

Experimental and DFT Investigation on the Influence of Electron Donour/Acceptor on the Hydrogen Bonding Interactions of 1-(1,3-Benzothiazol-2-yl)-3-(R-benzoylthiourea)

(Uji Kaji dan Penyiataan DFT mengenai Pengaruh Penderma/Penerima Elektron pada Interaksi Ikatan Hidrogen dalam 1-(1,3-Benzotiazol-2-yl)-3-(R-benzoylthiourea))

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ABSTRACT

The presence of two different chromophores in benzothiazole molecule namely benzothiazole and aromatic rings lead to interesting chemical and biological properties that attract more researches on the compounds. Three new benzothiazolyl-benzoylthiourea compounds namely 1-(1,3-benzothiazol-2-yl)-3-(benzoylthiourea) (BBT), 1-(1,3-benzothiazol-2-yl)-3-(4-chlorobenzoylthiourea) (BBT-4Cl) and 1-(1,3-benzothiazol-2-yl)-3-(4-methoxybenzoylthiourea) (BBT-4OCH₃) with different electron withdrawing substituents (R) at the para positions on the benzene ring of benzoylthiourea ring have been synthesized from the reaction of R-benzoyl isothiocyanate (R= H, Cl, and OCH₃) and 2-aminobenzothiazole. The compounds were characterized by spectroscopic techniques (infrared, ¹H proton NMR and UV-Vis). The IR spectra showed the frequency signals of ν (C=O), ν (C=S), ν (N-H) at 1664-1673, 1238-1249 and 3031-3055 cm⁻¹, respectively. The ¹H proton NMR spectra showed the presence of N-H amine and amide signals in the region of (12.14-12.35) and (14.17-14.43) ppm, respectively. The proton signals of the two benzothiazole and benzoylthiourea moieties appear at 7.08-8.16 ppm. A theoretical study based on Density Functional Theory (DFT) and Time-Dependent (TD) DFT was conducted to optimize the geometrical structure and investigate the electronic properties of title compounds. The highest occupied molecular orbital (HOMO) was found on the benzothiazole moiety; while, the lowest-unoccupied molecular orbital (LUMO) was located at the benzoylthiourea fragment. The DFT optimized structures possessed an intramolecular hydrogen bonding and the types of para substituents used influenced the properties of hydrogen bonding.

Keywords: Benzothiazolyl-benzoylthiourea; DFT; electron donating groups; electron withdrawing groups; hydrogen bonding interactions

ABSTRAK

Kehadiran dua kromofor yang berbeza di dalam molekul benzotiazol iaitu benzotiazol dan gelang aromatik menyebabkan molekul ini mempunyai ciri kimia dan biologi yang menarik minat para penyelidik terhadap sebatian tersebut. Tiga sebatian benzotiazolil-benzoiltiourea yang baru dengan kumpulan pengganti daripada kumpulan penderma dan kumpulan penerima elektron (R) pada kedudukan para pada gelang benzoiltiourea iaitu 1-(1,3-benzotiazol-2-il)-3-(benzoiltiourea) (BBT), 1-(1,3-benzotiazol-2-il)-3-(4-klorobenzoiltiourea) (BBT-4Cl) dan 1-(1,3-benzotiazol-2-il)-3-(4-metoksibenzoiltiourea) (BBT-4OCH₃) berjaya disintesis daripada tindak balas R- benzoil isotiosianat (R = H, Cl dan OCH₃) dan 2-aminobenzotiazol. Sebatian tersebut telah dicari dengan teknik spektroskopi (inframerah, ¹H proton RMN dan UV-Vis). Spektra inframerah sebatian menunjukkan frekuensi bagi jalur ν (C=O), ν (C=S), ν (N-H) masing-masing pada 1664-1673, 1238-1249 dan 3031-3055 cm⁻¹. Spektra ¹H proton NMR menunjukkan kehadiran proton pada moiety N-H amina dan amida masing-masing pada 12.14-12.35 and 14.17-14.43 ppm. Kehadiran dua moiety benzotiazol dan benzoiltiourea ditunjukkan oleh isyarat proton pada julat 7.08-8.16 ppm. Kajian teori berdasarkan pengiraan dengan kaedah teori fungsi ketumpatan (DFT) dan DFT bersandar masa (TD) telah dijalankan untuk mengoptimumkan struktur geometri dan mengkaji sifat elektronik sebatian tersebut. orbital molekul terisi dengan tenaga tertinggi (HOMO) didapati pada moiety benzotiazol; manakala orbital molekul tidak terisi dengan tenaga terendah (LUMO) didapati pada moiety benzoiltiourea. Ikatan intramolekul hidrogen dapat dioptimumkan melalui DFT dan jenis kumpulan pengganti yang digunakan mempengaruhi sifat ikatan hidrogen tersebut.

Kata kunci: Benzotiazolil-benzoiltiourea; DFT; ikatan hidrogen; kumpulan penarik elektron; kumpulan penderma elektron

INTRODUCTION

Thiourea compounds are unique and have interesting properties that lead to the development of various

applications such as non-linear optical materials that makes thioureas as a potential compound especially for a laser material (Weiqun et al. 2003). The principal

role of panchromatic dyes is to harvest light spectrum particularly the visible and near-infrared (Li et al. 2013). In addition, thioureas were found to be widely used in several applications such as in the development of electronic and optoelectronic devices (Yusof et al. 2010; Yutronic et al. 2000). Another interesting aspect of thioureas is this compound can act as chelating agents (Alkheraz et al. 2014; Das 1984; Shome et al. 1980) for various metal ions with electronic spectrum extended to the visible region (Mishra et al. 2009), hence, can be utilized as a molecular dye. Meanwhile, compounds based on benzothiazole derivative are known to be employed as organic dyes is photoelectrochemical (Sayama et al. 2002). The study has also shown that benzothiazole derivatives exhibited interesting photochemical properties due to the presence of two different chromophores in the molecule namely benzothiazole and aromatic moiety (Đaković et al. 2009).

Metal complexes of thiourea compounds have shown interesting biological activities such as anti-cancer, anti-microbe, anti-bacterial, anti-fungus, anti-malaria and anti-tuberculosis (Yang et al. 2012). Besides, thiourea compounds have also been used as building blocks in the synthesis of heterocyclic compounds and was claimed to be an important organic compound which acts as corrosion inhibitors and antioxidant (Alkheraz et al. 2014; Katritzky & Gordeev 1991). Benzoylthiourea and its derivatives are another class of thiourea compounds that have attracted tremendous research activities on their coordination chemistry, analytical and environmental application as well as their biological properties. Benzothiazole and its derivatives are also known to have biological activities such as anti-tumour, anti-bacterial, anti-fungus, anti-inflammatory and anti-allergy (Gao et al. 2007). In addition, rhenium complexes with benzothiazole derivatives were reported to have interesting biological activities and have been studied for application in technetium radiopharmaceuticals for radiotherapy and diagnostic imaging (Schoultz et al. 2016).

The previous study has shown that 1-(benzothiazol-2-ylidene)-3-methylthiourea, that contained a tertiary amide, behaves as a bidentate ligand through *S*, *N* coordination mode (Sathdeo et al. 2016). Benzoylthiourea contains *N*, *O* and *S* donor atoms that make coordination chemistry of this molecule more interesting as it can behave as a monodentate, bidentate or tridentate ligand (Kurt et al. 2009). The presence of intramolecular and intermolecular hydrogen bonding interactions that influence their coordination chemistry with the main group and transition metal elements (Domínguez et al. 2002). The *N*-carbamothioylbenzamide moiety in benzoylthiourea molecules plays an important role in determining their coordination modes that saw a ligand with secondary *N*-carbamothioylbenzamide moiety to favour a monodentate *S* coordination mode due to the presence of an intramolecular hydrogen bonding between the H-amide and the O-carbonyl group to form a 6-membered ring (NHOCNC) (Selvarakumar et al. 2009; Thompson et al. 1980). On the other hand, benzoylthiourea

with a tertiary *N*-carbamothioylbenzamide fragment tends to coordinate in a bidentate manner through OS donor atoms since the formation of intramolecular hydrogen bonding was eliminated from the structural feature (Mohammad Halim et al. 2012).

In this study, we report the synthesis of benzothiazole-benzoylthiourea molecules with chloro and methoxy substituent at the *para* position on the benzene ring of the benzoyl moiety. Chloro and methoxy have been chosen as the substituents since both are electron withdrawing and donating group, respectively, that may influence the formation of the intramolecular hydrogen bonding interactions. The findings from this work can facilitate a better understanding of the structural and intramolecular hydrogen bonding behaviour of these molecules.

EXPERIMENTAL DETAILS

SYNTHESIS OF 1-(1,3-BENZOTHIAZOL-2-YL)-3-(*R*-BENZOYL)THIOUREA (*R* = H, Cl AND OCH₃)

All the compounds were synthesized according to the previous literature methods (Al-abbasi et al. 2011; Perez et al. 2011; Raj et al. 1999; Tan et al. 2014) with some modification. The solution of *R*-benzoyl chloride (0.01 mol) in acetone (25 mL) was added drop-wise to a solution of potassium thiocyanate, KSCN (0.01 mol) in acetone (25 mL). The mixture was stirred for 30 min and the byproduct, potassium chloride, was removed by filtration to give *R*-benzoyl isothiocyanate as an intermediate product. Then, 2-aminobenzothiazole (0.01 mol) in acetone (25 mL) was added to the *R*-benzoyl isothiocyanate solution and left stirring for 2 h 30 min (Figure 1). Lastly, the product was precipitated by addition of 500 mL cold water and the mixture was left in an ice bath for 2 h. The precipitate was washed with a small volume of cold ethanol to give the desired product.

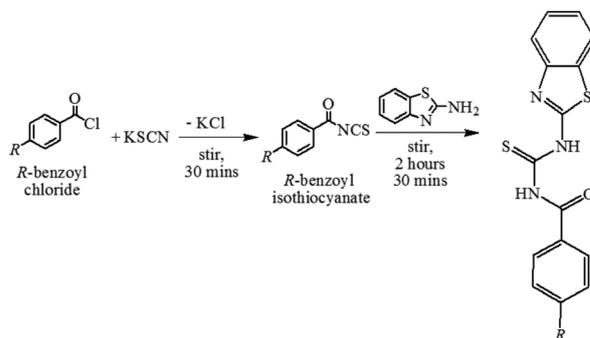


FIGURE 1. The a two-stage chemical reactions for the synthesis of the 1-(1,3-benzothiazol-2-yl)-3-(*R*-benzoyl)thiourea (*R* = H, Cl and OCH₃) molecules

INSTRUMENTATION

The IR spectra were obtained using ATR-FTIR Cary 630 FTIR spectrophotometer from Agilent Technologies. The

^1H NMR spectra were recorded by Bruker AVANCE 400 III HD. The analysis on UV-Vis absorption was conducted with AvaSpec-2048L (AVANTES).

COMPUTATIONAL METHODS

The structural geometry of the molecule was optimised with density functional theory (DFT) and their electronic and absorption properties were calculated with time-dependent (TD) DFT. The hybrid function of Lee–Yang–Parr (B3LYP) exchange–correlation functional and 6-311++G (d, p) basis-set with polarization and diffuse function was used in combination for the calculation (Becke 1993, 1988; Davidson & Feller 1986; Hehre et al. 1986; Lee et al. 1988). The vibrational frequencies were verified to ascertain that the optimized structure represents local minima. Acetonitrile ($\epsilon = 35.688$) was considered for the geometry optimization with Tomasi's polarizable continuum model (PCM) (Cossi et al. 2003; Miertuš et al. 1981). It is known that calculations based on the hybrid function (B3LYP) tend to over-estimate the optical energies compared to experimentally obtained results (Fui et al. 2016; Mark-Lee et al. 2017).

RESULTS AND DISCUSSION

All the three compounds, BBT, BBT-4Cl, and BBT-4OCH₃ were synthesized via a condensation reaction with benzoyl isothiocyanate and 2-aminobenzothiazole. The IR spectra of all molecules showed a band at 3303-3304 cm⁻¹, which is more intense than a normal N-H signal from amine group. This observation is attributed to the formation of hydrogen bonding between the N–H···O. Thus, the band was assigned as the $\nu(\text{N-H})$ signal for the amide group. The strong stretching vibration signal ascribed to be $\nu(\text{C=O})$ was recorded at 1664-1673 cm⁻¹ and the $\nu(\text{C=S})$ signal from the thiocyanide group was observed at 1238-1249 cm⁻¹ with a medium-weak intensity. In addition, stretching vibration for C=N from the benzoyl ring can be found at 1510-1525 cm⁻¹ and the band at 2912-3003 cm⁻¹ indicates the presence of C-H from the benzoyl ring. The stretching frequencies of C=O were relatively lower than a free C=O (< 1730 cm⁻¹) due to the formation of hydrogen bond (Saeed et al. 2010; Yusof et al. 2010). The functional groups and their vibration frequencies for BBT, BBT-4Cl, and BBT-4OCH₃ are collected in Table 1.

TABLE 1. Vibrational frequencies for BBT, BBT-4Cl and BBT-4OCH₃ ligands

Functional group	Frequency (cm ⁻¹)		
	BBT	BBT-4Cl	BBT-4OCH ₃
C=O	1672	1664	1673
N-H (amide)	3052	3031	3055
N-H (amine)	3327	3303	3304
C=S	1238	1239	1249
C=N	1510	1519	1525

The optimized structures of these compounds led to the lowest energy molecular structure with the presence of an intramolecular hydrogen bond. The optimized structure of BBT is shown in Figure 2. The geometrical parameters of selected bond lengths (Å) and angles (°) of the optimised BBT, BBT-4Cl and BBT-4OCH₃ structures are listed in Table 2. The structures of the compounds are almost planar due to the intramolecular hydrogen bonding interaction. In Figure 2, the intramolecular hydrogen bonding interaction is expected to occur in the N2–H7···O1 moiety. Table 2 shows the selected geometrical data of DFT for BBT, BBT-4Cl, and BBT-4OCH₃. The data shows that the length of hydrogen bonding for BBT-4Cl is longer than that of BBT-4OCH₃ because of the electron donating OCH₃ group which induced a better electron delocalization through resonance involving the two lone pairs of electrons on the oxygen (OCH₃) and hence, the C=O bond becomes slightly elongated compared to that of BBT ($\Delta = 0.002$ Å). Subsequently, the intramolecular hydrogen bonding involving O1 atom (C=O) with H7 became stronger (O1···H7; shorter by 0.011 Å) and form a pseudo six-membered ring as shown in Figure 2. The intramolecular hydrogen bonding (N2–H7···O1) essentially improves the planarity of the two moieties (benzothiazole and benzoylthiourea).

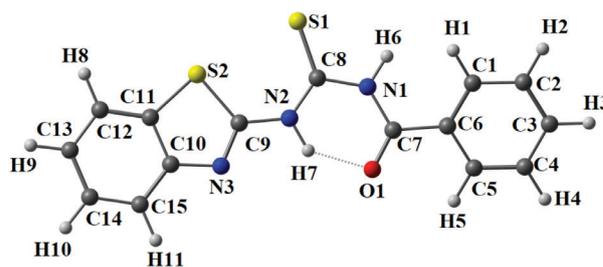


FIGURE 2. The optimised molecular structure of BBT in vacuo showing the intramolecular H-bond (dotted line); B3LYP/6-311++G (d, p)

TABLE 2. Selected geometrical data of DFT optimised (in vacuo) BBT, BBT-4Cl and BBT-4OCH₃

	BBT	BBT-4Cl	BBT-4OCH ₃
Bond (Å)			
S1-C8	1.665	1.665	1.667
O1-C7	1.225	1.225	1.227
N1-C7	1.387	1.386	1.390
N1-C8	1.402	1.403	1.400
N2-H7	1.027	1.027	1.028
H7-O1	1.833	1.837	1.822
Angle (°)			
O1-C7-N1	122.3	122.4	121.8
N1-C8-S1	118.5	118.4	118.5
N2-C8-S1	127.1	127.2	127.0
C8-N2-C9	130.0	130.0	130.0

Further insight into the structures of the product molecules was obtained from ^1H NMR spectroscopy. The ^1H NMR of BBT-4Cl ligand shows the proton signal belonging to aromatic rings at 7.34-8.16 ppm. The N-H signals appeared at the 12.35 ppm and 14.17 ppm which indicates the presence of N-H benzamine [(N-H)1] and the N-H thioamide [(N-H)2] moieties, respectively. Similarly, the BBT-4OCH₃ shows the signal of the corresponding benzothiazole and benzoylthiourea protons at 7.08-8.06. Whereas, the corresponding benzamide and thioamide proton resonances were detected at 12.14 and 14.43 ppm. The chemical shifts for all protons are collected in Table 3. The (N-H)2 chemical shift of BBT-4OCH₃ was further downshifted compared to BBT and BBT-4Cl. This observation is influenced by the presence of greater hydrogen bonding effect (Arslan et al. 2006; Kurt et al. 2009; Zhou et al. 2005).

TABLE 3. Chemical shift for BBT, BBT-4Cl and BBT-4OCH₃

Compound	$\delta_{(N-H)1}$	$\delta_{(N-H)2}$	$\delta_{\text{H (benzene ring)}}$
BBT	12.30	14.29	7.38-8.07
BBT-4Cl	12.35	14.17	7.34 - 8.16
BBT-4OCH ₃	12.14	14.43	7.08 - 8.06

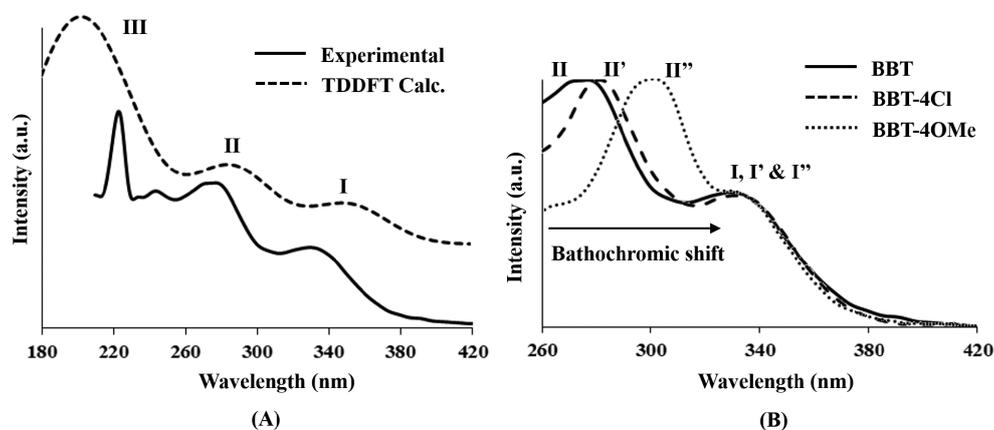


FIGURE 3. (A) Experimental (solid line) and DFT simulated (dashed line) UV-Vis spectra of BBT in acetonitrile with three dominant absorption bands: I, II and III. (B) Comparison of the first two absorption bands obtained experimentally for BBT (I, II), BBT-4Cl (I', II') and BBT-4OCH₃ (I'', II'')

TABLE 4. UV-Vis absorption data measured experimentally and theoretically in acetonitrile for BBT

Band	Expt.			TDDFT/B3LYP			
	λ_{max}^a (nm)	E_g^a (eV)	ϵ^a	λ_{max}^a (nm)	E_g^a (eV)	Osc. ^a (<i>f</i>)	Key transitions and character ^b
I	329	3.77	1.137	353	3.51	0.3470	(98%) HOMO _(btz) → LUMO _(btu)
II	277	4.47	2.049	291	4.26	0.4758	(91%) HOMO-3 _(*) → LUMO _(btu)
III	223	5.56	3.064	217	5.74	0.4446	(24%) HOMO-1 _(n) → LUMO+5 _(btz)

^a $\lambda_{\text{max}} / \text{nm}$, ($\epsilon (\times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$); $1.0 \times 10^{-4} \text{ M}$; $E_g = 1239.5 / \lambda_{\text{max}}$; Osc. = Oscillator strength (Fui et al. 2012; Mark-Lee et al. 2013).

^b n = non-bonding electron pair, btz = benzothiazolyl, btu = benzoylthiourea, * = spread across btz and btu with higher participation from S atom of thioamide

UV-VIS ABSORPTION STUDY

The experimental UV-Vis spectrum of BBT showed three prominent absorption bands labelled as I, II and III. A shoulder peak was also observed in the region, 230-250 nm. The TDDFT simulation of the electronic excitation bands has demonstrated a similar spectral profile. The TDDFT simulated band III is relatively broad compared to the experimental one, as a result, the apparent shoulder peak may not be observed due to overlapping absorption bands. A total of one hundred vertical excitation states were considered for the TDDFT calculation. The data obtained was subsequently interpolated with a Gaussian-type distribution curve in Figure 3(A). The UV-Vis absorption information i.e. maxima wavelength (λ_{max}), optical bandgap (E_g), extinction coefficient (ϵ), oscillator strengths (*f*), predominant transitions and orbitals involved are shown in Table 4.

Figure 4 illustrates the frontier molecular orbitals, HOMO and LUMO of the three titled compounds. The UV-Vis spectral description will focus on BBT since all three compounds have similar UV-Vis spectral profile in terms of the number of absorption bands. The most intense absorption peak with the highest extinction coefficient belongs to band III ($\lambda_{\text{max}} = 223 \text{ nm}$, $\epsilon = 3.064$

$\times 10^4 \text{ M}^{-1}\text{cm}^{-1}$; Calc: 217 nm, $f = 0.4446$). Based on TDDFT calculations, band III is assigned to the, $n \rightarrow \pi^*$ electronic transition where the free non-bonding electron pairs (n) of electron rich atoms i.e. S, N and O of the molecule populates the empty molecular orbitals found on the benzothiazole fragment. Moving towards the longer wavelengths, band II involves the photoexcitation of electrons from the lower occupied molecular orbital (HOMO-3) to LUMO. The HOMO-3 is located throughout the molecule which involves the filled- π molecular orbitals in the z -plane. While the LUMO is predominantly located at the benzoylthiourea moiety involving the empty π^* orbital in the same direction. The calculated probability of involvement for HOMO-3 \rightarrow LUMO was 91% since their molecular orbitals are congruent in terms of orientation. The electron excitation recorded at $\lambda_{\text{max}} = 329 \text{ nm}$, $E_{\text{g}} = 3.77$ is ascribed to band I. This electronic absorption is identified as the HOMO \rightarrow LUMO transition (98% probability). The HOMO is mainly found on the benzothiazolyl fragment and the photoexcited electrons move to the opposite end of the molecule towards the benzoylthiourea fragment where the LUMO, empty π^* molecular orbitals are located.

Among the three compounds, two of which are substituted with either an electron-donating (OCH_3) or withdrawing (Cl) group, situated at the *para* position of the benzoyl moiety. Concurrently, the substituent is also located where the mass accumulation of empty molecular orbitals, LUMO is found. Therefore, we would expect that the substituent would affect the LUMO energy level and shift the optical bandgap. The LUMO is basically involved in electronic transitions for the band I and

II (Table 4) and these absorption bands are illustrated in Figure 4(B) for BBT, BBT-4Cl and BBT-4OCH₃. It is observed that band I, I' and I'' have no significant changes in terms of band position despite the presence of substituents on the benzene ring of a benzoylthiourea fragment. Nevertheless, the position of band II is drastically affected with increasing bathochromic shift in the following order: II < II' < II''. In the unsubstituted compound, BBT, band II involves HOMO-3 where the filled- π molecular orbitals are distributed across the entire molecule with a slightly higher participation from the S atom of thioamide linkage. In comparison with band II, a band I encompass the filled- π molecular orbitals of benzothiazole moiety (HOMO), which are situated away from the benzoyl moiety (benzoylthiourea) with *para*-substituents (Cl and OCH₃). Therefore, the electron withdrawing and donating substituent of Cl and OCH₃, respectively, have a greater influence on the HOMO-3. As such, the electron-donating resonance effect induced by the methoxy group outweighed the inductive effect caused by the electron-withdrawing chlorine atom. The ease of electron delocalization within the BBT-4OCH₃ molecule has lowered the required energy for electronic photo-excitation of band II and hence, a blue-shift was observed. As per discussion, the reduction of optical bandgap which involves the lowest energy electronic absorption band (I) can essentially be achieved with the utilization of electron donors at the benzothiazole moiety, while, the benzoylthiourea moiety should be infused with electron acceptors. Hence, electrons will have a higher affinity to delocalized from the HOMO (benzothiazole) to the LUMO (benzoylthiourea).

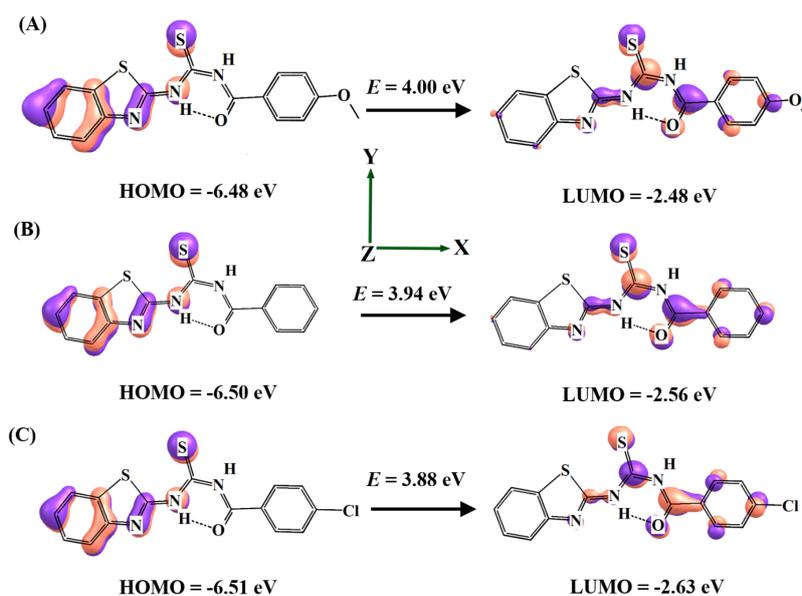


FIGURE 4. Isosurface illustration (contour value = 0.052) of HOMO and LUMO of (A) BBT-4OCH₃, (B) BBT and (C) BBT-4Cl with their ground state energy bandgaps

CONCLUSION

Three new compounds namely 1-(1,3-benzothiazol-2-yl)-3-(benzoylthiourea) (BBT), 1-(1,3-benzothiazol-2-yl)-3-(4-chlorobenzoylthiourea) (BBT-4Cl) and 1-(1,3-benzothiazol-2-yl)-3-(4-methoxybenzoylthiourea) (BBT-4OCH₃) were successfully synthesized and showed the presence of intramolecular hydrogen bonding interaction which enhanced the overall geometrical stability in the observed structural conformation. The Cl and OCH₃ substituents influenced the electron density of the benzene ring. The electron delocalization within the molecule was improved via the resonance effect of OCH₃ and hence, greatly strengthen the hydrogen bonding. On the contrary, the Cl substituent weakened the hydrogen bonding by inductively attracting the electron density away from the hydrogen bond. Essentially, the presence of intramolecular hydrogen bond induced structural planarity of the molecule. Tuning of the optical properties can be systematically accessed via the HOMO (benzothiazole) and LUMO (benzoylthiourea) by incorporating proper substituent groups.

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