# THEORETICAL STUDY ON STRUCTURE AND ELECTRONIC PROPERTIES OF 4H-CYCLOPENTA[2,1-B,3;4-B']DITHIOPENE S-OXIDE AND ITS CCl$_2$ AND CF$_2$ BRIDGED DERIVATIVES

## Banjo Semire[*] and Olusegun Ayobami Odunola

*Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology,*
*P.M.B. 4000, Ogbomoso, Oyo-State, Nigeria*

## ABSTRACT

*Quantum chemical calculations using semi-empirical, ab initio, density functional theory (DFT) and Møller plesset (MP2) methods were performed on 4H-Cyclopenta[2,1-b,3;4-b']dithiopene S-oxide derivatives (i.e. bridged dithiophene S-oxides, BTOs). The geometries, stabilities, electronic and thermodynamic properties of the compounds were studied. The thermodynamic parameters calculated at PM3 were in good agreement with those calculated at B3LYP/6-31G(d) level. The band gap energies calculated at B3LYP/6-31G(d) level for the BTOs were lower than the un-substituted trithiophene but higher than 4H-Cyclopenta[2,1-b,3;4-b']dithiopene. The absorption $\lambda_{max}$ calculated using TD-DFT was shifted to longer wavelength by successive replacement of methylene hydrogens of BTO by chlorine and fluorine atoms.*

*Keywords: electronic properties; bridged dithiophene S-oxides; quantum chemical methods*

## ABSTRAK

*Perhitungan kimia kuantum menggunakan metoda-metoda semiempiris, ab initio, teori kerapatan muatan (density functional theory, DFT) dan Møller plesset (MP2) telah dilakukan untuk turunan 4H-siklopenta [2,1-b,3;4-b']ditiopen-oksida S (ditiopen terhubung dengan jembatan oksida S, BTO). Bentuk geometri, kestabilan, sifat-sifat elektronik dan termodinamik dari senyawa-senyawa telah dikaji. Parameter-parameter termodinamik hasil perhitungan PM3 menunjukkan kesesuaian yang cukup baik dengan hasil perhitungan level B3LYP/6-31G(d). Energi celah BTO hasil perhitungan dengan B3LYP/6-31G(d) terlihat lebih rendah dari trithiopen tak tersubstitusi, tetapi lebih tinggi dari 4H-siklopenta[2,1-b,3;4-b']dithiopen. Nilai $\lambda_{max}$ hasil perhitungan TD-DFT mengalami pergeseran lebih tinggi akibat pertukaran suksesif dari hidrogen metilen pada BTO oleh atom-atom khlor dan fluor.*

*Kata Kunci: sifat elektronik; jembatan dithiopen; oksida S; metoda kimia kuantum*

## INTRODUCTION

The vast interests shown by polymer scientists towards conjugated organic polymers among others are mainly due to two important properties of conductivity and electroluminescence. Semiconducting polymers with band gaps in the range 0.5–3.5 eV have a number of potential advantages over their inorganic counterparts, such as ease of processing, cost of manufacture and greater varieties of large area panel displays [1-2]. The idea of using organic molecules in electronic devices has attracted tremendous attention in the past quarter century. Among various possible types and designs of such organic molecules, the π-conjugated molecules have been, perhaps, the most useful ones [3-4]. Oligo- and poly-thiophenes offer remarkable potential as active elements in electronic devices that exploit their semiconducting properties, such as light-emitting diodes (LED) and field-effect transistors (FET) [3]. Moreover,

the oligothiophenes provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in polythiophenes [5-7].

However, monitoring the decrease in band gap as a way of controlling the electric properties of polythiophenes are strongly governed by the intramolecular delocalization of π-electrons along the conjugation chain [8]. This delocalization has been found to depend on the extent of the overlapping between the p$_z$ orbitals of the carbon atoms in positions α and α' of adjacent thiophene rings, this is also strongly influenced by substituents [9-18].

In order to reduce energy band gaps, the geometric and electronic structures of some bridged octamer of oligothiophenes have been theoretically studied with bridging electron-accepting groups such as C=O, C=S and C=C(CN)$_2$ [18-21]. In one of our recent works, semi-empirical methods (AM1 and PM3)

* Corresponding author.
Email address : bsemire@lautech.edu.ng

**Table 1.** Calculated geometries of 4H-Cyclopenta[2,1-b,3;4-b']dithiopene S-oxide (BTO-$CH_2$) by means of different methods: Bond lengths are in Å, bond angles in degree and dihedral angles in degree

| Bond length | AM1 | RM1 | PM3 | HF/6-31G(d) | B3LYP/6-31G(d) | MP2/6-31G(d) |
|---|---|---|---|---|---|---|
| $C_1$-$S_1$ ($C_6$-$S_2$) | 1.733 | 1.749 | 1.800 | 1.784 | 1.804 | 1.786 |
| $C_4$-$S_1$ ($C_5$-$S_2$) | 1.710 | 1.723 | 1.778 | 1.770 | 1.798 | 1.774 |
| $C_1$-$C_2$ ($C_6$-$C_7$) | 1.357 | 1.347 | 1.351 | 1.329 | 1.353 | 1.361 |
| $C_2$-$C_3$ ($C_7$-$C_8$) | 1.446 | 1.446 | 1.446 | 1.463 | 1.446 | 1.441 |
| $C_3$-$C_4$ ($C_5$-$C_8$) | 1.399 | 1.374 | 1.383 | 1.337 | 1.371 | 1.380 |
| $C_4$-$C_5$ | 1.436 | 1.422 | 1.438 | 1.454 | 1.439 | 1.438 |
| $C_3$-X ($C_8$-X) | 1.499 | 1.494 | 1.497 | 1.511 | 1.513 | 1.507 |
| $C_1S_1C_4$ ($C_5S_2C_6$) | 91.65 | 89.44 | 88.59 | 88.87 | 88.96 | 89.38 |
| $C_1C_2C_3$ ($C_6C_7C_8$) | 110.74 | 110.05 | 111.24 | 111.66 | 112.36 | 111.74 |
| $C_2C_3C_4$ ($C_7C_8C_5$) | 112.82 | 112.91 | 114.03 | 113.56 | 114.22 | 113.87 |
| $C_3C_4C_5$ ($C_7C_5C_4$) | 108.36 | 108.39 | 108.36 | 108.99 | 109.27 | 109.07 |
| $C_1S_1C_4C_5$ ($C_6S_2C_5C_4$) | -179.54 | -179.12 | 178.97 | 175.27 | 170.39 | 175.23 |
| $C_2C_1S_1C_4$ ($C_7C_6S_2C_5$) | -8.41 | -6.66 | -6.92 | -8.61 | -12.13 | 12.88 |
| $C_1C_2C_3X$ ($C_6C_7C_8X$) | 179.69 | 179.88 | 178.55 | -178.67 | -176.50 | 176.76 |
| $C_2C_3C_4C_5$ ($C_7C_8C_5C_4$) | 179.56 | 179.29 | -179.91 | -177.44 | -174.32 | 178.76 |
| $C_1C_2C_3C_4$ ($C_6C_7C_8C_5$) | 0.01 | 0.08 | -0.18 | 0.64 | 0.41 | -1.76 |
| $C_4C_3XC_8$ ($C_3C_8XC_3$) | 0.08 | 0.22 | -0.12 | -0.72 | -1.32 | 0.21 |
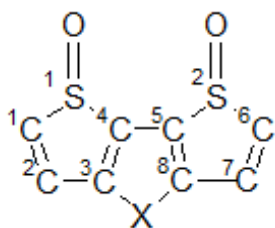


**Fig 1.** The structure and atomic numbering of 4H-Cyclopenta[2,1-b,3;4-b']dithiopene S-oxide (BTO); X=$CH_2$ for BTO-$CH_2$, X= CHCl for BTO-CHCl, X=$CCl_2$ for BTO-$CCl_2$, X=CHF for BTO-CHF and X=$CF_2$ for BTO-$CF_2$

and density functional theory (B3LYP/6-31G(d) were used to study geometries, electronic and thermodynamic properties of 4H-cyclopenta[2,1-b,3;4-b']dithiopene S-oxide derivatives (BTO-X, with X = $BH_2$, $SiH_2$, S, S=O or O bridge). The results showed that geometries and thermodynamic parameters calculated by PM3 were in good agreement with those calculated with B3LYP/6-31 G*; and also there was correlation between terminal C=C vibrational frequencies and the absorption $\lambda_{max}$ of the BTO-X [22].

In this paper we reported the theoretical investigation on structure of 4H-Cyclopenta[2,1-b,3;4-b']dithiopene S-oxide (the methylene -$CH_2$- bridged dithiophene S-oxide) using semi-empirical and *ab initio* (HF/6-31G(d), B3LYP/6-31G(d)) and MP2/6-31G(d) methods as shown in Fig. 1. Halogens have been found to increase the electrical conductivity conjugated polymers when incorporated [23-26], therefore attempt was also made to decrease the band gap by successive replacement of bridged methylene hydrogen with chlorine and fluorine atoms.

## COMPUTATIONAL METHODS

Calculations were performed by Spartan 06 program implemented on an Intel Pentium M 1.7GHz Computer. The geometries of bridged dithiophene S-oxide (BTO) derivatives were maximally optimized at Semi-empirical methods (AM1, RM1 and PM3), *ab initio* (Hatree Fock and Density Functional Theory (Beckes's Three Parameter Hybrid [27] Functional) using the Lee, Yang and Parr correlation Functional B3LYP [28] (Lee, 1988)) and Møller Plesset (MP2). The basis set 6-31G(d) was used for all atoms *ab initio* methods which were used by several researchers in studying heterocycles [1,19-20,29], all optimizations were without symmetry restrictions.

## RESULT AND DISCUSSION

### Geometries and Stabilities

The calculation time required for DFT-B3LYP and MP2 (some hours) was drastically reduced in semi-empirical calculations into some minutes at detriment of the accuracy of the theoretical calculations (the developments of semi-empirical methods involved restriction of parameterizations to the valence electrons). Table 1 showing a list of the geometrical parameters of BTO-$CH_2$ calculated at different methods.

Generally, the bond lengths calculated by MP2/6-31G(d) were slightly different from those calculated using other methods, however those calculated at PM3 and DFT methods were very close (i.e. mean deviation of bond lengths calculated at PM3 from that DFT was about 0.009Å). The mean deviations (δ) of the bond lengths calculated at AM1, RM1, PM3, HF/6-31G(d) and

**Table 2.** Calculated geometries of BTO-CHCl, BTO-CCl$_2$, BTO-CHF and BTO-CF$_2$ by B3LYP/6-31G(d) and MP2/6-31G(d) methods: Bond lengths are in Å, bond angles in degree and dihedral angles in degree

| | BTO-CHCl | BTO-CCl$_2$ | BTO-CHF | BTO-CF$_2$ |
|---|---|---|---|---|
| C$_1$-S$_1$ (C$_6$-S$_2$) | 1.803 (1.801) | 1.801 | 1.802 (1.799) | 1.798 |
| | **1.784** | **1.785** | **1.782** | **1.781** |
| C$_4$-S$_1$ (C$_5$-S$_2$) | 1.796 (1.797) | 1.797 | 1.795 (1.798) | 1.795 |
| | **1.774** | **1.772** | **1.773** | **1.769** |
| C$_1$-C$_2$ (C$_6$-C$_7$) | 1.353 (1.355) | 1.354 | 1.354 (1.356) | 1.356 |
| | **1.362** | **1.362** | **1.363** | **1.362** |
| C$_2$-C$_3$ (C$_7$-C$_8$) | 1.444 (1.442) | 1.441 | 1.444 (1.441) | 1.440 |
| | **1.438** | **1.436** | **1.437** | **1.435** |
| C$_3$-C$_4$ (C$_5$-C$_8$) | 1.368 (1.367) | 1.366 | 1.367 | 1.364 |
| | **1.377** | **1.374** | **1.376** | **1.373** |
| C$_4$-C$_5$ | 1.445 | 1.448 | 1.448 | 1.445 |
| | **1.443** | **1.447** | **1.448** | **1.457** |
| C$_3$-X (C$_8$-X) | 1.513 (1.515) | 1.518 | 1.520 (1.522) | 1.527 |
| | **1.507** | **1.508** | **1.512** | **1.517** |
| C$_1$S$_1$C$_4$ (C$_5$S$_2$C$_6$) | 89.10 (89.15) | 89.23 | 89.15 (89.25) | 89.39 |
| | **89.51** | **89.56** | **89.64** | **89.80** |
| C$_1$C$_2$C$_3$ (C$_6$C$_7$C$_8$) | 111.91 (111.93) | 111.56 | 112.05 (111.99) | 111.70 |
| | **111.29** | **110.88** | **111.35** | **110.97** |
| C$_2$C$_3$C$_4$ (C$_7$C$_8$C$_5$) | 114.88 (114.95) | 115.50 | 114.78 (114.98) | 115.41 |
| | **114.57** | **115.18** | **114.56** | **115.12** |
| C$_3$C$_4$C$_5$ (C$_7$C$_5$C$_4$) | 109.38 (109.37) | 109.48 | 109.59 (109.22) | 109.65 |
| | **109.51** | **109.20** | **109.20** | **109.43** |
| C$_1$S$_1$C$_4$C$_5$ (C$_6$S$_2$C$_5$C$_4$) | 170.02 (168.42) | 168.39 | 170.91 (166.48) | 167.26 |
| | **-173.68** | **174.27** | **-171.80** | **173.17** |
| C$_2$C$_1$S$_1$C$_4$ (C$_7$C$_6$S$_2$C$_5$) | -13.03 (-12.68) | -31.11 | -13.14 (-12.48) | -13.24 |
| | **13.23** | **-13.82** | **13.21** | **-14.11** |
| C$_1$C$_2$C$_3$X (C$_6$C$_7$C$_8$X) | -173.37 (-178.21) | -175.23 | -172.39 (-178.42) | -174.49 |
| | **178.78** | **-175.19** | **178.66** | **-174.45** |
| C$_2$C$_3$C$_4$C$_5$ (C$_7$C$_8$C$_5$C$_4$) | -174.39 (-173.17) | -173.33 | -174.69 (-171.80) | -172.15 |
| | **178.03** | **-178.49** | **176.71** | **-177.51** |
| C$_1$C$_2$C$_3$C$_4$ (C$_6$C$_7$C$_8$C$_5$) | 0.75 (0.78) | 0.93 | 0.32 (0.96) | 0.63 |
| | **-2.21** | **2.00** | **-2.39** | **1.89** |
| C$_4$C$_3$XC$_8$ (C$_3$C$_8$XC$_3$) | 2.20 (-5.06) | -1.46 | 4.34 (-7.38) | -1.62 |
| | **4.07** | **0.89** | **6.11** | **0.33** |

*geometries parameters calculated in MP2/6-31G(d) in bold

DFT methods were 0.022, 0.024, 0.016, 0.019 and 0.014Å respectively as compared to that obtained at MP2/6-31G(d). The δ calculated with respect to bond angles in BTO-CH$_2$ at AM1, RM1, PM3, HF/6-31G(d) and DFT methods were 1.26°, 0.59°, 0.39°, 0.25° and 0.40° respectively compared to that of MP2 method, this showed that bond angles calculated at PM3 and HF/6-31(d) were more closer to that of MP2. For instance, the values of C$_1$S$_1$C$_4$ (C$_1$C$_2$C$_5$) bond angles were 91.65° (110.74°), 89.44° (110.05°), 88.59° (111.24°), 88.87° (111.66°) and 88.96° (112.36°) at AM1, RM1, PM3, HF/6-31G(d) and B3LYP/6-31G(d) respectively compared 89.38° (111.74°) at MP2/6-31G(d).

Dihedral angles calculated for BTO-CH$_2$ using various methods showed that there was little distortion of the molecule from planarity. For instance, the dihedral angles C$_1$S$_1$C$_4$C$_5$ (C$_1$C$_2$C$_3$C$_4$) were -179.54° (0.01°), -179.12° (0.08°), 178.977° (-0.18°), 175.27° (0.64°), 170.39° (0.41°) and 175.23° (-1.76°) at AM1, RM1, PM3, B3LYP/6-31G(d) and MP2/6-31G(d) respectively. In

case of BTO-CHCl, BTO-CCl$_2$, BTO-CHF and BTO-CF$_2$, there was little or no difference in bond lengths compared to BTO-CH$_2$. However, there were little differences in dihedral angles between symmetrical BTOs (i.e. BTO-CCl$_2$, BTO-CH$_2$ and BTO-CF$_2$) and unsymmetrical BTOs (i.e. BTO-CHCl and BTO-CHF), thus symmetrical BTO derivatives were more planar as shown in Table 2). In the process of calculation of energies, the predictive order of stability for BTOs at B3LYP/6-31G(d) and MP2/6-31G(d) were the same, although the energies predicted by MP2 were slightly lower. The results showed that BTO with CHCl and CCl$_2$ were more stable than their fluorine analogues, therefore the order of stability was BTO-CCl$_2$ > BTO-CHCl > BTO-CF$_2$ > BTO-CHF > BTO-CH$_2$.

**Electronic Properties**

The Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO) and band

**Table 3.** Calculated HOMO, LUMO, Energy band gap BTOs by various methods

| Compound | Calculation method | HOMO (eV) | LUMO (eV) | Energy band gap (eV) | Shift in energy band gap (eV) |
|---|---|---|---|---|---|
| BTO-CH$_2$ | AM1 | -9.04 | -1.51 | 7.53 | - |
| | RM1 | -9.07 | -1.18 | 7.89 | - |
| | PM3 | -9.35 | -1.69 | 7.66 | - |
| | HF/6-31G(d) | -8.46 | 1.14 | 9.60 | - |
| | B3LYP/6-31G(d) | -6.06 | -2.56 | 3.50 | - |
| BTO-CHCl | AM1 | -9.27 | -1.84 | 7.43 | -0.08 |
| | RM1 | -9.40 | -1.76 | 7.64 | -0.25 |
| | PM3 | -9.54 | -1.99 | 7.55 | -0.11 |
| | HF/6-31G(d) | -8.84 | 0.64 | 9.48 | -0.12 |
| | B3LYP/6-31G(d) | -6.36 | -3.04 | 3.32 | -0.18 |
| BTO-CCl$_2$ | AM1 | -9.44 | -2.06 | 7.38 | -0.15 |
| | RM1 | -9.64 | -2.09 | 7.55 | -0.34 |
| | PM3 | -9.69 | -2.20 | 7.49 | -0,17 |
| | HF/6-31G(d) | -9.01 | 0.34 | 9.35 | -0.28 |
| | B3LYP/6-31G(d) | -6.53 | -3.33 | 3.20 | -0.30 |
| BTO-CHF | AM1 | -9.82 | -1.32 | 7.52 | -0.01 |
| | RM1 | -9.39 | -1.51 | 7.88 | -0.01 |
| | PM3 | -9.63 | -2.00 | 7.63 | -0.03 |
| | HF/6-31G(d) | -8.78 | 0.68 | 9.46 | -0.14 |
| | B3LYP/6-31G(d) | -6,32 | -2.98 | 3.34 | -0.16 |
| **BTO-CF$_2$** | **AM1** | **-9.59** | **-2.09** | **7.50** | **-0.03** |
| | **RM1** | **-9.69** | **-1.83** | **7.86** | **-0.03** |
| | **PM3** | **-9.88** | **-2.29** | **7.59** | **-0.07** |
| | **HF/6-31G(d)** | **-9.03** | **0.37** | **9.40** | **-0.20** |
| | **B3LYP/6-31G(d)** | **-6.51** | **-3.26** | **3.25** | **-0.25** |
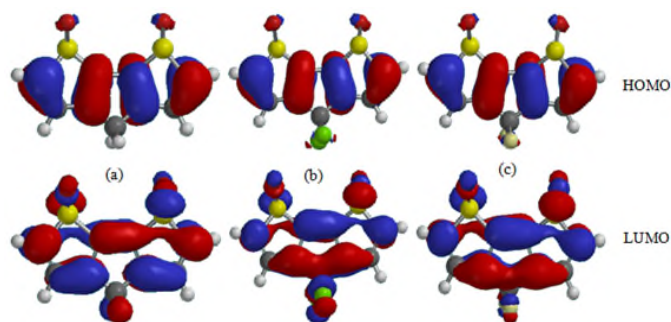


**Fig 2.** Frontier molecular orbital: (a) BTO-CH$_2$, (b) BTO-CCl$_2$ and (c) BTO-CF$_2$
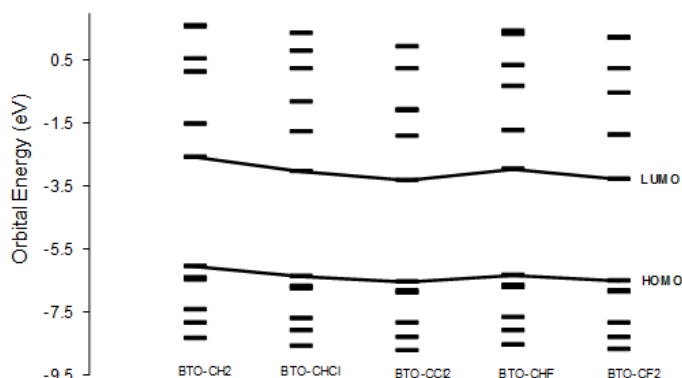


**Fig 3.** Partial molecular orbital energy diagram for BTO-X calculated by B3LYP/6-31G(d) method

gap energy calculated by all theoretical methods employed were displaced in Table 3. To further understand the electronic properties of BTO derivatives, some frontier molecular orbitals levels obtained at B3LYP/6-31G(d) were shown in Fig. 2 and 3. All the bridged BTOs showed HOMO-1 degeneracy and there was a systematic change in the HOMO and LUMO energies as halogens (Cl and F) were successively introduced to replace the bridged methylene hydrogen of 4H-Cyclopenta[2,1-b,3;4-b']dithiopene S-oxide (BTO-CH$_2$). The HOMO and LUMO energies decreased upon such substitution, although the decrease in the LUMO energy was significantly pronounced with the increase in strength/number of electron withdrawing group (halogen) [32].

The band gap energy of BTO containing chlorine atom was less than that of fluorine analogues which could be attributed to the larger atomic size of chlorine atom which makes chlorine acts as electrons donor compared to fluorine atom. The band gap energies calculated ranged from 3.50 eV – 3.20 eV for B3LYP/6-31G(d), 9.60 eV – 9.35 eV for HF/6-31D(d), 7.66 eV – 7.49 eV for PM3, 7.89 eV – 7.55 eV for RM1 and 7.53 eV – 7.35 eV AM1. The band gaps calculated at B3LYP/6-31G(d) were larger than those calculated for 4H-Cyclopenta[2,1-b,3;4-b']dithiopene with CH$_2$ and SiH$_2$ bridged but lower than that of un-substituted

**Table 4.** Calculated transitions, oscillation strength (*f*) and transitions generated calculated at TD-DFT B3LYP/6-31G(d)

| λ_max (mn) | f | MO involves in transition |
|---|---|---|
| **BTO-CH_2** | | |
| **308.15** | 0.0015 | HOMO-1 → LUMO+1 (93%) |
| **369.68** | 0.2275 | HOMO → LUMO (91%) |
| **394.83** | 0.0129 | HOMO-2 → LUMO (94%) |
| **400.22** | 0.0310 | HOMO → LUMO (95%) |
| **BTO-CCl_2** | | |
| **426.91** | 0.1181 | HOMO-2 → LUMO (69%) |
| | | HOMO → LUMO (26%) |
| **438.45** | 0.0424 | HOMO-1→ LUMO (96%) |
| **439.30** | 0.0501 | HOMO → LUMO (68%) |
| | | HOMO-2 → LUMO (27%) |
| **BTO-CF_2** | | |
| **414.27** | 0.2245 | HOMO → LUMO (68%) |
| | | HOMO-2 → LUMO (25%) |
| **427.41** | 0.0044 | HOMO-2 → LUMO (71%) |
| | | HOMO → LUMO (25%) |
| **430.26** | 0.0350 | HOMO-1 → LUMO (96%) |

**Table 5.** Selected vibrational frequencies (cm⁻¹) calculated at B3LYP/6-31G(d)

| BTO-CH_2 | BTO-CCl_2 | BTO-CF_2 | Assignment |
|---|---|---|---|
| 1596, 1591 | 1594, 1593 | 1600, 1598 | $\nu C_1 = C_2/C_6 = C_{7*}$ |
| 1504, 1471 | 1509, 1477 | 1506, 1476 | $\nu C_3 = C_4/C_5 = C_8$ |
| 1350 | 1321 | 1309 | $\nu C_4 - C_5$ |
| 1080, 1085 | 1092, 1088 | 1089, 1089 | $\nu S = O$ |
| 3076, 3043 | 1009 | 1270, 1190 | $\nu C - X_2$ |

*terminal C=C stretching modes

dithiophene and trithiophene [19]. The order of decrease in energy band gap was BTO-CCl_2 < BTO-CF_2 < BTO-CHCl < BTO-CHF < BTO-CH_2.

The electronic spectra involving transition of valence electrons that occur in the UV-visible absorption was calculated at TD-B3LYP/6-31G(d) level in order to investigate the molecular orbitals that involved in electronic transitions in bridged BTO derivatives. The absorption peaks, oscillation strength and percentage of the molecular orbitals involved in transitions are displayed in Table 4. The results show that λ_max shifted to a longer wavelength with increase in the number of halogen atoms, due to enhancement of π-conjugated system/increase in electron(s) contribution from the halogen to the π-rings. For instance, the calculated λ_max for BTO-CCl_2 and BTO-CF_2 are 426.91 and 414.27 nm respectively compared to 361.68 nm for BTO-CH_2. However, the calculated λ_max for BTO-CH_2 is higher than the experimental by 49nm [33]. The chlorine derivatives of methylene bridged BTO have lower band gaps than the corresponding fluorine analogues, hence longer wavelengths.

The oscillator strength (*f*), a parameter that shows the probability of the transition which accomplishes the transition in question (oscillate) revealed that BTO-CH_2 bridge molecule has the highest probability of electrons

transition from ground state to the excited state. The transitions arising from low absorption bands i.e. oscillator strength (*f*) values less than 0.005 are considered in this paper. BTO-CH_2 has three strong absorption (i.e. > 0.005*f*) at 369.68, 394.83 and 400.22 nm arising from HOMO → LUMO (91%), HOMO-2 → LUMO (94%) and HOMO → LUMO (95%) respectively; the 369.6 nm absorption peak with 0.2275*f* is characterized as π-π* transition. For BTO-CCl_2, all calculated transitions showing strong absorption peaks at 426.91, 438.45 and 439.30 nm with *f* values of 0.1181, 0.0424 and 0.0501 respectively. The 426.91 nm absorption peak is characterized as π-π* and n- π* transitions arise from HOMO-2 → LUMO (69%) and HOMO → LUMO+1 (26%); 438.45 nm absorption peak is from HOMO-1 → LUMO (96%) and 439.30 nm absorption peak arises from HOMO → LUMO (68%) and HOMO-2 → LUMO (27%). However, for BTO-CF_2 the absorption peaks calculated are 414.27, 427.41 and 430.26 nm with 0.2245, 0.0044 and 0.035*f* respectively. The 414.27 nm absorption arises from HOMO → LUMO (68%) and HOMO-2 → LUMO (25%); 427.41 nm absorption peak is from HOMO-2 → LUMO (71%) and HOMO → LUMO (25%); and 430.26 absorption is from HOMO-1 → LUMO (96%) (Table 4). The 414.27 nm absorption peak is characterized as π-π* and n- π* transitions.

**Selected Vibrational Frequencies for BTO Derivatives**

Vibrational spectroscopy is one of the powerful methods that has been extensively used in by organic chemists for the identification of functional groups and also used to distinguish molecular conformers,

**Table 6.** Standard enthalpy ($H^o_m$), standard entropy ($S^o_m$), standard Gibb's free energy ($G^o_m$) and heat of formation ($H^o_f$) calculated by various methods at 298K

| Compound | Calculation method | $H^o_m$ (kJ/mol) | $S^o_m$ (J/mol) | $G^o_m$ (kJ/mol) | $H_f^o$ (kJ/mol) |
|---|---|---|---|---|---|
| BTO-$CH_2$ | AM1 | 375.54 | 418.00 | 250.91 | **73.52** |
| | RM1 | 370.30 | 420.56 | 244.91 | **69.00** |
| | PM3 | 365.71 | 426.15 | 238.65 | **57.00** |
| | HF/6-31G(d) | 392.28 | 413.40 | 269.02 | - |
| | B3LYP/6-31G(d) | 364.74 | 427.99 | 237.13 | - |
| BTO-CHCl | AM1 | 345.92 | 449.26 | 220.97 | **75.80** |
| | RM1 | 350.61 | 456.20 | 214.59 | **49.35** |
| | PM3 | 345.08 | 458.50 | 208.37 | **64.97** |
| | HF/6-31G(d) | 370.49 | 449.39 | 236.51 | - |
| | B3LYP/6-31G(d) | 344.22 | 465.72 | 205.36 | - |
| BTO-$CCl_2$ | AM1 | 333.21 | 474.95 | 191.61 | **84.73** |
| | RM1 | 328.02 | 484.95 | 183.43 | **42.14** |
| | PM3 | 323.33 | 487.76 | 177.90 | **63.84** |
| | HF/6-31G(d) | 345.77 | 474.65 | 204.24 | - |
| | B3LYP/6-31G(d) | 320.74 | 493.53 | 173.58 | - |
| BTO-CHF | AM1 | 359.41 | 437.58 | 228.94 | **72.91** |
| | RM1 | 359.41 | 437.58 | 223.82 | **80.86** |
| | PM3 | 348.92 | 446.10 | 215.92 | **78.15** |
| | HF/6-31G(d) | 374.23 | 429.16 | 243.29 | - |
| | B3LYP/6-31G(d) | 347.02 | 455.50 | 211.21 | - |
| BTO-$CF_2$ | AM1 | 341.26 | 452.98 | 206.20 | **243.63** |
| | RM1 | 340.49 | 454.68 | 204.93 | **287.26** |
| | PM3 | 332.99 | 461.78 | 195.31 | **265.59** |
| | HF/6-31G(d) | 353.33 | 454.26 | 217.89 | - |
| | B3LYP/6-31G(d) | 327.25 | 472.49 | 186.37 | - |

tautiomers and isomers [34]. The comparison of the experimental and theoretical vibrational modes with proper assignment is helpful to understand a fairly complex system. However in the absence of experimental data, calculated vibrational frequencies could be used with reasonable degree of accuracy to understand the properties of molecules and to study effect of functional groups on molecules. The selected vibrational frequencies calculated at B3LYP/6-311G(d) were presented in Table 5 for the BTOs. The prominent terminal C=C stretching bands (i.e. $C_1 = C_2/C_6 = C_7$) were 1596 and 1591 $cm^{-1}$ for BTO-$CH_2$, 1594 and 1593 $cm^{-1}$ for BTO-$CCl_2$ and 1600 and 1598 $cm^{-1}$ for BTO-$CF_2$. The terminal C=C stretching modes for the rings in the dithiophene derivatives and the Raman-active (C=C) stretch mode in the oligoene have been used to establish a structure–property relationship for the compounds [35-37]. In this work, the terminal C=C stretching modes were not correlated with the $\lambda_{max}$ in the UV-visible absorption spectrum, however there was correlation between $C_3=C_4/C_5=C_8$ vibrational frequencies and $\lambda_{max}$. The higher the stretch mode, the greater the value of $\lambda_{max}$; i.e. 1509 $cm^{-1}$ (BTO-$CCl_2$, $\lambda_{max}$ = 426.91 nm) → 1506 $cm^{-1}$ (BTO-$CF_2$, $\lambda_{max}$ = 414.27 nm) → 1504 $cm^{-1}$ (BTO-$CCl_2$, $\lambda_{max}$ = 369.68 nm).

The splitting of $C_3=C_4/C_5=C_8$ stretching bands into two components has been attributed to a typical indicator of the attainment of a heteroquinonoid-like pattern for the π-conjugated path [38-39]. The $C_4$–$C_5$ stretching bands were 1350, 1321 and 1309 $cm^{-1}$ for BTO-$CH_2$, BTO-$CCl_2$ and BTO-$CF_2$ respectively. The stretching vibrations of S=O groups were 1085 and 1080 $cm^{-1}$ in BTO-$CH_2$ and 1092 and 1088 $cm^{-1}$ in BTO-$CCl_2$ and 1089 and 1087 in BTO-$CF_2$.

**Thermodynamic Properties**

The calculated standard thermodynamic properties at 298 K and 1 were listed in Table 6; these were used to determine the thermodynamic of successive halogen substitution of methylene hydrogen in BTO-$CH_2$. It was observed that the thermodynamic properties calculated at PM3 were in good agreement with that of DFT calculation [34]. The values of thermodynamic quantities calculated for BTO-$CH_2$ were higher than the derivatives, this indicated that ΔG°, ΔH° and ΔS° were negative upon halogen substitutions of methylene hydrogen.

**CONCLUSION**

The geometrical and electronic structure, UV-visible absorption bands, thermodynamic parameters of standard enthalpy, standard entropy and standard

*Indones. J. Chem., 2015, 15 (1), 93 - 100*

**99**

Gibb's free energy of bridged bithiophene-S-oxide derivatives were investigated through quantum chemistry calculations using semi-empirical (AM1, RM1 and PM3), Hatree Fock (6-31G(d)), B3LYP/6-31G(d) and MP2/6-31G(d) methods. The results showed that Bridged BTO derivatives with $CH_2$, $CCl_2$ and $CF_2$ were more planar than CHCl and CHF. Also, there were decreased in the thermodynamic parameters upon successive halogen substitution of methylene hydrogen of BTO-$CH_2$. The UV-visible absorption $\lambda_{max}$ was shifted to longer wavelength with increasing in number of halogen atoms due to enhancement of π-conjugated system, thus halogen atoms behaved as weak electron donors rather than electron abstractors in the bridged bithiophene-S-oxides.

## REFERENCES

1. Amazonas, J.G., Guimarães, J.R., Costa, S.C.S., Laks, B., and Nero, J.D.J., 2006, *J. Mol. Struct. THEOCHEM*, 759(1-3), 87–91.
2. Xing, Y., Xu, X., Wang, F., and Lu, P., 2006, *Opt. Mater.*, 29(4), 407–409.
3. Geiger, F., Stoldt, M., Schweizer, H., Bäuerle, P., and Umbach, E., 1993, *Adv. Mater.*, 5(2), 922–925; Garnier, F., Horowitz, G., Peng, X., and Fichou, D., 1990, *Adv. Mater.*, 2, 562–568.
4. Gill, R.E., Malliaras, G.G., Wildeman, J., and Hadziioannou, G., 1994, *Adv. Mater.*, 6, 132–139.
5. Bauerle, P., "Sulfur-Containing Oligomers" in *Electronic Materials: The Oligomer Approach*, Mullen, K., and Wegner G., Eds., Wiley–VCH, Weinheim, NY, 1998, 105–197.
6. Cornil, J., Beljonne, D., and Bredas, J.L., "A Quantum Chemical Approach to Conjugated Oligomers: The Case of Oligothiopenes", in *Electronic Materials: The Oligomer Approach*, Mullen, K., and Wegner G., Eds., Wiley–VCH, Weinheim, NY, 1998, 432–447.
7. Hasnaoui, K., Makayssi, A., Hamidi, M., and Bouachrine, M., 2008, *J. Iran. Chem. Res.*, 1, 67–77.
8. Bredas, J.L., 1985, *J. Chem. Phys.*, 82, 3808–3816.
9. Ferraris, J.P., and Lambert, T.L., 1991, *J. Chem. Soc., Chem. Commun.*, 18, 1268–1270.
10. Gunataunga, S.R., Jones, G.W., Kalaji, M., Murphy, P.J., Taylor, D.M., and Williams, G.O., 1997, *Synth. Met.*, 84, 973–974.
11. De Oliveira, M.A., Duarte, H.A., Pernaut, J.M., and de Almeida, W.B., 2000, *J. Phys. Chem. A.*, 104(35), 8256–8262.
12. De Oliveira, M.A., Dos Santos, H.F., and de Almeida, W.B., 2002, *Int. J. Quantum Chem.*, 90(2), 603–610.
13. Odunola O.A., and Semire, B., 2008, *Asian J. Chem.*, 20(6), 4343–4352.
14. Bundgaard, E., and Krebs, F.C., 2006, *Macromolecules*, 39(8), 2823–2831.
15. Van Duren, J.K.J., Dhanabalan, A., van Hal, P.A., and Janssen, R.A.J., 2001, *Synth. Met.*, 121(1-3), 1587–1588.
16. Yoshino, K., Park, D.H., Park B.K., Onoda, M., and Sugimoto, R., 1998, *Solid State Commun.*, 67(12), 1119–1121.
17. Petersen, M.H., Hagemann, O., Nielsen, K.T., Jørgensen, M., and Krebs, F.C., 2007, *Sol. Energy Mater. Sol. Cells*, 91, 996–1009.
18. Ashraf, R.S., and Klemm, E.J., 2006, *J. Polym. Sci., Part A: Polym. Chem.*, 43(24), 6445–6454.
19. Bouzzine, S.M., Bouzakraoui, S., Bouachrine, M., and Hamidi. M., 2005, *J. Mol. Struct. THEOCHEM*, 726, 271–276.
20. Bouzzine, S.M. Hamidi, M., and Bouachrine, M., 2009, *Orbital*, 1(2), 203–210.
21. Aouchiche, H.A., Djennane, S., and Boucekkine, A., 2004, *Synth. Met.*, 140(2-3), 127–134.
22. Semire, B., Odunola, O.A., and Adejoro, I.A., 2012, *J. Mol. Model.*, 18(6), 2755–2760.
23. Shirakawa, H., Louis, E.J., Macdiarmid, .A.G., Chang, C.K., and Heeger A.J., 1977, *J. Chem. Soc. D*, 16, 578–580.
24. Springborg M., 2003, *Synth. Met.*, 135, 347–353.
25. Bakhshi, A.K., Yamagudi, Y., Ago, H., and Yamabe, T., 1998, *J. Mol. Struct. THEOCHEM*, 437, 211–229.
26. Inagi, S., Hosaka, K., Hayashi, S., and Funchigami, T., 2010, *J. Electrochem. Soc.*, 157 (5), E88–E91.
27. Becke, A.D., 1993, *J. Chem. Phys.*, 98(7), 5648–5652.
28. Lee, C., Yang, W., and Parr, R.G., 1988, *Phys. Rev. B: Condens. Mater.*, 37(2), 785–789.
29. Brasca, R., Kneeteman, M.N., and Mancini, P.M.E., 2007, *IDECEFYN*, 12, 54–57.
30. Armelin, E., Bertran, O., Estrany, F., Salvatella, R., and Alemán, C., 2009, *Eur. Polym. J.*, 45(8), 2211–2221.
31. De Olivera, M.A., De Almeida, W.B., and Dos Santon, H.F., 2004, *J. Braz. Chem. Soc.*, 15(6), 832–838.
32. Kim, K-D., Park, J-S., Kim, H-K., Lee, T-B., and No, K-T., 1998, *Macromolecules*, 31(21), 7267–7272.
33. Coppo, P., and Turner, M.L., 2005, *J. Mater. Chem.*, 15, 1123–1133.
34. Silverstein M., Basseler, G.C., and Morill, C., *Spectrometric Identification of Organic compounds*, Wiley, New York, 1981.
35. Liu, G., and Yu, J., 2005, *J. Mol. Struct. THEOCHEM,* 717(1-3), 15–19.
36. Semire, B., Oyebamiji, B., and Ahmad, M., 2012, *Pak. J. Chem.*, 2(4), 166–173.

37. Oliva M.M., Gonzalez, S.R., Casado, J., Lopez Navarrete, J.T., Seixasde Melo, J.S., and Rojen, S., 2009, *Port. Electrochim. Acta*, 27(5), 531–537.
38. Casado, J., Hernández, V., Kim, O-K., Lehn, J-M., Navarrete, J.T.L., Ledesma, S.D., Ortiz, R.P., Delgado, M.C.R., Vida, Y., and Pérez-Inestrosa, E., 2004, *Chem. Eur. J.*, 10(6), 3805–3816.
39. Casado ,J., Hernández, V., Delgado, M.C.R, Ortiz, R.P., Navarrete, J.T.L., Facchetti A., and Marks, T.J., 2005, *J. Am. Chem. Soc.*, 127(38), 13364–13372.