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.

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.

| Conformer | E (Hartree) | ΔE (kcal/mol) | Dipole moment (D) |
|-----------|-------------|---------------|-------------------|
| 1         | -1063.40977 | 0.0000        | 2.2783            |
| 2         | -1063.40973 | 0.0249        | 1.3747            |

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

|          |     |     |     |     |     |     |
|----------|-----|-----|-----|-----|-----|-----|
| A(12,13,14) | 121.49 | 121.19 | 121.26 | 121.13 | 121.13 | 121.84(15)
| A(13,14,15) | 122.42 | 122.64 | 122.53 | 122.51 | 122.46 | 121.80(17)
| A(13,14,16) | 119.38 | 119.35 | 119.90 | 119.24 | 119.21 | 119.73(18)
| A(15,14,16) | 118.20 | 118.01 | 118.17 | 118.25 | 118.33 | 118.48(17)
| A(14,15,17) | 121.07 | 121.13 | 121.05 | 121.02 | 120.98 | 119.71(18)
| A(14,16,19) | 121.36 | 121.37 | 121.30 | 121.26 | 121.22 | 121.56(19)
| A(15,17,21) | 120.19 | 120.23 | 120.23 | 120.21 | 120.19 | 120.0(3)
| A(16,19,21) | 119.74 | 119.81 | 119.81 | 119.80 | 119.78 | 120.0(3)
| A(17,21,19) | 119.45 | 119.45 | 119.46 | 119.45 | 118.9(3)
| A(17,21,24) | 115.93 | 115.54 | 115.79 | 115.86 | 115.88 | 115.8(3)
| A(19,21,24) | 124.62 | 125.00 | 124.75 | 124.68 | 124.62 | 125.1(3)
| A(21,24,25) | 120.11 | 118.40 | 118.70 | 118.37 | 118.30 | 118.3(3)

a Obtained from [31]; b Obtained from [32]; c 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\(^{-1}\) 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 \(\nu_{CH}\) stretching vibrations of heteroaromatic structure are expected to appear in 3000-3100 cm\(^{-1}\) frequency ranges. The \(\nu_{CH}\) stretching vibrations of the title compound were assigned to four bands observed at 3111, 3084, 3076, and 3062 cm\(^{-1}\) in the infrared spectrum. The B3LYP calculated wavenumbers of these bands very well reproduced the experimental ones. The difference between experimental and calculated \(\nu_{CH}\) is about 3, 7, 4, and 4 cm\(^{-1}\) [37].
Figure 2. FT-IR spectrum of 2-(4-methoxyphenyl)benzo[d]thiazole recorded at room temperature.

For the assignments of CH$_3$ group frequencies, eight fundamental vibrations can be associated to CH$_3$ groups. Three stretching, one umbrella, one rocking and three deformation vibration mode designated the motion of the methyl group. The CH$_3$ asymmetric and symmetric stretching frequencies are established at 3034, 2968, and 2910 cm$^{-1}$ 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$^{-1}$ in the infrared. The calculated band at 1433 and 1122 cm$^{-1}$ are attributed to an umbrella and a CH$_3$ rocking vibration, respectively [38].

The characteristic region of the benzothiazole derivatives on the spectrum is 1500-1650 cm$^{-1}$ 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$^{-1}$ range for benzothiazole derivatives. The observed vibrational frequencies (1591 and 1558 cm$^{-1}$) 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$^{-1}$ 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$^{-1}$ are assigned to $\nu$C=N vibrations and 1267, 1253, and 1207 cm$^{-1}$ 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 | BLYP | B3LYP | B3PW91 | mPW1PW91 |
|----|------|----|------|-------|--------|----------|
|    |      | Wave number | Rel. | Wave number | Rel. | Wave number | Rel. | Wave number | Rel. | Wave number | Rel. | Assignments, PED (%) |
|    |      | Unscal. Scaled | Inten. | Unscal. Scaled | Inten. | Unscal. Scaled | Inten. | Unscal. Scaled | Inten. | Unscal. Scaled | Inten. |
| 1  | 3111 | 3380 3059 | 2 | 3111 3110 | 4 | 3211 3108 | 3 | 3219 3101 | 3 | 3238 3098 | 3 | ν_{CH}, sym, ring 1, (99) |
| 2  | 3084 | 3363 3044 | 1 | 3118 3097 | 2 | 3198 3095 | 1 | 3210 3092 | 4 | 3229 3090 | 4 | ν_{CH}, asym, ring 1, (93) |
| 3  | 3084 | 3362 3043 | 1 | 3117 3097 | 6 | 3198 3095 | 5 | 3210 3091 | 1 | 3229 3089 | 1 | ν_{CH}, sym, ring 2, (87) |
| 4  | 3084 | 3359 3040 | 3 | 3117 3096 | 5 | 3197 3094 | 2 | 3205 3087 | 1 | 3224 3084 | 1 | ν_{CH}, asym, ring 1, (89) |
| 5  | 3084 | 3351 3033 | 5 | 3110 3090 | 9 | 3190 3088 | 6 | 3203 3085 | 5 | 3223 3083 | 5 | ν_{CH}, asym, ring 2, (99) |
| 6  | 3076 | 3338 3021 | 2 | 3100 3079 | 4 | 3180 3078 | 2 | 3192 3075 | 2 | 3122 3073 | 2 | ν_{CH}, asym, ring 2, (100) |
| 7  | 3076 | 3337 3020 | 2 | 3093 3073 | 3 | 3172 3070 | 3 | 3180 3063 | 1 | 3200 3061 | 1 | ν_{CH}, sym, ring 1, (100) |
| 8  | 3062 | 3324 3008 | 0 | 3088 3068 | 0 | 3168 3066 | 0 | 3180 3063 | 2 | 3198 3060 | 3 | ν_{CH}, asym, ring 2, (95) |
| 9  | 3034 | 3289 2977 | 9 | 3061 3041 | 9 | 3137 3037 | 8 | 3152 3036 | 7 | 3171 3034 | 8 | ν_{CH}, sym, CH₃, (92) |
| 10 | 2968 | 3230 2923 | 10 | 2988 2969 | 15 | 3067 2969 | 12 | 3082 2969 | 11 | 3100 2966 | 12 | ν_{CH}, asym, CH₃, (100) |
| 11 | 2910 | 3167 2867 | 11 | 2932 2912 | 29 | 3007 2911 | 21 | 3015 2904 | 21 | 3032 2901 | 22 | ν_{CH}, sym, CH₃, (92) |
| 12 | 1604 | 1797 1627 | 43 | 1585 1574 | 63 | 1651 1598 | 62 | 1666 1604 | 66 | 1681 1608 | 73 | ν_{C=C}, ring 1, (43) |
| 13 | 1591 | 1790 1620 | 4 | 1571 1560 | 2 | 1638 1586 | 2 | 1653 1592 | 2 | 1669 1597 | 2 | ν_{C=C}, ring 2, (59) + ν_{CC} (10) |
| 14 | 1571 | 1759 1592 | 11 | 1540 1530 | 2 | 1608 1556 | 3 | 1623 1563 | 4 | 1639 1568 | 4 | ν_{C=C}, ring 1, (42) + δ_{CCC} (12) |
| 15 | 1558 | 1749 1583 | 1 | 1533 1523 | 2 | 1597 1546 | 2 | 1611 1551 | 2 | 1626 1555 | 2 | ν_{C=C}, ring 2, (57) + ν_{CC} (13) |
| 16 | 1521 | 1728 1564 | 13 | 1495 1485 | 8 | 1560 1510 | 5 | 1575 1517 | 6 | 1591 1522 | 7 | ν_{CC} (38)+ν_{CC} (12)+ δ_{CCC} (23) |
| 17 | 1483 | 1676 1517 | 55 | 1471 1462 | 22 | 1533 1483 | 67 | 1540 1483 | 77 | 1552 1485 | 89 | ν_{CC} (31)+δ_{CHCH}, deform. (26) |
| 18 | 1467 | 1630 1476 | 9 | 1463 1453 | 58 | 1505 1457 | 24 | 1501 1445 | 23 | 1509 1444 | 24 | ν_{C=C} (12)+ δ_{CHCH}, deform. (58) |
| 19 | 1454 | 1622 1468 | 1 | 1453 1444 | 3 | 1494 1446 | 3 | 1493 1438 | 3 | 1504 1439 | 3 | δ_{CHCH}, deform. (91) |
| 20 | 1442 | 1609 1457 | 4 | 1440 1430 | 3 | 1489 1441 | 3 | 1489 1434 | 3 | 1497 1432 | 3 | ν_{C=C} ring 2, (26) + δ_{CH} (47) |
| 21 | 1433 | 1608 1455 | 8 | 1435 1426 | 12 | 1480 1433 | 6 | 1475 1421 | 4 | 1484 1420 | 3 | δ_{CH}, umbrella (76) |
| 22 | 1412 | 1600 1448 | 12 | 1413 1404 | 9 | 1465 1418 | 12 | 1470 1415 | 11 | 1481 1416 | 14 | δ_{CH}, ring 2, (45) |
Table 3. Cont.

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

|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 48 | 815 | 930 | 842 | 1 | 812 | 807 | 19 | 848 | 821 | 18 | 847 | 816 | 19 | 854 | 817 |
| 49 | 791 | 918 | 831 | 0 | 787 | 782 | 0 | 822 | 795 | 0 | 821 | 791 | 0 | 828 | 793 |
| 50 | 779 | 866 | 784 | 2 | 774 | 769 | 3 | 805 | 780 | 3 | 811 | 781 | 3 | 818 | 782 |
| 51 | 756 | 852 | 771 | 13 | 742 | 738 | 16 | 772 | 747 | 14 | 772 | 744 | 15 | 778 | 744 |
| 52 | 729 | 812 | 735 | 4 | 710 | 705 | 6 | 738 | 714 | 7 | 737 | 709 | 7 | 742 | 710 |
| 53 | 709 | 797 | 722 | 0 | 705 | 701 | 2 | 732 | 708 | 1 | 730 | 703 | 1 | 735 | 704 |
| 54 | 692 | 771 | 698 | 0 | 690 | 686 | 1 | 717 | 694 | 0 | 721 | 694 | 0 | 726 | 695 |
| 55 | 662 | 748 | 677 | 4 | 658 | 654 | 4 | 689 | 667 | 6 | 697 | 671 | 7 | 704 | 673 |
| 56 | 623 | 689 | 624 | 2 | 619 | 615 | 1 | 640 | 619 | 4 | 639 | 615 | 6 | 643 | 615 |
| 57 | 607 | 688 | 623 | 3 | 611 | 607 | 11 | 635 | 614 | 5 | 634 | 611 | 1 | 638 | 610 |
| 58 | 608 | 680 | 615 | 1 | 600 | 596 | 1 | 625 | 605 | 1 | 626 | 603 | 1 | 631 | 604 |
| 59 | 551 | 613 | 555 | 2 | 546 | 543 | 12 | 564 | 546 | 8 | 562 | 542 | 7 | 565 | 541 |
| 60 | 540 | 604 | 546 | 4 | 540 | 536 | 2 | 561 | 543 | 2 | 560 | 539 | 2 | 564 | 539 |
| 61 | -   | 566 | 512 | 2 | 494 | 491 | 3 | 514 | 498 | 3 | 514 | 495 | 3 | 518 | 496 |
| 62 | -   | 550 | 497 | 0 | 490 | 486 | 1 | 509 | 493 | 0 | 512 | 493 | 0 | 516 | 494 |
| 63 | -   | 507 | 459 | 0 | 460 | 457 | 4 | 476 | 461 | 0 | 476 | 459 | 0 | 480 | 459 |
| 64 | -   | 482 | 436 | 1 | 422 | 419 | 2 | 438 | 424 | 1 | 436 | 420 | 2 | 439 | 420 |
| 65 | -   | 459 | 416 | 0 | 406 | 403 | 0 | 421 | 407 | 0 | 422 | 406 | 1 | 425 | 407 |
| 66 | -   | 451 | 408 | 1 | 399 | 396 | 0 | 418 | 405 | 0 | 419 | 403 | 0 | 422 | 403 |
| 67 | -   | 398 | 360 | 0 | 349 | 347 | 0 | 363 | 352 | 0 | 364 | 350 | 0 | 367 | 351 |
| 68 | -   | 349 | 316 | 1 | 314 | 312 | 1 | 326 | 315 | 1 | 326 | 314 | 1 | 329 | 314 |
| 69 | -   | 300 | 272 | 0 | 262 | 260 | 0 | 274 | 265 | 0 | 275 | 264 | 0 | 277 | 265 |
| 70 | -   | 267 | 242 | 0 | 245 | 243 | 1 | 252 | 244 | 1 | 253 | 244 | 1 | 255 | 244 |
| 71 | -   | 252 | 228 | 0 | 219 | 217 | 0 | 230 | 222 | 0 | 232 | 223 | 0 | 234 | 224 |
| 72 | -   | 227 | 206 | 0 | 205 | 204 | 0 | 213 | 206 | 0 | 214 | 206 | 0 | 216 | 207 |
|    | Harmonic frequencies (in cm$^{-1}$) and IR intensities (km mol$^{-1}$). |
|----|---------------------------------------------------------------------------------------------------------------|
| 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 | $90$ | $81$ | $0$ | $92$ | $91$ | $0$ | $93$ | $90$ | $0$ | $94$ | $91$ | $0$ | $95$ | $91$ | $0$ | $\tau_{CN}(13) + \tau_{CG}(51)$ |
| 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 | $17$ | $16$ | $0$ | $30$ | $30$ | $0$ | $29$ | $28$ | $0$ | $30$ | $29$ | $0$ | $31$ | $30$ | $0$ | $\tau_{CC}(91)$ |

$^a$ Harmonic frequencies (in cm$^{-1}$) and IR intensities (km mol$^{-1}$).

$^b$ Scaling factor = 0.9051.

$^c$ Scaling factor = 0.9934.

$^d$ Scaling factor = 0.9679.

$^e$ Scaling factor = 0.9631.

$^f$ Scaling factor = 0.9567.

$v$, 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–CH₃ mode is assigned in the region 1000–1100 cm⁻¹ for anisole and its derivatives [38,40,43-45]. In this work, the O–CH₃ stretching mode is assigned to medium IR band at 1010 cm⁻¹. The theoretically computed value at 1005 cm⁻¹ exactly coincides with the experimental results. The C–O–CH₃ angle bending mode is assigned near 300 cm⁻¹ for anisole by and at 421 cm⁻¹ 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–CH₃ angle bending mode in the region 300–670 cm⁻¹ 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⁻¹ as C–O–CH₃ 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 |
|----------------|------|------|-------|--------|----------|
| Mean absolute deviation | 153.80 | 23.14 | 12.90 | 12.90 | 54.13 | 7.14 | 64.50 | 7.46 |
| RMS Moy         | 167.10 | 28.19 | 17.37 | 16.25 | 64.00 | 9.02 | 75.23 | 9.22 |
| RMS over        | 146.56 | 24.72 | 15.23 | 14.25 | 50.43 | 7.65 | 56.13 | 7.91 | 65.98 | 8.09 |
| Scaling Factor  | 1.0000 | 0.9051 | 1.0000 | 0.9934 | 1.0000 | 0.9679 | 1.0000 | 0.9631 | 1.0000 | 0.9567 |
| r               | 0.9997 | 0.9999 | 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⁻¹. 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⁻¹). 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 diethyl ether (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) \[61\]. $^1$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 C$_{14}$H$_{11}$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 $^1$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 (4000–525 cm$^{-1}$; number of scans: 250; resolution: 1 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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