

THEORETICAL STUDY ON STRUCTURE AND ELECTRONIC PROPERTIES OF 4H-CYCLOPENTA[2,1-B,3;4-B']DITHIOPENE S-OXIDE AND ITS CCL₂ AND CF₂ BRIDGED DERIVATIVES

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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']dithiophene 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']dithiophene (Bouzzine, 2005). The absorption λ_{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, theoretical methods

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 0.5–3.5eV 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 (Amazonas *et al.*, 2006). 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 (Gill, 1994 and Geiger, 1993). 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) (Geiger, 1993). Moreover, the oligothiophenes provide interesting models for understanding the structural and electronic peculiarities which control the charge transport and optical properties in polythiophenes (Bauerle, 1998; Cornil *et al.*, 1998; Hasnaoui *et al.*, 2007).

However, monitoring the decrease in band gap as a way of controlling the electric properties of polythiophenes is strongly governed by the intramolecular delocalization of π -electrons along the conjugation chain (Bredas, 1985). 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 (Ferraris & Lambert, 1991; Gunataunga *et al.*, 1997; de Oliveira *et al.*, 2000; de Oliveira *et al.*, 2002; Odunola & Semire, 2008; Bundgaard & Krebs, 2006; Van Duren *et al.*, 2001; Yoshino *et al.*, 2008; Petersen *et al.*, 2007; Ashraf & Klemm, 2005).

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 (Ashraf, 2005; Bouzzine, 2005; Bouzzine, 2009; Aouchiche, 2004). In one of our recent works, semi-empirical methods (AM1 and PM3) 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']dithiophene S-oxide derivatives (BTO-X, with X = BH₂, SiH₂, 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 λ_{\max} of the BTO-X (Semire *et al.*, 2012).

In this paper is reported the theoretical investigation on structure of 4H-Cyclopenta[2,1-b,3;4-b']dithiophene S-oxide (the methylene -CH₂- 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 Figure 1. Halogens have been found to increase the electrical conductivity of conjugated polymers when incorporated (Shirakawa *et al.*, 1977; Springborg, 2003; Bakhshi *et al.*, 1998; Inagi *et al.*, 2010), therefore attempt was also made to decrease the band gap by successive replacement of bridged methylene hydrogen with chlorine and fluorine atoms.

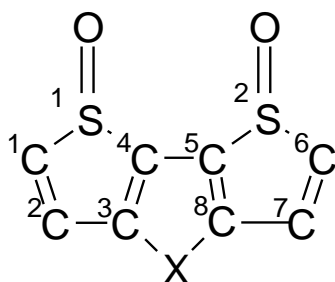


Figure 1. The structure and atomic numbering of 4H-Cyclopenta[2,1-b,3;4-b'] dithiophene S-oxide (BTO); X=CH₂ for BTO-CH₂, X= CHCl for BTO-CHCl, X=CCl₂ for BTO-CCl₂, X=CHF for BTO-CHF and X=CF₂ for BTO-CF₂.

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* (Hartree Fock and Density Functional Theory (Becke's Three Parameter Hybrid (Becke, 1993) Functional) using the Lee, Yang and Parr correlation Functional B3LYP (Lee *et al.*, 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 (Bouzzine *et al.*, 2005; Bouzzine *et al.*, 2009; Brasca *et al.*, 2007; Armelin *et al.*, 2009; De Olivera *et al.*, 2004; Amazonas *et al.*, 2006), all optimizations were without symmetry restrictions.

RESULTS 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-CH₂ 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 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-CH₂ at AM1, RM1, PM3, HF/6-31G(d) and DFT methods were 1.26°, 0.59°, 0.39°, 0.25° and 0.40° respectively as compared to that of MP2 method, this showed that bond angles calculated at PM3 and HF/6-31G(d) were more closer to that of MP2. For instance, the values of C₁S₁C₄ (C₁C₂C₃) 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 as compared 89.38° (111.74°) at MP2/6-31G(d).

Dihedral angles calculated for BTO-CH₂ using various methods showed that there was little distortion of the molecule from planarity. For instance, the dihedral angles C₁S₁C₄C₅ (C₁C₂C₃C₄) 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-CCl₂, BTO-CHF and BTO-CF₂, there was little or no difference in bond lengths as compared to BTO-CH₂. However, there were little differences in dihedral angles between symmetrical BTOs (i.e. BTO-CCl₂, BTO-CH₂ and BTO-CF₂) 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 CCl₂ were more stable than their fluorine analogues, therefore the order of stability was BTO-CCl₂ > BTO-CHCl > BTO-CF₂ > BTO-CHF > BTO-CH₂.

TABLE 1

Calculated Geometries of 4H-Cyclopenta[2,1-b,3;4-b']Dithiopene S-Oxide (BTO-CH₂) 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 ₁ S ₁ C ₄ (C ₅ S ₂ C ₆)	91.65	89.44	88.59	88.87	88.96	89.38
C ₁ C ₂ C ₃ (C ₆ C ₇ C ₈)	110.74	110.05	111.24	111.66	112.36	111.74
C ₂ C ₃ C ₄ (C ₇ C ₈ C ₅)	112.82	112.91	114.03	113.56	114.22	113.87
C ₃ C ₄ C ₅ (C ₇ C ₅ C ₄)	108.36	108.39	108.36	108.99	109.27	109.07
C ₁ S ₁ C ₄ C ₅	-179.54	-179.12	178.97	175.27	170.39	175.23
(C ₆ S ₂ C ₅ C ₄)	-8.41	-6.66	-6.92	-8.61	-12.13	12.88
C ₂ C ₁ S ₁ C ₄	179.69	179.88	178.55	-178.67	-176.50	176.76
(C ₇ C ₆ S ₂ C ₅)	179.56	179.29	-179.91	-177.44	-174.32	178.76
C ₁ C ₂ C ₃ X	0.01	0.08	-0.18	0.64	0.41	-1.76
(C ₆ C ₇ C ₈ X)	0.08	0.22	-0.12	-0.72	-1.32	0.21
C ₂ C ₃ C ₄ C ₅						
(C ₇ C ₈ C ₅ C ₄)						
C ₁ C ₂ C ₃ C ₄						
(C ₆ C ₇ C ₈ C ₅)						
C ₄ C ₃ XC ₈						
(C ₃ C ₈ XC ₃)						

Electronic properties

The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and band gap energy calculated by all theoretical methods employed were shown 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 Figures 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-CH₂). 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) (Kim *et al.*, 1998).

The band gap energy of BTO containing chlorine atom was less than that of fluorine analogues which could be attributed to the ability of chlorine atom, due to its larger atomic size to act as electrons donor as 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']dithiophene with CH₂ and SiH₂ bridged but lower than that of unsubstituted dithiophene and trithiophene (Bouzzine, 2005). The order of decrease in energy band gap was BTO-CCl₂ < BTO-CF₂ < BTO-CHCl < BTO-CHF < BTO-CH₂.

TABLE 2

Calculated Geometries of BTO-CHCl, BTO-CCl₂, BTO-CHF and BTO-CF₂ 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) 1.784	1.801 1.785	1.802 (1.799) 1.782	1.798 1.781
C ₄ -S ₁ (C ₅ -S ₂)	1.796 (1.797) 1.774	1.797 1.772	1.795 (1.798) 1.773	1.795 1.769
C ₁ -C ₂ (C ₆ -C ₇)	1.353 (1.355) 1.362	1.354 1.362	1.354 (1.356) 1.363	1.356 1.362
C ₂ -C ₃ (C ₇ -C ₈)	1.444 (1.442) 1.438	1.441 1.436	1.444 (1.441) 1.437	1.440 1.435
C ₃ -C ₄ (C ₅ -C ₈)	1.368 (1.367) 1.377	1.366 1.374	1.367 1.376	1.364 1.373
C ₄ -C ₅	1.445 1.443	1.448 1.447	1.448 1.448	1.445 1.457
C ₃ -X (C ₈ -X)	1.513 (1.515) 1.507	1.518 1.508	1.520 (1.522) 1.512	1.527 1.517
C ₁ S ₁ C ₄ (C ₅ S ₂ C ₆)	89.10 (89.15) 89.51	89.23 89.56	89.15 (89.25) 89.64	89.39 89.80
C ₁ C ₂ C ₃ (C ₆ C ₇ C ₈)	111.91 (111.93) 111.29	111.56 110.88	112.05 (111.99) 111.35	111.70 110.97
C ₂ C ₃ C ₄ (C ₇ C ₈ C ₅)	114.88 (114.95) 114.57	115.50 115.18	114.78 (114.98) 114.56	115.41 115.12
C ₃ C ₄ C ₅ (C ₇ C ₅ C ₄)	109.38 (109.37) 109.51	109.48 109.20	109.59 (109.22) 109.20	109.65 109.43
C ₁ S ₁ C ₄ C ₅ (C ₆ S ₂ C ₅ C ₄)	170.02 (168.42) -173.68	168.39 174.27	170.91 (166.48) -171.80	167.26 173.17
C ₂ C ₁ S ₁ C ₄ (C ₇ C ₆ S ₂ C ₅)	-13.03 (-12.68) 13.23	-31.11 -13.82	-13.14 (-12.48) 13.21	-13.24 -14.11
C ₁ C ₂ C ₃ X (C ₆ C ₇ C ₈ X)	-173.37 (-178.21) 178.78	-175.23 -175.19	-172.39 (- 178.42) 178.66	-174.49 -174.45
C ₂ C ₃ C ₄ C ₅ (C ₇ C ₈ C ₅ C ₄)	-174.39 (-173.17) 178.03	-173.33 -178.49	-174.69 (- 176.71	-172.15 -177.51
C ₁ C ₂ C ₃ C ₄ (C ₆ C ₇ C ₈ C ₅)	0.75 (0.78) -2.21	0.93 2.00	171.80) 176.71	0.63 1.89
C ₄ C ₃ XC ₈ (C ₃ C ₈ XC ₃)	2.20 (-5.06) 4.07	-1.46 0.89	0.32 (0.96) -2.39	-1.62 0.33
			4.34 (-7.38) 6.11	

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

TABLE 3

Calculated HOMO(eV), LUMO(eV), Energy Band Gap (eV), λ_{\max} (nm) and Oscillator Strength (OS) BTOs by Various Methods

Compound	Calculation method	HOMO	LUMO	Energy band gap	Shift in energy band gap	λ_{\max} (OS)
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	-	369.68 (0.28)
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	405.80 (0.19)
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	426.91 (0.12)
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	396.94 (0.23)
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	414.27 (0.23)

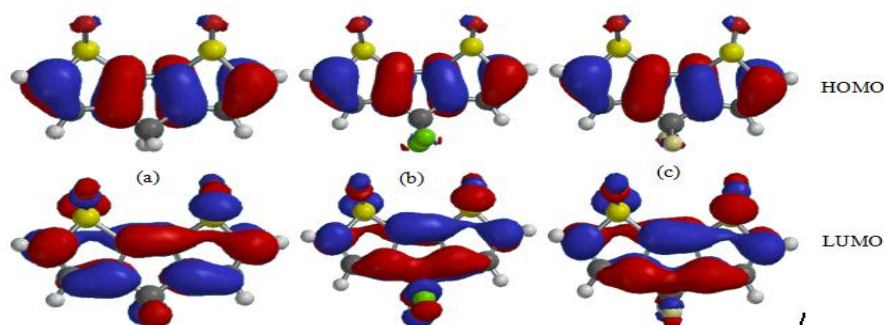


Figure 2. Frontier molecular orbital: (a) BTO-CH₂, (b) BTO-CCl₂ and (c) BTO-CF₂.

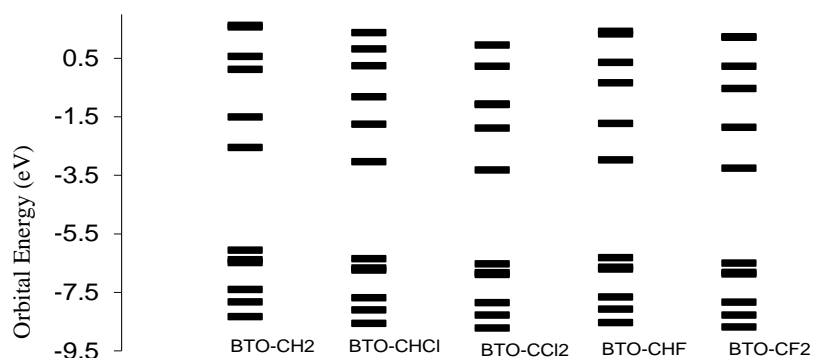


Figure 3. Partial molecular orbital energy diagram for BTO-X calculated by B3LYP/6-31G(d) method.

The electronic spectra involving transition of valence electrons that occur in the UV-visible absorption was calculated at TD-B3LYP/6-31G* level in order to investigate the effect of bridged BTO derivatives (Table 3). It was found that λ_{\max} shifted to a longer wavelength with increase in the number of halogen atoms, due to enhancement of π -conjugated system. For example, the calculated λ_{\max} for BTO-CCl₂ and BTO-CF₂ were 426.91nm and 414.27nm respectively as compared to 361.68nm for BTO-CH₂. However, the calculated λ_{\max} for BTO-CH₂ was higher than the experimental by 49nm (Coppo & Turner, 2005). The chlorine derivatives of methylene bridged BTO have lower band gaps than the corresponding fluorine analogues, hence longer wavelengths.

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, tautomers and isomers (Silverstein *et al.*, 1981). 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 4 for the BTOs. The prominent terminal C=C stretching bands (*i.e.* C₁ = C₂/C₆ = C₇) were 1596 and 1591 cm⁻¹ for BTO-CH₂, 1594 and 1593 cm⁻¹ for BTO-CCl₂ and 1600 and 1598 cm⁻¹ for BTO-CF₂. 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 (Semire *et al.*, 2012; Oliva *et al.*, 2009; Liu & Yu, 2005). In this work, the terminal C=C stretching modes were not correlated with the λ_{\max} in the UV-visible absorption spectrum, however there was correlation between C₃=C₄/C₅=C₈ vibrational frequencies and λ_{\max} . The higher the stretch mode, the

greater the value of λ_{\max} ; i.e. 1509 cm^{-1} (BTO- CCl_2 , $\lambda_{\max} = 426.91 \text{ nm}$) 1506 cm^{-1} (BTO- CF_2 , $\lambda_{\max} = 414.27 \text{ nm}$) 1504 cm^{-1} (BTO- CCl_2 , $\lambda_{\max} = 369.68 \text{ nm}$).

TABLE 4

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	$\nu\text{C}_1 = \text{C}_2/\text{C}_6 = \text{C}_{7*}$
1504, 1471	1509, 1477	1506, 1476	$\nu\text{C}_3 = \text{C}_4/\text{C}_5 = \text{C}_8$
1350	1321	1309	$\nu\text{C}_4 - \text{C}_5$
1080, 1085	1092, 1088	1089, 1089	$\nu\text{S}=\text{O}$
3076, 3043	1009	1270, 1190	$\nu\text{C}-\text{X}_2$

*Terminal C=C stretching modes

TABLE 5

Standard Enthalpy (H_m°), Standard Entropy (S_m°), Standard Gibb's Free Energy (G_m°) and Heat of Formation (H_f°) Calculated by Various Methods at 298K

Compound	Calculation method	H_m° (kJ/mol)	S_m° (J/mol)	G_m° (kJ/mol)	H_f° (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	-

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 (Casado *et al.*, 2004; Casado *et al.*, 2005; Semire *et al.*, 2012). The C_4-C_5 stretching bands were 1350, 1321 and 1309 cm^{-1} for BTO-CH₂, BTO-CCl₂ and BTO-CF₂ respectively. The stretching vibrations of S=O groups were 1085 and 1080 cm^{-1} in BTO-CH₂ and 1092 and 1088 cm^{-1} in BTO-CCl₂ and 1089 and 1087 in BTO-CF₂.

Thermodynamic properties

The calculated standard thermodynamic properties at 298 K and 1 were listed in Table 5; these were used to determine the thermodynamic of successive halogen substitution of methylene hydrogen in BTO-CH₂. It was observed that the thermodynamic properties calculated at PM3 were in good agreement with that of DFT calculation (Liu & Yu, 2005). The values of thermodynamic quantities calculated for BTO-CH₂ 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 band, thermodynamic parameters of standard enthalpy, standard entropy and standard Gibb's free energy of bridged bithiophene-S-oxide derivatives have been 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. In the study, one found out that:

- Bridged BTO derivatives with CH₂, CCl₂ and CF₂ were more planar than those CHCl and CHF. The mean deviation of bond lengths at PM3 and DFT were very small about 0.009Å, but they were 0.016 and 0.014Å respectively if compared to PM2 method.
- There was a decrease in the thermodynamic parameters upon successive halogen substitution of methylene hydrogen of BTO-CH₂.
- The UV-visible absorption λ_{max} was shifted to longer wavelength with increasing in number of halogen atoms due to enhancement of π -conjugated system with BTO-CCl₂ having the longest wavelength.

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