup>a</sup>
R(1,6)	1.378	1.401	1.390	1.388	1.386	1.384(2) <sup>a</sup>
R(2,3)	1.391	1.428	1.414	1.412	1.410	1.402(17) <sup>a</sup>
R(2,12)	1.743	1.767	1.750	1.740	1.737	1.7367(13) <sup>a</sup>
R(3,4)	1.393	1.411	1.401	1.399	1.397	1.3950(18) <sup>a</sup>
R(3,11)	1.382	1.387	1.379	1.374	1.373	1.3854(16) <sup>a</sup>
R(4,5)	1.377	1.397	1.387	1.384	1.382	1.381(2) <sup>a</sup>
R(5,6)	1.397	1.412	1.403	1.401	1.400	1.390(2) <sup>a</sup>
R(11,13)	1.270	1.308	1.295	1.295	1.293	1.3150(15) <sup>a</sup>
R(12,13)	1.766	1.822	1.792	1.778	1.772	1.764(4) <sup>a</sup>
R(13,14)	1.475	1.469	1.464	1.461	1.459	1.463(2) <sup>b</sup>
R(14,15)	1.394	1.416	1.405	1.402	1.400	1.400(4) <sup>c</sup>
R(14,16)	1.387	1.413	1.401	1.398	1.396	1.377(4) <sup>c</sup>
R(15,17)	1.374	1.392	1.383	1.381	1.379	1.381(4) <sup>c</sup>
R(16,19)	1.384	1.398	1.389	1.387	1.386	1.375(5) <sup>c</sup>
R(17,21)	1.392	1.412	1.402	1.400	1.398	1.391(4) <sup>c</sup>
R(19,21)	1.388	1.411	1.400	1.398	1.396	1.376(5) <sup>c</sup>
R(21,24)	1.341	1.374	1.359	1.353	1.350	1.352(4) <sup>c</sup>
R(24,25)	1.401	1.442	1.423	1.416	1.412	1.424(4) <sup>c</sup>
<b>Bond angles (°)</b>						
A(2,1,6)	118.08	118.16	118.12	118.05	118.03	117.95(14) <sup>a</sup>
A(1,2,3)	121.65	121.50	121.54	121.61	121.62	121.44(12) <sup>a</sup>
A(1,2,12)	129.51	129.12	129.28	129.27	129.29	129.55(10) <sup>a</sup>
A(3,2,12)	108.84	109.39	109.18	109.12	109.09	109.01(9) <sup>a</sup>
A(2,3,4)	119.73	119.26	119.37	119.33	119.35	119.31(1) <sup>a</sup>
A(2,3,11)	115.26	115.51	115.35	115.33	115.34	115.97(11) <sup>a</sup>
A(4,3,11)	125.00	125.23	125.28	125.34	125.31	124.70(11) <sup>a</sup>
A(3,4,5)	118.86	119.20	119.12	119.10	119.08	119.31(13) <sup>a</sup>
A(4,5,6)	120.90	120.87	120.88	120.92	120.92	120.74(14) <sup>a</sup>
A(1,6,5)	120.78	121.01	120.97	121.00	121.00	121.22(14) <sup>a</sup>
A(3,11,13)	112.11	112.43	112.21	111.89	111.78	110.72(10) <sup>a</sup>
A(2,12,13)	88.78	88.38	88.66	88.85	88.88	89.50(6) <sup>a</sup>
A(11,13,12)	115.01	114.30	114.59	114.80	114.92	114.78(9) <sup>a</sup>
A(11,13,14)	123.50	124.51	124.16	124.07	123.95	122.78(19) <sup>b</sup>

**Table 2.** Cont.

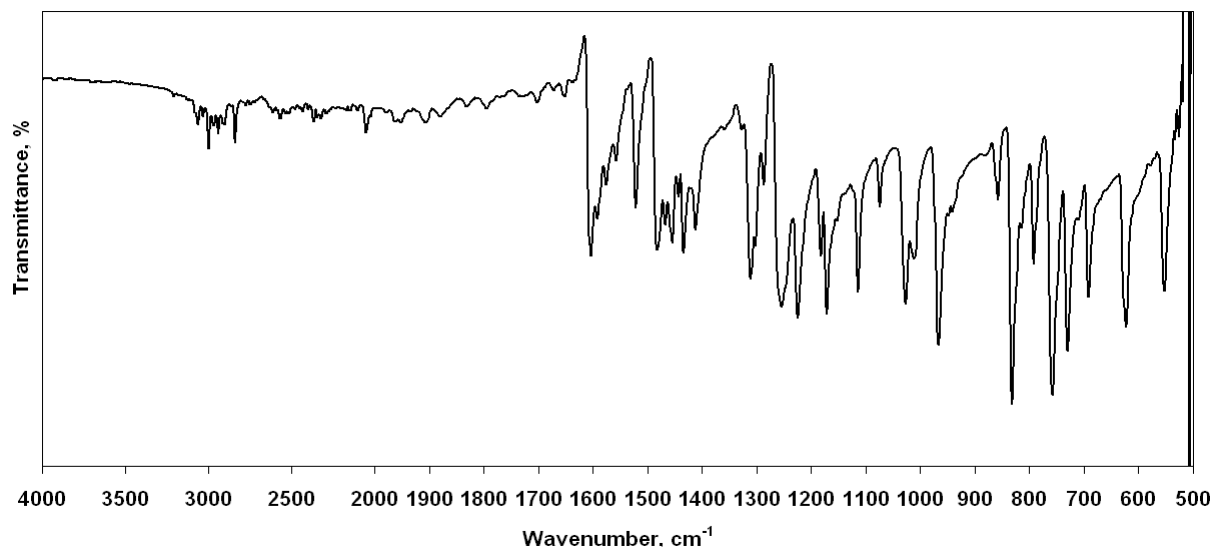
A(12,13,14)	121.49	121.19	121.26	121.13	121.13	121.84(15) <sup>b</sup>
A(13,14,15)	122.42	122.64	122.53	122.51	122.46	121.80(17) <sup>b</sup>
A(13,14,16)	119.38	119.35	119.30	119.24	119.21	119.73(18) <sup>b</sup>
A(15,14,16)	118.20	118.01	118.17	118.25	118.33	118.48(17) <sup>b</sup>
A(14,15,17)	121.07	121.13	121.05	121.02	120.98	119.71(18) <sup>b</sup>
A(14,16,19)	121.36	121.37	121.30	121.26	121.22	121.56(19) <sup>b</sup>
A(15,17,21)	120.19	120.23	120.23	120.21	120.19	120.0(3) <sup>c</sup>
A(16,19,21)	119.74	119.81	119.81	119.80	119.78	120.0(3) <sup>c</sup>
A(17,21,19)	119.45	119.45	119.45	119.46	119.50	118.9(3) <sup>c</sup>
A(17,21,24)	115.93	115.54	115.79	115.86	115.88	115.8(3) <sup>c</sup>
A(19,21,24)	124.62	125.00	124.75	124.68	124.62	125.1(3) <sup>c</sup>
A(21,24,25)	120.11	118.40	118.70	118.37	118.30	118.3(3) <sup>c</sup>

<sup>a</sup> Obtained from [31]; <sup>b</sup> Obtained from [32]; <sup>c</sup> Obtained from [33].

### 2.3. Vibrational assignments

The vibrational spectra of benzo[d]thiazole derivatives have not been described in detail in any literature. Therefore, we focused on a benzo[d]thiazole derivative, 2-(4-methoxyphenyl)benzo[d]thiazole. The FT-IR spectrum of the title compound is shown in Fig. 2. We have calculated the theoretical vibrational spectra of 2-(4-methoxyphenyl)benzo[d]thiazole by using HF, B3LYP, BLYP, B3PW91 and mPW1PW91 methods with 6-311G(d,p) basis set. None of the predicted vibrational spectra has no imaginary frequency, implying the optimized geometry is located at the local lowest point on the potential energy surface. It is known that *ab initio* and DFT potentials systematically overestimate the vibrational wavenumbers. These discrepancies can be corrected either by computing anharmonic corrections explicitly or by introducing a scaled field [33] or directly scaling the calculated wavenumbers with the proper factor [34]. Considering systematic errors with scaling factor of 0.9051, 0.9679, 0.9934, 0.9631 and 0.9567, we calibrated the vibrational wavenumbers calculated by HF, B3LYP, BLYP, B3PW91 and mPW1PW91, respectively. After scaled with a scaling factor, the deviation from experiments is less than 10 cm<sup>-1</sup> with a few exceptions. Theoretical and experimental results of the title compound are shown in Table 3. The vibrational bands' assignments have been made by using both the animation option of GaussView 3.0 graphical interface for Gaussian programs [35] and VEDA 4 program [36]. All the calculated spectra are in a good agreement with the experimental data. All DFT methods are superior to HF method in terms of realistic reproduction of both band intensity distribution and general spectral features.

The characteristic  $\nu_{\text{CH}}$  stretching vibrations of heteroaromatic structure are expected to appear in 3000-3100 cm<sup>-1</sup> frequency ranges. The  $\nu_{\text{CH}}$  stretching vibrations of the title compound were assigned to four bands observed at 3111, 3084, 3076, and 3062 cm<sup>-1</sup> in the infrared spectrum. The B3LYP calculated wavenumbers of these bands very well reproduced the experimental ones. The difference between experimental and calculated  $\nu_{\text{CH}}$  is about 3, 7, 4, and 4 cm<sup>-1</sup> [37].



**Figure 2.** FT-IR spectrum of 2-(4-methoxyphenyl)benzo[d]thiazole recorded at room temperature.

For the assignments of CH<sub>3</sub> group frequencies, eight fundamental vibrations can be associated to CH<sub>3</sub> groups. Three stretching, one umbrella, one rocking and three deformation vibration mode designated the motion of the methyl group. The CH<sub>3</sub> asymmetric and symmetric stretching frequencies are established at 3034, 2968, and 2910 cm<sup>-1</sup> in infrared spectra. The three methyl hydrogen deformation modes are also well established in the spectra. We have observed the methyl deformation mode at 1483, 1467, and 1454 cm<sup>-1</sup> in the infrared. The calculated band at 1433 and 1122 cm<sup>-1</sup> are attributed to an umbrella and a CH<sub>3</sub> rocking vibration, respectively [38].

The characteristic region of the benzothiazole derivatives on the spectrum is 1500-1650 cm<sup>-1</sup> as benzimidazole derivatives. The vibrational frequencies and intensities for all substituted benzothiazole derivatives in this range differ from the position of the substituent [39]. Generally, two bands observed in 1500-1650 cm<sup>-1</sup> range for benzothiazole derivatives. The observed vibrational frequencies (1591 and 1558 cm<sup>-1</sup>) are generally intense because of the conjugation between the benzene and thiazole rings. In addition, the vibrational frequencies in this range vary with the electronegativity of the substituent. The 4-methoxyphenyl group in position 2 is less apt to influence the vibrational frequencies in this range. Additionally, we obtained another vibrational frequency at 1604 and 1571 cm<sup>-1</sup> which comes from 4-methoxyphenyl group.

The identification of  $\nu_{C-N}$  vibrations is a difficult task since the mixing of vibrations is possible in this region. However, with the help of the animation option of GaussView 3.0 graphical interface for gaussian programs and VEDA 4 program, the  $\nu_{C-N}$  vibrations are identified and assigned in this study. The IR bands appearing at 1521, 1483, and 1467 cm<sup>-1</sup> are assigned to  $\nu_{C=N}$  vibrations and 1267, 1253, and 1207 cm<sup>-1</sup> are assigned to  $\nu_{C-N}$  vibrations with the  $\delta_{CH}$  for the title compound. All these results agree with Sundaraganesan et al. [40] and Krishnakumar et al. [41,42].

**Table 3.** Vibrational wavenumbers obtained for the title compound at 6-311G(d,p) level.

No	Exp.	HF		DFT												Assignments, PED (%) <sup>g</sup>	
				BLYP			B3LYP			B3PW91			mPW1PW91				
		Wave number <sup>a</sup>		Rel.	Wave number <sup>a</sup>		Rel.	Wave number <sup>a</sup>		Rel.	Wave number <sup>a</sup>		Rel.	Wave number <sup>a</sup>			Rel.
		Unscal.	Scaled <sup>b</sup>	Inten.	Unscal.	Scaled <sup>c</sup>	Inten.	Unscal.	Scaled <sup>d</sup>	Inten.	Unscal.	Scaled <sup>e</sup>	Inten.	Unscal.	Scaled <sup>f</sup>		Inten.
1	3111	3380	3059	2	3131	3110	4	3211	3108	3	3219	3101	3	3238	3098	3	$\nu_{\text{CH}}$ , sym, ring 1, (99)
2	3084	3363	3044	1	3118	3097	2	3198	3095	1	3210	3092	4	3229	3090	4	$\nu_{\text{CH}}$ , asym, ring 1, (93)
3	3084	3362	3043	1	3117	3097	6	3198	3095	5	3210	3091	1	3229	3089	1	$\nu_{\text{CH}}$ , sym, ring 2, (87)
4	3084	3359	3040	3	3117	3096	5	3197	3094	2	3205	3087	1	3224	3084	1	$\nu_{\text{CH}}$ , asym, ring 1, (89)
5	3084	3351	3033	5	3110	3090	9	3190	3088	6	3203	3085	5	3223	3083	5	$\nu_{\text{CH}}$ , asym, ring 2, (99)
6	3076	3338	3021	2	3100	3079	4	3180	3078	2	3192	3075	2	3212	3073	2	$\nu_{\text{CH}}$ , asym, ring 2, (100)
7	3076	3337	3020	2	3093	3073	3	3172	3070	3	3180	3063	1	3200	3061	1	$\nu_{\text{CH}}$ , asym, ring 1, (100)
8	3062	3324	3008	0	3088	3068	0	3168	3066	0	3180	3063	2	3198	3060	3	$\nu_{\text{CH}}$ , asym, ring 2, (95)
9	3034	3289	2977	9	3061	3041	9	3137	3037	8	3152	3036	7	3171	3034	8	$\nu_{\text{CH}}$ , asym, CH <sub>3</sub> , (92)
10	2968	3230	2923	10	2988	2969	15	3067	2969	12	3082	2969	11	3100	2966	12	$\nu_{\text{CH}}$ , asym, CH <sub>3</sub> , (100)
11	2910	3167	2867	11	2932	2912	29	3007	2911	21	3015	2904	21	3032	2901	22	$\nu_{\text{CH}}$ , sym, CH <sub>3</sub> , (92)
12	1604	1797	1627	43	1585	1574	63	1651	1598	62	1666	1604	66	1681	1608	73	$\nu_{\text{C=C}}$ , ring 1, (43)
13	1591	1790	1620	4	1571	1560	2	1638	1586	2	1653	1592	2	1669	1597	2	$\nu_{\text{C=C}}$ , ring 2, (59) + $\nu_{\text{CN}}$ (10)
14	1571	1759	1592	11	1540	1530	2	1608	1556	3	1623	1563	4	1639	1568	4	$\nu_{\text{C=C}}$ , ring 1, (42) + $\delta_{\text{CCC}}$ (12)
15	1558	1749	1583	1	1533	1523	2	1597	1546	2	1611	1551	2	1626	1555	2	$\nu_{\text{C=C}}$ , ring 2, (57) + $\nu_{\text{CN}}$ (13)
16	1521	1728	1564	13	1495	1485	8	1560	1510	5	1575	1517	6	1591	1522	7	$\nu_{\text{CN}}$ (38)+ $\nu_{\text{CC}}$ (12)+ $\delta_{\text{CCC}}$ (23)
17	1483	1676	1517	55	1471	1462	22	1533	1483	67	1540	1483	77	1552	1485	89	$\nu_{\text{CN}}$ (31) + $\delta_{\text{CH}_3}$ , deform. (26)
18	1467	1630	1476	9	1463	1453	58	1505	1457	24	1501	1445	23	1509	1444	24	$\nu_{\text{CN}}$ (12) + $\delta_{\text{CH}_3}$ , deform. (58)
19	1454	1622	1468	1	1453	1444	3	1494	1446	3	1493	1438	3	1504	1439	3	$\delta_{\text{CH}_3}$ , deform. (91)
20	1442	1609	1457	4	1440	1430	3	1489	1441	3	1489	1434	3	1497	1432	3	$\nu_{\text{CC}}$ , ring 2, (26) + $\delta_{\text{CH}}$ (47)
21	1433	1608	1455	8	1435	1426	12	1480	1433	6	1475	1421	4	1484	1420	3	$\delta_{\text{CH}_3}$ , umbrella (76)
22	1412	1600	1448	12	1413	1404	9	1465	1418	12	1470	1415	11	1481	1416	14	$\delta_{\text{CH}}$ , ring 2, (45)

Table 3. Cont.

23	1400	1560	1412	3	1404	1394	9	1450	1404	5	1456	1402	3	1465	1402	3	$\nu_{CC}$ , ring 1, (40) + $\delta_{CH}$ (13)
24	1309	1448	1310	6	1312	1304	3	1346	1303	2	1369	1318	5	1377	1317	5	$\nu_{CC}$ , ring 2, (52)
25	1303	1422	1287	100	1307	1299	27	1342	1299	39	1366	1316	28	1375	1315	35	$\nu_{CC}$ , ring 1, (53)
26	1286	1414	1280	1	1297	1288	1	1334	1291	1	1329	1280	15	1340	1282	25	$\delta_{CH}$ , ring 1, (80)
27	1267	1372	1242	11	1272	1264	3	1316	1273	9	1325	1276	10	1333	1275	11	$\nu_{CC}$ , ring 2, (13) + $\delta_{CH}$ (15) + $\nu_{CN}$ (19)
28	1253	1367	1237	8	1235	1227	21	1289	1247	100	1302	1254	100	1314	1257	100	$\nu_{CN}$ (13) + $\delta_{CH}$ (18), ring 2
29	1224	1335	1208	1	1229	1221	100	1274	1234	3	1277	1230	2	1285	1230	2	$\nu_{CO}$ (39) + $\delta_{CH}$ (20), ring 1
30	1207	1322	1196	11	1201	1193	15	1250	1210	24	1262	1216	18	1274	1219	20	$\nu_{CN}$ (21) + $\nu_{CC}$ (29)
31	1170	1287	1165	29	1168	1160	1	1206	1167	1	1205	1160	1	1213	1160	2	$\delta_{CH}$ , (74)
32	1157	1282	1161	1	1158	1151	83	1193	1155	51	1190	1146	38	1196	1145	40	$\delta_{CH}$ (51), ring 1
33	1141	1270	1149	2	1155	1147	0	1183	1145	1	1183	1139	2	1188	1137	2	$\delta_{CH}$ (73), ring 2
34	1122	1240	1122	2	1130	1123	0	1171	1134	0	1171	1128	0	1179	1128	0	$\delta_{CH3}$ , rock. (99)
35	1114	1209	1094	1	1110	1103	2	1144	1107	2	1146	1104	2	1153	1103	2	$\nu_{CC}$ (28) + $\delta_{CH}$ (32), ring 2
36	1084	1200	1087	2	1108	1100	5	1139	1102	4	1136	1094	4	1141	1092	4	$\delta_{CH}$ (29), ring 1
37	1037	1174	1062	7	1040	1033	3	1082	1048	2	1089	1049	2	1098	1050	3	$\nu_{SC}$ (22) + $\delta_{CCC}$ (46)
38	1026	1169	1058	5	1007	1000	3	1060	1026	20	1079	1039	18	1093	1046	18	$\nu_{CC}$ (29) + $\delta_{CH}$ (52), ring 2
39	1010	1107	1002	1	997	990	13	1039	1005	2	1043	1005	2	1050	1005	2	$\nu_{CC}$ (11) + $\nu_{O-CH3}$ (45)
40	985	1104	999	0	993	986	15	1026	993	1	1026	988	1	1033	988	1	$\nu_{O-CH3}$ (30) + $\delta_{CCC}$ (55)
41	968	1104	999	0	946	940	0	989	957	0	990	953	0	998	955	0	$\gamma_{CH}$ , (85), ring 2
42	947	1103	998	1	943	936	0	985	953	0	983	947	0	992	949	0	$\gamma_{CH}$ , (89), ring 1
43	941	1072	970	0	927	921	25	970	939	20	976	940	18	985	942	19	$\nu_{CC}$ (11) + $\delta_{CNC}$ (34) + $\delta_{CCN}$ (11)
44	925	1069	967	0	916	910	0	957	926	0	956	921	0	964	922	0	$\gamma_{CH}$ , (86), ring 1
45	910	1058	958	10	906	900	1	950	919	0	952	916	0	960	918	1	$\gamma_{CH}$ , (81), ring 2
46	858	968	876	0	845	839	0	873	845	0	876	844	0	882	844	0	$\nu_{CN}$ (12) + $\delta_{CCC}$ (32)
47	831	942	853	14	830	825	1	866	838	1	866	834	1	873	835	1	$\gamma_{CH}$ , (87), ring 2



Table 3. Cont.

48	815	930	842	1	812	807	19	848	821	18	847	816	19	854	817	20	$\gamma_{\text{CH}}$ , (49), ring 1
49	791	918	831	0	787	782	0	822	795	0	821	791	0	828	793	0	$\gamma_{\text{CH}}$ , (98), ring 1
50	779	866	784	2	774	769	3	805	780	3	811	781	3	818	782	3	$\nu_{\text{CN}}$ (34) + $\nu_{\text{CO}}$ (20)
51	756	852	771	13	742	738	16	772	747	14	772	744	15	778	744	17	$\gamma_{\text{CH}}$ , (53), ring 2+ $\gamma_{\text{C}}$ , (17)
52	729	812	735	4	710	705	6	738	714	7	737	709	7	742	710	7	$\gamma_{\text{C}}$ (21) + $\gamma_{\text{CH}}$ , (10)
53	709	797	722	0	705	701	2	732	708	1	730	703	1	735	704	1	$\gamma_{\text{C}}$ , (46)
54	692	771	698	0	690	686	1	717	694	0	721	694	0	726	695	0	$\nu_{\text{CS}}$ (23) + $\delta_{\text{CCC}}$ (47)
55	662	748	677	4	658	654	4	689	667	6	697	671	7	704	673	8	$\delta_{\text{CCC}}$ (33) + $\delta_{\text{CCN}}$ (16)
56	623	689	624	2	619	615	1	640	619	4	639	615	6	643	615	6	$\delta_{\text{CCC}}$ (54)
57	617	688	623	3	611	607	11	635	614	5	634	611	1	638	610	1	$\delta_{\text{CNC}}$ (11) + $\delta_{\text{CCN}}$ (11) + $\delta_{\text{CCC}}$ (26)
58	605	680	615	1	600	596	1	625	605	1	626	603	1	631	604	1	$\gamma_{\text{C}}$ (52) + $\tau_{\text{CN}}$ (25)
59	551	613	555	2	546	543	12	564	546	8	562	542	7	565	541	8	$\delta_{\text{CCC}}$ (15) + $\delta_{\text{CCO}}$ (15) + $\delta_{\text{COC}}$ (18)
60	540	604	546	4	540	536	2	561	543	2	560	539	2	564	539	2	$\tau_{\text{CC}}$ (26) + $\gamma_{\text{C}}$ (10)
61	-	566	512	2	494	491	3	514	498	3	514	495	3	518	496	3	$\tau_{\text{CN}}$ (10) + $\gamma_{\text{C}}$ (35)
62	-	550	497	0	490	486	1	509	493	0	512	493	0	516	494	0	$\nu_{\text{CS}}$ (30) + $\delta_{\text{CCC}}$ (28) + $\delta_{\text{SCC}}$ (19)
63	-	507	459	0	460	457	0	476	461	0	476	459	0	480	459	0	$\delta_{\text{C-O-CH}_3}$ (25) + $\delta_{\text{CCC}}$ (10) + $\delta_{\text{CCO}}$ (15)
64	-	482	436	1	422	419	2	438	424	1	436	420	2	439	420	2	$\tau_{\text{CC}}$ (81), ring 2
65	-	459	416	0	406	403	0	421	407	0	422	406	1	425	407	1	$\tau_{\text{CC}}$ (93), ring 1
66	-	451	408	1	399	396	0	418	405	0	419	403	0	422	403	0	$\delta_{\text{SCC}}$ (38) + $\delta_{\text{CCN}}$ (12)
67	-	398	360	0	349	347	0	363	352	0	364	350	0	367	351	0	$\tau_{\text{CN}}$ (101) + $\tau_{\text{CC}}$ (26)
68	-	349	316	1	314	312	1	326	315	1	326	314	1	329	314	1	$\delta_{\text{CCN}}$ (19) + $\delta_{\text{CCC}}$ (21) + $\delta_{\text{COC}}$ (16)
69	-	300	272	0	262	260	0	274	265	0	275	264	0	277	265	0	$\tau_{\text{CO}}$ (17) + $\tau_{\text{CC}}$ (17) + $\tau_{\text{CN}}$ (18)
70	-	267	242	0	245	243	1	252	244	1	253	244	1	255	244	1	$\tau_{\text{CC}}$ (18) + $\delta_{\text{CCC}}$ (22) + $\delta_{\text{CCO}}$ (11)
71	-	252	228	0	219	217	0	230	222	0	232	223	0	234	224	0	$\tau_{\text{CO}}$ (47)
72	-	227	206	0	205	204	0	213	206	0	214	206	0	216	207	0	$\delta_{\text{CNC}}$ (15) + $\delta_{\text{OCC}}$ (22) + $\delta_{\text{COC}}$ (21)

Table 3. Cont.

73	-	209	189	0	185	184	1	192	186	0	193	186	1	194	186	1	$\tau_{CC}(57) + \gamma_C(30)$
74	-	147	133	1	136	135	1	140	136	1	142	137	1	143	137	1	$\tau_{CC}(22) + \tau_{CO}(31)$
75	-	90	81	0	92	91	0	93	90	0	94	91	0	95	91	0	$\tau_{CN}(13) + \tau_{CO}(51)$
76	-	87	79	0	81	80	0	83	81	0	83	79	0	83	79	0	$\delta_{CNC}(42) + \delta_{CCC}(38)$
77	-	47	42	0	43	43	0	45	43	0	45	43	0	45	43	0	$\tau_{CC}(11) + \tau_{CN}(35) + \gamma_C(26)$
78	-	17	16	0	30	30	0	29	28	0	30	29	0	31	30	0	$\tau_{CC}(91)$

<sup>a</sup> Harmonic frequencies (in  $\text{cm}^{-1}$ ) and IR intensities ( $\text{km mol}^{-1}$ ).

<sup>b</sup> Scaling factor = 0.9051.

<sup>c</sup> Scaling factor = 0.9934.

<sup>d</sup> Scaling factor = 0.9679.

<sup>e</sup> Scaling factor = 0.9631.

<sup>f</sup> Scaling factor = 0.9567.

<sup>g</sup>  $\nu$ , stretching;  $\delta$ , bending; ipb, in-plane bending;  $\gamma$ , out-of-plane bending;  $\tau$ , torsion; sym, symmetric; asym, asymmetric; Ring 1: C14-C15-C17-C21-C19-C16; Ring 1: C1-C2-C3-C4-C5-C6; PED less than 10% are not shown.

The O–CH<sub>3</sub> mode is assigned in the region 1000–1100 cm<sup>-1</sup> for anisole and its derivatives [38,40,43-45]. In this work, the O–CH<sub>3</sub> stretching mode is assigned to medium IR band at 1010 cm<sup>-1</sup>. The theoretically computed value at 1005 cm<sup>-1</sup> exactly coincides with the experimental results. The C–O–CH<sub>3</sub> angle bending mode is assigned near 300 cm<sup>-1</sup> for anisole by and at 421 cm<sup>-1</sup> for *p*-methoxy benzaldehyde by Campagnaro and Wood [46]. Owen and Hester [47], Sundaraganesan et al. [40] and Ramana Rao et al. [43-45,48] have proposed assignment for C–O–CH<sub>3</sub> angle bending mode in the region 300–670 cm<sup>-1</sup> for anisole and its derivatives. As this mode lies in the region of the ring planar C–C–C angle bending modes, a strong mixing amongst these two modes and other planar modes is expected. Accordingly, we have assigned the theoretically calculated value by B3LYP/6–311G(d,p) at 461 cm<sup>-1</sup> as C–O–CH<sub>3</sub> angle bending mode.

A better performance of B3LYP, BLYP, B3PW91 and mPW1PW91 versus HF in general can be quantitatively characterized by using the mean absolute deviation, root mean square values and coefficients of correlation (cc) between the calculated and observed vibration frequencies and given in Table 4. The root mean square (RMS) values were obtained in this study using the equations (12) and (13) from Ref. [22]. The cc values for all three DFT methods were bigger than 0.9998, whereas for HF it was 0.9997. These values are very close to those reported for the literature data [49-59].

**Table 4.** Mean absolute deviation, correlation coefficient, and root mean square between the calculated and observed fundamental vibrational frequencies for the title compound.

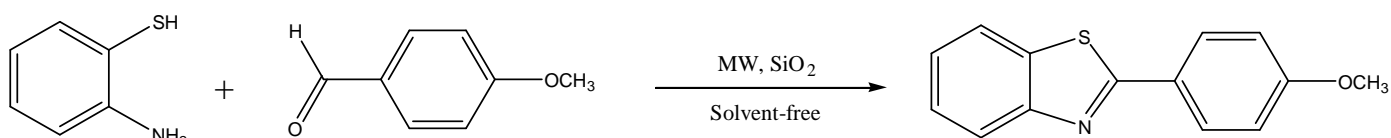
	HF		BLYP		B3LYP		B3PW91		mPW1PW91	
<b>Mean absolute deviation</b>	153.80	23.14	12.90	12.90	48.68	6.62	54.13	7.14	64.50	7.46
<b>RMS<sub>mol</sub></b>	167.10	28.19	17.37	16.25	57.50	8.73	64.00	9.02	75.23	9.22
<b>RMS<sub>over</sub></b>	146.56	24.72	15.23	14.25	50.43	7.65	56.13	7.91	65.98	8.09
<b>Scaling Factor</b>	1.0000	0.9051	1.0000	0.9934	1.0000	0.9679	1.0000	0.9631	1.0000	0.9567
<b><i>r</i></b>	0.9997		0.9999		0.9999		0.9999		0.9999	

These results indicate that the fundamental frequencies calculated (DFT) for the title compound show quite good agreement with experimental values. Furthermore, the B3LYP method calculations approximate the observed fundamental frequencies much better than results of the other investigated DFT methods. This is also proved by the low RMS deviation values of about 7.7 cm<sup>-1</sup>. The RMS value obtained with the B3LYP method is smaller than those obtained by Rauhut and Pulay [60] for a group of 20 molecules (RMS = 13 cm<sup>-1</sup>). The small difference between experimental and calculated vibrational modes is observed. This discrepancy can come from the formation of intermolecular hydrogen bonding. Also, we note that the experimental results obtained from solid phase and theoretical calculations belong to gaseous phase.

### 3. Experimental Section

#### 3.1. Synthesis of 2-(4-methoxyphenyl)benzothiazol

All chemicals used for the preparation of the title compound were reagent grade quality. To a solution of 4-methoxybenzaldehyde (3 mmol) and *o*-aminothiophenol (6 mmol) in diethylether (10 mL) silica gel (3 g) was added (Scheme 1). The slurry was mixed thoroughly and the solvent was removed by rotary evaporation. The resultant solid was subjected to microwave irradiation using microwave oven operating at 300W for 6 min. After cooling, the product was extracted with ethyl acetate. The extract was then filtered and the filtrate was evaporated under reduced pressure to yield the crude product. The product was purified by recrystallization in methanol. (Yield 94%), M.p. 393 K (392-394 K) [61].  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 8.04 ( $J=2$ , d, 1H), 8.02 ( $J=2.4$ , 1H, s), 7.87 ( $J=8$ , 1H, d), 7.46 (1H, t), 7.35 (1H, t), 7.00 ( $J=2$ , d, 1H), 6.90 ( $J=2$ , 2H, d), 3.87 (3H, s, OMe). MS (70 eV)  $m/z$  (%): 242 (M+1, 80). Anal. required for  $\text{C}_{14}\text{H}_{11}\text{NSO}$ : C, 69.68; H, 4.59; N, 5.80; Found: C, 69.45; H, 4.51; N, 5.82% [62].



**Scheme 1.** Synthesis of the title compound.

#### 3.2. Instrumentation

Microwave reaction was carried out in 10 mL sealed glass tubes in focused mono-mode microwave oven (Discover by CEM). Melting points were determined using an Electrothermal-9300 Digital Melting Points Apparatus (Electrothermal Inc., Essex, UK). The  $^1\text{H}$ -NMR spectra were recorded on Bruker 400 MHz NMR spectrometer. Chemical shifts are reported in parts per million relative to internal standard tetramethylsilane. Microanalyses were performed by TUBITAK Analytical Laboratory (Ankara, Turkey). Mass spectra were recorded on a VG Autospec, using the FAB technique. The room temperature attenuated total reflection Fourier transform infrared (FT-IR ATR) spectrum of the 2-(4-methoxyphenyl)benzo[d]thiazole was recorded using Varian FTS1000 FT-IR spectrometer with Diamond/ZnSe prism ( $4000\text{--}525\text{ cm}^{-1}$ ; number of scans: 250; resolution:  $1\text{ cm}^{-1}$ ) in the solid (Fig. 2).

#### 3.3. Calculation details

The conformation analysis study was carried out by Spartan 06 program package [29]. All the other calculations were performed with the Gaussian 03W program package on a double Xeon/3.2 GHz processor with 8 GB Ram [63]. The molecular structure of the title compound, in the ground state are optimized by using the Hartree-Fock (HF) [20], density functional using Becke's three-parameter hybrid method [21] with the Lee, Yang, and Parr correlation functional methods [22] (B3LYP), Becke's exchange functional in combination with the Lee, Yang and Parr correlation functional methods (BLYP) [22,23], the Barone and Adamo's Becke-style one-parameter functional using the

modified Perdew–Wang exchange and Perdew–Wang 91 correlation method, (mPW1PW91) [24,25], Becke's three parameter exchange functional combined with gradient corrected correlation functional of Perdew and Wang's 1991 (B3PW91) [23,26], and 6-311G(d,p) basis set. The vibrational frequencies were also calculated with these methods. The frequency values computed at these levels contain known systematic errors [64]. Therefore, we have used the scaling factor values of 0.9051, 0.9679, 0.9934, 0.9631 and 0.9567 for HF, B3LYP, BLYP, B3PW91 and mPW1PW91, respectively [34,49]. The assignment of the calculated wave numbers 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 [35]. Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of PEDs using VEDA 4 program [36].

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