

# Structural and electronic properties of 4*H*-cyclopenta[2,1-*b*,3;4-*b'*]dithiophene *S*-oxide (BTO) derivatives with an S, S=O, O, SiH<sub>2</sub>, or BH<sub>2</sub> bridge: semi-empirical and DFT study

Semire Banjo · Odunola Olusegun Ayobami ·  
Adejoro Isaiah Ajibade

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**Abstract** In this paper, we theoretically studied the geometries, stabilities, and the electronic and thermodynamic properties of 4*H*-cyclopenta[2,1-*b*,3;4-*b'*]dithiophene *S*-oxide derivatives (BTO-X, with X = BH<sub>2</sub>, SiH<sub>2</sub>, S, S=O, or O) using semi-empirical methods, ab initio methods, and density functional theory. The geometries and thermodynamic parameters calculated by PM3 were in good agreement with those calculated with B3LYP/6-31 G\*. The band gap calculated using B3LYP/6-31 G\* ranged from 3.94 eV (BTO-O) to 3.16 eV (BTO-B). The absorption  $\lambda_{\text{max}}$  calculated using B3LYP/6-31 G\* was shifted to longer wavelengths when X = BH<sub>2</sub>, SiH<sub>2</sub>, or S=O (due to their electron-withdrawing effects) and to shorter wavelengths for BTO-S and BTO-O as compared to the  $\lambda_{\text{max}}$  for the thiophene *S*-oxide (2TO) dimer. The changes in  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  calculated using both semi-empirical and DFT methods were quite similar.

**Keywords** Density functional theory (DFT) · Semi-empirical (PM3) · 4*H*-cyclopenta[2,1-*b*,3;4-*b'*]dithiophene *S*-oxide derivatives

## Introduction

Conjugated polymers have attracted considerable interest in recent years because of their promise in electronic applications, such as in batteries [1–5], electroluminescent devices [6], field-effect transistors [7], and photovoltaics [8].

Oligothiophenes are perhaps the most thoroughly investigated and well-characterized conjugated polymer systems [9–12]. These one-dimensional semiconductors are potentially important candidates for a broad range of applications in the ever-growing field of molecular electronics, including molecular wires and switches—for example as light-emitting diodes and field-effect transistors [13–18]. However, monitoring changes in the band gap is a way to control the electrical properties of polythiophenes, which are strongly governed by the intramolecular delocalization of  $\pi$ -electrons along the conjugation chain [19]. Thiophene-related molecules such as thiophene 1,1-dioxide and thiophene *S*-oxide have also been investigated [20] in studies of their synthesis, their reactivity as dienes in Diels–Alder reactions [21], and their photochemical and electrochemical behavior [22]. The orbital energies and electrochemical properties of thiophene *S*-oxide monomers have been studied theoretically using PM2/6-31 G\* [23].

In this paper, we describe theoretical studies performed by the authors on the geometric and electronic structures of some bridged oligothiophene octamers with bridges containing electron-accepting groups such as C=O, C=S and C=C(CN)<sub>2</sub> [24–26], as part of an overall strategy to reduce the band gap. In this paper, we will theoretically investigate the structure, electronic, and thermodynamic properties of bridged bithiophene *S*-oxide (BTO-X) with the bridges X = S, S=O, O, SiH<sub>2</sub>, and BH<sub>2</sub>. The results will be compared

S. Banjo (✉) · O. O. Ayobami  
Department of Pure and Applied Chemistry,  
Ladoke Akintola University of Technology,  
Ogbomoso, Nigeria  
e-mail: semireban@yahoo.com

S. Banjo  
e-mail: bsemire@lautech.edu.ng

A. I. Ajibade  
Department of Chemistry, University of Ibadan,  
Ibadan, Nigeria







**Table 1** Calculated geometries of bridged BTO-X derivatives (with X = BH<sub>2</sub>, SiH<sub>2</sub>, S, S=O, or O) obtained using PM3 and B3LYP/6-31G\* methods. Bond lengths are in Å; bond angles and dihedral angles are in degrees

	2TO		BTO-B		BTO-Si		BTO-S		BTO-SO		BTO-O	
	PM3	B3LYP/ 6-31G*	PM3	B3LYP/ 6-31G*	PM3	B3LYP/ 6-31G*	PM3	B3LYP/ 6-31G*	PM3	B3LYP/ 6-31G*	PM3	B3LYP/ 6-31G*
C1–S1 (C6–S2)	1.783	1.784	1.803	1.816	1.788	1.794	1.795	1.814	1.788	1.801	1.813	1.822
C4–S1 (C5–S2)	1.812	1.826	1.793	1.808	1.796	1.805	1.787	1.812	1.789	1.811	1.774	1.807
C1–C2 (C6–C7)	1.346	1.352	1.369	1.364	1.350	1.353	1.348	1.349	1.351	1.354	1.351	1.350
C2–C3 (C7–C8)	1.461	1.449	1.431	1.435	1.446	1.452	1.452	1.450	1.448	1.442	1.448	1.440
C3–C4 (C5–C8)	1.355	1.363	1.445	1.422	1.371	1.372	1.398	1.382	1.378	1.365	1.401	1.337
C4–C5	1.440	1.433	1.374	1.386	1.442	1.445	1.411	1.408	1.435	1.431	1.418	1.419
C3–X (C8–X)	-	-	1.574	1.607	1.835	1.888	1.717	1.747	1.787	1.822	1.374	1.366
C1–S1–C4 (C5–S2–C6)	89.17	90.18	88.29	86.85	88.89	89.15	88.87	88.67	88.79	89.06	88.76	88.72
C1–C2–C3 (C6–C7–C8)	113.28	114.04	113.11	114.21	112.59	113.76	111.88	111.83	111.98	111.67	109.57	110.01
C2–C3–C4 (C7–C8–C5)	113.08	114.15	111.70	110.38	113.42	112.66	111.33	114.94	113.45	115.66	115.78	117.49
C3–C4–C5 (C7–C5–C4)	124.64	128.99	110.49	111.49	115.45	117.52	111.44	112.66	112.40	113.68	105.42	105.51
C1–S1–C4–C5 (C6–S2–C5–C4)	−175.04	−175.15	−178.29	−177.68	−179.52	177.68	−179.53	175.40	178.63	173.55	178.37	164.63
C2–C1–S1–C4 (C7–C6–S2–C5)	−7.25	−13.12	−7.07	−9.89	−6.77	11.81	−6.34	−10.31	−7.03	−11.24	−6.68	−11.59
C1–C2–C3–X (C6–C7–C8–X)	-	-	178.60	176.78	178.53	179.75	178.81	−178.75	172.83	171.02	179.83	−174.82
C2–C3–C4–C5 (C7–C8–C5–C4)	176.69	178.91	178.37	177.57	179.82	−177.20	179.48	−176.93	−179.06	−176.25	179.88	−172.70
C1–C2–C3–C4 (C6–C7–C8–C5)	0.07	0.22	−0.12	0.78	0.03	0.22	−0.23	0.01	−0.13	1.95	−0.29	0.47
C4–C3–X–C8 (C5–C8–X–C3)	-	-	0.26	0.04	−0.37	−0.89	−0.09	−0.76	−8.09	−12.06	0.03	−1.39

of BTO-S, HOMO and HOMO-3 were doubly degenerate, whereas in BTO-SO, HOMO-1 and HOMO-3 were doubly degenerate. However, in BTO-O and BTO-Si, HOMO-1 was degenerate, while HOMO-1, LUMO+2 and LUMO+3 were degenerate in 2TO (Fig. 2).

There were systematic changes in the HOMO and LUMO energies as various X groups (X = BH<sub>2</sub>, SiH<sub>2</sub>, S, S=O, or O) were introduced to bridge the dithiophene S-oxide dimer. The band gap energies ( $E_{\text{HOMO-LUMO}}$ ) calculated for bridged BTO derivatives containing X (X = S or O) were larger than that of 2TO, so there was more localization of the  $\pi$ -electrons in BTO-S and BTO-O. However, BTO-BH<sub>2</sub>, BTO-Si, and BTO-SO had smaller band gaps than 2TO, which could ease the oxidation of these molecules, leading to better conductivity. The band gap calculated using B3LYP/6-31 G\* ranged from 3.94 eV (BTO-O) to 3.16 eV (BTO-B), as compared to 3.45 eV for 2TO. The DFT band gaps of the compounds studied in this work can be ordered as follows: BTO-B < BTO-SO < BTO-Si < 2TO < BTO-S < BTO-O.

The electronic spectra derived from transitions of valence electrons (which lead to adsorption in the UV-visible) were studied theoretically, in order to investigate the differences between 2TO and the X-bridged derivatives (X = BH<sub>2</sub>, SiH<sub>2</sub>, S, S=O, or O), and the results are shown in Table 2. It was found that with X = BH<sub>2</sub>, SiH<sub>2</sub>, and S=O,  $\lambda_{\text{max}}$  was shifted to longer wavelengths due to the electron-withdrawing effects of these groups, while  $\lambda_{\text{max}}$  was shifted to shorter wavelengths for BTO-S and BTO-O due to the electron-donating effects of the bridging groups for these compounds, as compared to  $\lambda_{\text{max}}$  for the BTO-CH<sub>2</sub> analog [37, 38]. For example, the calculated  $\lambda_{\text{max}}$  values for BTO-B and BTO-O were 536.21 and 328.53 nm, respectively, as compared to 360.95 nm for 2TO, which were in accordance with the band gap shifts calculated with the DFT method (Table 2).

The IR frequencies calculated with the DFT method for the molecular structures in their S<sub>0</sub> ground electronic states are shown in Table 3. The prominent bands in the calculated spectra were 1320 cm<sup>−1</sup> in BTO-B, 1450 cm<sup>−1</sup>



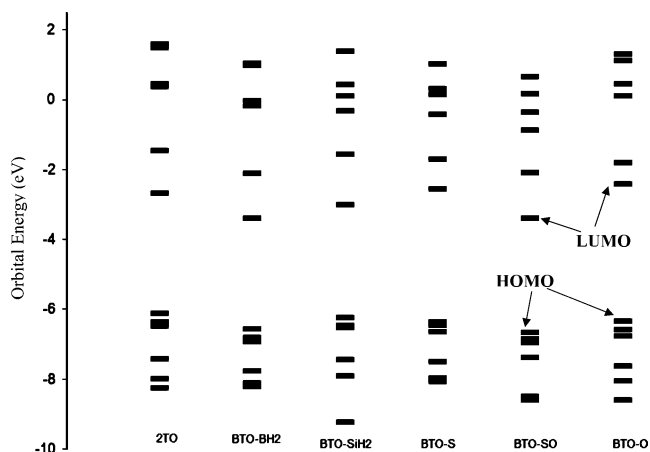
**Table 2** Calculated HOMO energies (eV), LUMO energies (eV), band gaps (eV),  $\lambda_{\max}$  (nm), and oscillator strengths (OS) for BTO derivatives, as obtained by various methods

Compound	Calculation method	HOMO	LUMO	Band gap	<sup>a</sup> Shift in band gap	$\lambda_{\max}$ (OS)
2TO	AM1	−9.29	−1.45	7.84	-	-
	PM3	−9.51	−1.43	8.08	-	-
	B3LYP/6-31G*	−6.12	−2.67	3.45	-	360.95 (0.26)
BTO-B	AM1	−9.49	−2.34	7.15	−0.69	-
	PM3	−9.60	−2.64	6.96	−1.12	-
	B3LYP/6-31G*	−6.55	−3.39	3.16	−0.29	536.21 (0.05)
BTO-Si	AM1	−9.26	−1.71	7.55	−0.23	-
	PM3	−9.26	−1.60	7.66	−0.42	-
	B3LYP/6-31G*	−6.24	−3.00	3.24	−1.12	411.97 (0.20)
BTO-S	AM1	−9.21	−1.48	7.73	−0.11	-
	PM3	−9.36	−1.89	7.47	−0.62	-
	B3LYP/6-31G*	−6.36	−2.55	3.81	+0.36	341.79 (0.23)
BTO-SO	AM1	−9.62	−2.20	7.42	−0.42	-
	PM3	−9.66	−2.35	7.31	−0.77	-
	B3LYP/6-31G*	−6.66	−3.39	3.27	−0.18	478.60 (0.04)
BTO-O	AM1	−9.25	−1.42	7.83	−0.01	-
	PM3	−9.49	−1.58	7.91	−0.17	-
	B3LYP/6-31G*	−6.34	−2.40	3.94	+0.48	328.53(0.30)

<sup>a</sup> The shift in the band gap (eV) was the difference between the band gaps of the bridged BTO-X and 2TO

in BTO-Si, 1510  $\text{cm}^{-1}$  in BTO-SO, 1516  $\text{cm}^{-1}$  in BTO-O, 1485  $\text{cm}^{-1}$  in BTO-S, and 1521  $\text{cm}^{-1}$  in 2TO. The terminal C=C stretching modes for the rings in the dithiophene derivatives and the Raman-active  $(\text{C}=\text{C})_{\text{stretch}}$  mode in the oligoene were used to establish a structure–property relationship for the compounds [39, 40]. In this work, an attempt was made to correlate the terminal C=C stretching modes (i.e., the stretching modes of  $\text{C}_1\text{--C}_2$  and  $\text{C}_6\text{--C}_7$ ) in

the IR spectra as calculated with DFT for the modeled molecules. It was found that the terminal C=C stretching modes of BTO-B, BTO-SO, and BTO-Si were correlated with the  $\text{C}_4\text{--C}_5$  bond length and  $\lambda_{\max}$  in the UV-visible absorption spectrum. The higher the terminal stretch mode, the greater the value of  $\lambda_{\max}$ , and the shorter the  $\text{C}_4\text{--C}_5$  bond length; i.e., 1486  $\text{cm}^{-1}$  (BTO-B)  $\rightarrow$  1575  $\text{cm}^{-1}$  (BTO-SO)  $\rightarrow$  1577  $\text{cm}^{-1}$  (BTO-Si), and 1.386 Å (BTO-B,  $\lambda_{\max}=536.21$ )  $\rightarrow$  1.431 Å (BTO-SO,  $\lambda_{\max}=478.60$ )  $\rightarrow$  1.445 Å (BTO-Si,  $\lambda_{\max}=411.92$ ).

**Fig. 2** Partial molecular orbital energy diagram for bridged BTO-X compounds and 2TO, as calculated with the B3LYP/6-31 G\* method

### Thermodynamic properties

The standard thermodynamic properties at 298 K calculated with all of the methods used in this work are listed in Table 4. These data were used to determine the thermodynamics of the insertion of X to bridge 2TO. It was observed that the Gibbs free energy values obtained from PM3 were in good agreement with those from DFT calculations [39], except in the cases of BTO-B and BTO-Si, which could be due to poor parameterization of boron and silicon in the PM3 method [41]. For instance, the values of  $G^\circ$  calculated with PM3 (DFT) for 2TO, BTO-S, BTO-SO, and BTO-O were 217.48 (218.64), 167.82 (166.45), 170.94 (167.70), and 178.85 (175.74), respectively. The calculated values of  $\Delta H^\circ$  showed that the insertion of X into 2TO was always an exothermic process (except for the insertion of  $\text{BH}_2$ ) and



**Table 3** Vibrational frequencies ( $\text{cm}^{-1}$ ) for C–C double bonds calculated with the DFT/B3LYP/6-31G\* method<sup>a</sup> Terminal C=C stretching modes

BTO-B	BTO-Si	BTO-SO	BTO-O	BTO-S	2TO	Assignment
1320	1450	1510	1414	1471	1521	(C=C) <sub>stretch</sub>
1486 <sup>a</sup>	1479	1575 <sup>a</sup>	1516	1485	1618 <sup>a</sup>	
	1577 <sup>a</sup>		1592 <sup>a</sup>	1587 <sup>a</sup>		

was feasible based on the results of  $\Delta G^\circ$ , so these insertion reactions were thermodynamically favorable. The  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  values calculated using both the semi-empirical and DFT methods were quite similar. The heats of formation calculated with PM3 for 2TO, BTO-B, BTO-Si, BTO-S, and BTO-SO were higher than that of AM1, which could be due to the overestimation of the bond dissociation energy (BDE) by the AM1 method, since the BDE represents the difference between the enthalpies of the molecules (Table 3).

## Conclusions

The geometric and electronic structures, UV-visible absorption bands, and changes in the thermodynamic parameters (standard enthalpy, standard entropy, and standard Gibb's free energy) of bridged dithiophene *S*-

oxide (BTO-X) derivatives were investigated through quantum chemistry calculations using semi-empirical (AM1 and PM3) and B3LYP/6-31 G\* methods. The mean differences between the bond lengths calculated by PM3 and DFT were 0.014, 0.032, and 0.018 Å for BTO-S, BTO-SO, and BTO-O, respectively, and 0.015 Å for both BTO-B and BTO-Si. However, the insertion of the bridge X has a profound effect on the geometries of the bridged dithiophene *S*-oxide derivatives as compared to that of 2TO. The values of the thermodynamic parameters calculated by PM3 and DFT were in good agreement, except in the cases of BTO-B and BTO-Si, due to the poor parameterization of boron and silicon in the PM3 method. The wavelength of most intense UV-visible absorption  $\lambda_{\text{max}}$  was shifted to longer wavelengths in BTO-B, BTO-Si, and BTO-SO and to shorter wavelengths in BTO-S and BTO-O compared to that of the BTO-CH<sub>2</sub> analog.

**Table 4** Standard enthalpies ( $H^\circ$ ), standard entropies ( $S^\circ$ ), standard Gibb's free energies ( $G^\circ$ ), and heats of formation ( $H_f$ ) of the compounds calculated using various methods at 298 K

Compound	Calc. method	$H^\circ$ (kJ/mol)	$S^\circ$ (J/mol)	$G^\circ$ (kJ/mol)	$H_f$ (kJ/mol)	$^*\Delta H^\circ$ (kJ/mol)	$^*\Delta S^\circ$ (kJ/mol)	$^*\Delta G^\circ$ (kJ/mol)
2TO	AM1	355.94	419.73	230.80	119.07	-	-	-
	PM3	345.66	429.92	217.48	144.58	-	-	-
	B3LYP/6-31G*	346.63	429.26	218.64	-	-	-	-
BTO-B	AM1	363.96	429.91	225.78	343.50	+8.02	+10.91	-5.80
	PM3	342.83	439.76	211.72	346.38	-2.82	+9.84	-5.76
	B3LYP/6-31G*	346.74	444.52	214.43	-	+0.11	+15.26	-4.21
BTO-Si	AM1	347.84	441.36	216.25	128.10	-8.10	+21.63	-14.55
	PM3	336.15	448.89	202.31	169.38	-9.51	+18.91	-15.17
	B3LYP/6-31G*	340.35	452.86	205.33	-	-6.28	+23.60	-13.31
BTO-S	AM1	305.66	422.00	179.84	130.50	-50.28	+2.27	-50.96
	PM3	296.96	433.13	167.82	186.53	-48.70	+3.21	-49.66
	B3LYP/6-31G*	296.13	434.98	166.45	-	-50.70	+5.71	-52.19
BTO-S = O	AM1	316.74	448.13	186.55	84.05	-39.20	+28.40	-44.25
	PM3	307.46	457.90	170.94	125.77	-38.20	+27.98	-46.54
	B3LYP/6-31G*	307.40	468.55	167.70	-	-39.23	+39.29	-50.94
BTO-O	AM1	313.16	414.47	189.58	106.20	-42.78	-5.26	-41.22
	PM3	304.61	421.81	178.85	82.08	-42.05	-8.11	-38.63
	B3LYP/6-31G*	302.87	427.09	175.54	-	-43.76	-2.17	-43.10

<sup>\*</sup> $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  are the differences in the values of  $H^\circ$ ,  $S^\circ$ , and  $G^\circ$  for BTO-X and 2TO, respectively



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