



## RESEARCH ARTICLE

## Density functional theoretical computations of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole

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### Abstract

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. The small and simple benzothiazole nucleus if present in compounds involved in research aimed at evaluating new products that possess interesting biological activities. Many of them reported to have antimicrobial, anti-diabetic, anti-inflammatory and anti-tumor activities. The compound 2-[2,4- is(4-methylphenylamino)thiazol-5-oyl]benzothiazole was synthesized. Theoretical information on the optimized geometry, vibrational frequencies and atomic charges in the ground state were obtained by means of Density Functional Theory (DFT) using standard B3LYP/6-31G basis sets with Gaussian '09 software. The results indicate that the B3LYP method is able to provide satisfactory results for predicting vibrational frequencies and structural parameters. Mulliken population analysis was performed on the atomic charges and the HOMO-LUMO energies were calculated.

### Keywords

Gaussian  
DFT  
B3LYP  
Vibrational  
Assignment  
Mullikencharges  
HOMO  
LUMO

### Introduction

Benzothiazole derivatives are fascinating chemical products used in the field of medicine as they have been found to possess a wide spectrum of biodynamic properties. Benzothiazole analogs of dendrodione derivatives have attracted a great deal of interest due to their biological and commercial importance [1]. The

study of benzothiazoles is, therefore, of practical and theoretical importance. A density functional theory of different benzothiazole derivatives have been calculated by using DFT/B3LYP method.

Marine organisms are known to contain several pharmacologically active compounds [2]. Many marine natural products have unique structural features and substitutions, such as the presence of unusual heterocyclic ring systems or halogen substituents [3]. A few marine natural products or their synthetic analogs are in clinical use or at various

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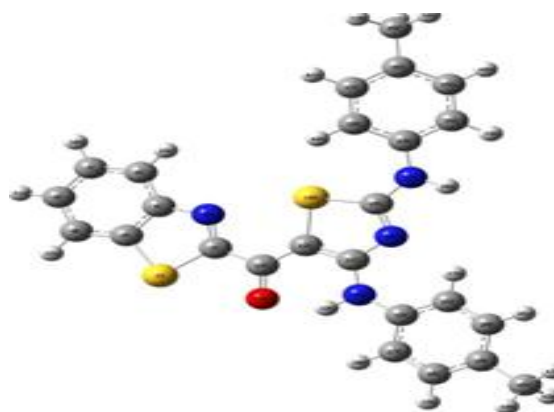
stages of drug development. Many alkaloids are derived from marine organisms such as sponges, coelenterates, tunicates (ascidiuans), bryozoans, red algae and symbiotic bacteria [4]. Indole derivatives are quite common among marine alkaloids which possess excellent in vitro cancer cell cytotoxicity. In addition, benzothiazole exhibit several biological activities just as indoles.

Patil *et al.* reported the DFT study on dihydroxyphenyl benzothiazole [5] by using B3LYP/6-31G(d). The main objective of this paper is to present, more accurate vibrational assignments, bond lengths, bond angles, atomic charges and HOMO-LUMO of 2-[2,4-bis(4-methylphenylamino)-thiazol-5-oyl]benzothiazole using DFT/B3LYP method. A systematic study on vibrational spectra and structure of 2-[2,4-bis(4-methylphenylamino)-thiazol-5-oyl]benzothiazole.

### Computational

The DFT computation of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole has been performed using Gaussian '09 program package at the Becke-3Lee-Yang-Parr (B3LYP) level with standard 6-31G basis set [6]. The optimized structural parameters are used in the vibrational frequency calculations at DFT level. At the

optimized geometry of the title molecule no imaginary frequency modes are obtained, so there is a true minimum potential energy surface is found [7]. The assignments of the normal modes of vibration for the titled compound have been made by visual inspection of the individual mode using the Gauss view software. The optimized structure of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole is given in **Fig 1**. The optimized structural parameter calculated by B3LYP level with 6-31G basis set are given in **Table 1**.



**Fig 1** Optimized structure of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole.

**Table 1** Optimized geometrical parameters of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole at B3LYP with 6-31G level.

Para	Bond len. (Å)	Parameters	Bond angles(°)	Parameters	Dihedral angle(°)
meters	Calculated		Calculated		Calculated
S1-C2	1.8423	S1-C2-N3	120.093	S1-C5-C4-C6	-0.3499
C2-C3	1.30061	C2-N3-C4	115.1965	C9-H32-C5-S1	179.0499
C3-C4	1.39713	N3-C4-C5	124.7096	C8-C9-C5-S1	179.8134
C4-C5	1.40369	C4-C5-S1	120.9802	H30-C7-C8-C9	-0.7869
C5-C6	1.39245	C5-S1-C2	110.344	H31-C8-C7-C6	0.2514
C6-C7	1.40978	C4-C6-H29	128.6726	C7-C6-C4-N3	-179.6848
C7-C8	1.39763	C6-H29-C7	118.2985	H30-C7-C6-C4	-179.9283
C8-C9	1.39633	C6-C7-H30	121.0738	C6-C4-C5-N3	-179.9283
C9-C5	1.81474	H30-C7-C8	120.6275	C4-C5-C6-S1	0.1354
C5-S1	1.08369	C7-C8-H31	121.1024	C4-N3-C2-C13	0.0317
C6-H29	1.08474	H31-C8-C9	119.3143	N3-C2-C13-O14	-179.7965
C7-H30	1.08511	C8-C9-H32	119.5833	N3-C2-C13-S1	0.2001
C8-C31	1.08402	H32-C9-C5	120.6216	C2-C13-C12-C11	-179.978
C9-H32	1.47124	C9-C5-C4	119.5211	O14-C13-C12-S10	-179.079
C2-C13	1.28739	C5-C4-N3	119.8573	C13-N3-C2-C12	0.7429
C13-O14	1.41442	C5-C4-C6	118.9029	C12-C13-O14-C11	0.9275

C13-C12	1.41891	N3-C2-C13	119.0731	C13-C12-C11-N44	-179.7316
C12-C11	1.83735	S1-C2-C13	122.024	C12-S10-C43-N22	0.0389
C12-S10	1.82821	C2-C13-O14	127.9005	S10-C43-N22-H38	179.9329
S10-C43	1.32402	C13-C2-C12	115.0886	C43-S10-N22-C23	-179.738
C43-N44	1.37674	O14-C13-C12	116.8074	C43-N22-H38-N44	0.1101
C11-N44	1.35739	C13-C12-S10	113.0213	N22-C43-N44-C11	-0.1326
C43-N22	1.01373	C12-C11-N44	117.2708	C43-N44-C11-N15	179.8422
N22-H38	1.41857	C11-N44-C43	121.6109	N44-C11-N15-H33	179.9737
N22-C23	1.402801	S10-C43-N22	120.9257	C11-N15-C16-N44	-0.0514
C23-C28	1.08227	C43-N22-H38	137.9546	C11-N15-C16-C21	-0.0156
C28-H42	1.39807	C23-N22-C24	113.0485	N15-C16-C17-H34	179.9187
C28-C27	1.08597	C23-C24-H39	108.0485	C16-C21-H37-C17	-179.9904
C27-H41	1.40631	C23-C28-H42	116.2979	C17-H34-C18-C19	-0.0561
C23-C24	1.08641	H41-C27-C28	130.8737	C17-C16-C21-H37	175.3504
C24-H39	1.39339	C26-C27-H41	112.7896	C16-C21-C20-H36	0.7466
C24-C25	1.08611	C25-C24-H39	86.4782	C21-C20-C19-C45	-158.4195
C25-H40	1.40655	C26-C25-H40	114.9915	C21-C20-H36-C19	16.5803
C25-C26	1.51202	C26-C49-H51	121.2594	C20-H36-C19-C18	16.1047
C26-C49	1.09577	C49-C26-H50	123.7076	C20-C19-C45-H47	-168.3955
C49-H50	1.09475	H52-C49-H50	112.9138	C20-C19-C45-H46	-0.99
C49-H52	1.09855	H52-C49-H51	111.8568	C19-H46-C45-H48	-176.2208
H51-C49	1.35653	C12-C11-N44	131.2734	C19-C45-H47-H48	18.289
C11-N15	1.02874	N44-C11-N15	115.7882	C19-C45-H48-H47	-155.3912
N15-H33	1.4112	H33-C11-N15	122.7441	H36-C20-C19-C45	-166.8924
N15-C16	1.40567	N15-C16-C21	117.8376	C21-C20-C19-C45	-19.4274
C16-C21	1.39794	C21-H37-C20	119.2895	C43-N22-C23-C24	-166.1854
C21-C20	1.4033	C20-H36-C21	119.8922	C23-C24-C25-H40	16.2746
C20-C19	1.4067	C21-C16-C17	120.1678	C26-C25-C24-H39	7.6733
C19-C18	1.39209	C16-C17-H34	119.8972	H40-C25-C26-C49	-169.8668
C18-C17	1.41024	C17-C18-H35	120.1678	C49-C26-C27-C28	-169.0022
C17-C16	1.0864	H35-C18-C19	119.9307	C27-C28-H42-C26	-6.5321
C17-H34	1.0865	C18-C19-C20	120.3804	C27-C28-C23-N22	-4.3876
C18-H35	1.07965	C21-C20-H36	119.3941	H52-C49-C26-C27	173.5951
C21-H37	1.08675	H37-C21-C20	120.2213	H51-C49-C26-C27	-165.5769
C20-H36	1.51243	C20-C19-C45	120.8346	H50-C49-C26-C27	27.0683
C19-H45	1.09495	C2-C13-O14	119.1106	H52-C49-C26-C25	16.8151
C45-H47	1.09881	O14-C13-C12	120.0535	C49-C26-C25-H40	-150.5397
C45-H46	1.09643	C19-C45-H47	120.3656	C26-C25-H40-C24	4.6345
C45-H48	1.09754	C45-H48-H46	119.4681	C25-C24-H39-C26	-177.624
		C19-C45-H47	120.1632	C49-C26-C27-C25	-1.327
		C20-C19-C45	119.2278	C27-C28-H50-C26	-179.0061
		C19-C45-H46	120.3694	C27-C28-C23-N22	6.4241
				H52-C49-C26-C27	-177.715
				H51-C49-C23-C27	-176.0368
				H50-C423-C26-C27	-0.1759
				H52-C49-C26 -C27	19.8626

## Results and discussion

### Molecular geometry

The optimized structure of 2-[2,4-bis(4-methylphenyl-amino)thiazol-5-oyl]benzothiazole is given in **Fig 1**. The optimized structural parameter calculated by B3LYP level with 6-31G basis. The self-consistent field (SCF) energy of 2-[2,4-bis(4-methylphenyl-amino)thiazol-5-oyl]benzothiazole at B3LYP level with the basis set 6-31G is found to be -2054.96 a.u; with dipole moment 5.4781 Debye. The bond lengths of C4-C5, C5-C9, C9-C8, C8-C7, C7-C6 and C6-C4 shows double bond character (aromatic bond). Similarly the bond lengths of C16-C21, C21-C20, C20-C19, C19-C18, C17-C16 and C16-C21 shows double bond characters (aromatic bond). Similarly the bond lengths of C23-C24, C24-C25, C25-C26, C26-C27, C27-C28 and C28-C23 shows double bond characters.

### Vibrational assignments

Vibrational frequency were calculated by using B3LYP/6-31G, method. 2-[2,4-bis(4-methylphenyl-amino)thiazol-5-oyl]benzothiazole molecules consists of 52 atom therefore it got 150 normal modes of vibrations. The scaling factor of 0.96 is used for getting theoretical vibrational frequency [8]. Comparison of the frequencies calculated at DFT method using 6-31G basis set with experimental values reveal that the B3LYP method shows very good agreement with the literature observation [9-12].

The hetero aromatic molecule containing an N-H group and its stretching absorption occurs in the region 3500-3220  $\text{cm}^{-1}$ . Primary amine examined in dilute solution display two weak absorption bands [13] one near 3500 and 3400  $\text{cm}^{-1}$ . These bands represent, the asymmetric and symmetric N-H stretching modes. In the present work, the theoretical calculation indicate the scaled frequency values at 3484 and 3448  $\text{cm}^{-1}$  is assigned to N-H stretching vibration. Primary aromatic amines normally [14] absorb at 1615-1580  $\text{cm}^{-1}$ . The N-H in-plane bending vibration computed by B3LYP/6-31G method good agreement with literature values. The presence of aromatic N-H out-of-plane bending vibration are appeared with in the region 767-673  $\text{cm}^{-1}$ . In the present work, the theoretical calculation indicates, the scaled frequency values at 706 and 688  $\text{cm}^{-1}$  is assigned to N-H out-of-plane bending vibration.

The assignments of methyl group vibration make a significant contribution to the titled compound. The asymmetric C-H vibration for methyl group usually [15] occurs in the region between 2975  $\text{cm}^{-1}$  and 2920  $\text{cm}^{-1}$ . The theoretically computed values by B3LYP/6-31G

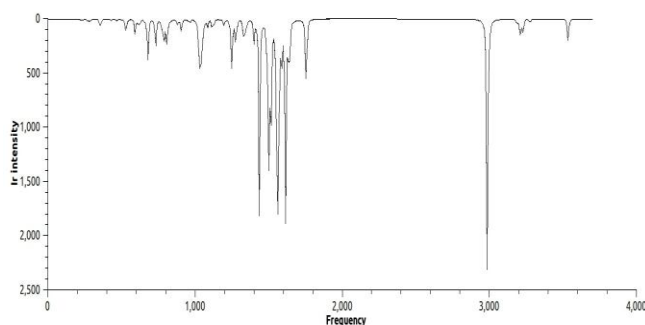
method for C-H vibrations are found at 2992, 2988, 2913  $\text{cm}^{-1}$ . Thus the theoretically computed values for C-H vibrations nearly coincide with literature values. In the title compound the methyl in-plane bending modes occur in the range 1479-1411  $\text{cm}^{-1}$ . The C-H out-of plane bending vibrations occur at 888  $\text{cm}^{-1}$  and 774  $\text{cm}^{-1}$ . The assignments are in agreement with the literature values.

The aromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000  $\text{cm}^{-1}$  which is the characteristic region for the ready identification of the C-H stretching vibrations [16]. The C-H stretching vibration computed by B3LYP/6-31G method good agreement with literature observations. The C-H in-plane bending vibrations were observed in the region 1420-1000  $\text{cm}^{-1}$ . These bands represents, the C-H in-plane-bending vibrations. In the present work, the theoretical calculation indicate the scaled frequency value at 1395  $\text{cm}^{-1}$  is assigned to C-H in-plane-bending vibration. The presence of C-H out-of plane vibrations were observed in the region 999-750  $\text{cm}^{-1}$ .

In the present work, the C-H out-of-plane bending vibration computed by B3LYP/6-31G method good agreement with literature observation. Generally, the c-c stretching vibrations in aromatic compound from the band in the region [17] 1650-1430  $\text{cm}^{-1}$ . In the present study, the scaled frequency value at 1478  $\text{cm}^{-1}$  are assigned to c-c stretching vibration. The assignments of methyl group vibration make a significant contribution to the titled compound. The asymmetric C-H vibration for methyl group usually occurs in the region 2975  $\text{cm}^{-1}$  and 2920  $\text{cm}^{-1}$ . The theoretically computed values by B3LYP/6-31G method for C-H vibrations are found at 2964, 2864  $\text{cm}^{-1}$ . Thus the theoretically computed values for C-H vibrations nearly coincide with literature values.

In the title compound the methyl in-plane bending modes occur in the range 1479-1411  $\text{cm}^{-1}$ . The C-H out-of plane bending vibrations occur at 888  $\text{cm}^{-1}$  and 774  $\text{cm}^{-1}$ . The carbonyl group is present in a large number of different classes of compounds, for which a strong band observed due to the C=O stretching vibration is in the region of 1850-1550  $\text{cm}^{-1}$ . The intensity of these bands can be increase due to conjugation or formation of hydrogen bonds. The lone pair of electrons on oxygen also determined the nature of the carbonyl group.

In our present study the theoretically computed wavenumber for C=O stretching vibrations occur at  $1571\text{ cm}^{-1}$ . The in-plane and out-of plane C=O bending mode occur at  $1522\text{ cm}^{-1}$  and  $849\text{ cm}^{-1}$ . The identifications of C-N, C=N vibrations is a difficult task, since the mixing of several bands are possible in the region. Silverstein *et al.* assigned C=N stretching absorption in the region  $1382\text{--}1226\text{ cm}^{-1}$  for aromatic amines. The identification of wavenumber for C-N stretching in the side chains is rather difficult since there are problems in differentiating wavenumber from others. The band at  $1357\text{ cm}^{-1}$  corresponds C-N, C=N stretching vibrations. The C-S stretching vibration is expected in the region  $710\text{--}685\text{ cm}^{-1}$ . While DFT calculations give the C-S stretching vibration at  $637\text{ cm}^{-1}$  is assigned to C-S stretching vibration. The carbonyl group is important and its characteristic frequency has been extensively used to study a wide range of compounds.



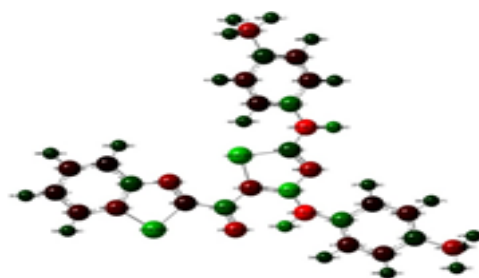
**Fig 2** Calculated IR spectrum of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole.

### Mulliken atomic charges

The atomic charges are very much dependent on how the atoms are defined. It also plays an important role in the application of quantum chemical calculation to molecular systems. The atomic charge values have been obtained by Mulliken population analysis. The Mulliken atomic charges calculated at B3LYP level with 6-31G basis set. As seen in **Fig 3**, show that N (15) has more negative charge ( $-0.825\text{eV}$ ) and C(11) has more positive charge ( $0.528\text{eV}$ ). The Mulliken atomic charge of all hydrogen and sulphur carries positive charge.

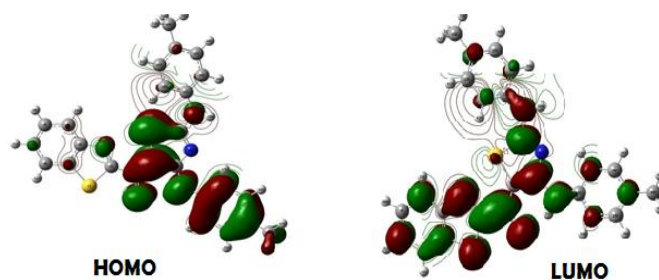
### HOMO-LUMO energy gaps

The HOMO-LUMO energy is calculated at B3LYP-6-31G level and energies of HOMO and LUMO are:  $-0.08258, -0.19139\text{ a.u.}$ , respectively and energy gap ( $\Delta E$ ) is  $0.10881\text{ a.u.}$   $\Delta E$  reveals the chemical activity of the molecule. LUMO is an electron acceptor that represents



**Fig 3** Mulliken charge distribution of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole

the ability to obtain an electron and HOMO represents the ability to donate an electron. The HOMO-LUMO energy gap of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole have been calculated at the B3LYP/6-31G level is shown in **Fig 4**.



**Fig 4** HOMO-LUMO of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole.

### Conclusions

To study the vibrational assignments of 2-[2,4-bis(4-methylphenylamino)thiazol-5-oyl]benzothiazole using DFT method (B3LYP) with 6-31G basis set. The optimized molecular geometry, atomic charges in the ground state were also calculated. The results indicate that the B3LYP Method is able to provide satisfactory results for predicting vibrational frequencies and structural parameters. Atomic charge distributions were calculated by determining the electron population of each atom. The lowering in the HOMO and LUMO energy gap explains the eventual charge transfer interactions that take place within the molecule.

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