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STRUCTURAL AND ELECTRONIC PROPERTIES OF BRIDGED BITHIOPHENE S-OXIDES (BTO) WITH S, S=O, O, SiH_2 and BH_2 BRIDGE: SEMI-EMPIRICAL AND AB INITIO STUDY.

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ABSTRACT

In this paper, we theoretically studied the geometries, stabilities, electronic and thermodynamic properties of bridged bithiophene S-oxide (BTO-X) derivatives (with X= BH_2, SiH_2, S, S=O and O) by using semi-empirical methods, ab initio and Density functional theory. The geometries and thermodynamic parameters calculated by PM3 were in good agreement with that of B3LYP/6-31G(d). The band gap calculated by B3LYP/6-31G(d) ranged from 3.94eV (BTO-O) – 3.16eV (BTO-BH_2). The absorption λ_{max} calculated using B3LYP/6-31G(d) shifted to longer wavelength with X= BH_2, SiH_2 and S=O due to enhancement of π-conjugated system whereas, BTO-S and BTO-O shifted to shorter wave lengths as compared to dimmer thiophene S-oxide (2TO).

***Keywords*:** Density functional theory (DFT), Semi-empirical (PM3), Bridged bithiophene S-oxides.

RESUMO

Este trabalho apresenta os resultados obtidos por nossos estudos teóricos das geometrias, estabilidades e propriedades eletrônicas e termodinâmicas de S-óxidos de derivados de bitiofenos (BTO-X) com pontes, (X=BH_2,,SiH_2 ,S=O e O) usando métodos semi-empíricos, ab-initio e teoria funcional de densidade. Os parâmetros geométricos e termodinâmicos calculados por PM3 concordaram bem com aqueles de B3LYP/6-31G(d). O intervalo de banda calculado com B3LYP/6-31G(d) variou entre 3.94eV (BTO-O) e 3.16eV (BTO-BH_2). A banda máxima de absorção calculada com o mesmo método deslocou-se para comprimentos de onda maiores com X=BH_2, SiH_2 e S=O devido ao sistema de elétrons pi conjugados. No caso de BTO-S e BTO-O o deslocamento foi para comprimentos de onda menores em comparação a tiofeno S-óxido.

Palavras Chave: Teoria DFT,Método semi-empirico PM3 , S-óxidos de bitiofeno

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1. INTRODUCTION

Since their discovery, conjugated polymers have attracted considerable interest during recent years because of their promising electronic applications such as in batteries [1,2], electroluminescent devices [3], field-effect transistors [4] and photovoltaics [5]. Oligothiophenes are perhaps the most thoroughly investigated and well-characterized systems [7-9]. 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 [10–12]. However, monitoring the decrease in band gap as a way controlling of the electric properties of polythiophenes are strongly governed by the intramolecular delocalization of π-electrons along the conjugation chain [6]. Thiophene related molecules such as thiophene 1,1-dioxide and thiophene S-oxide have been investigated [13], this includes the synthesis, reactivity as dienes in Diels-Alder reactions [14], photochemical and electrochemical behavior [15]. The orbital energies and electrochemical properties of monomer of thiophene S-oxides have been theoretically studied using PM2/6-31G* [16].

In regard to reduce energy band gaps, the geometric and electronic structures of some bridged octamer of oligothiophenes have been theoretically studied with bridging containing electron-accepting groups are C=O, C=S and $C=C(CN)_2$ [17-19]. In this paper, we will theoretically investigate the structure, electronic and thermodynamic properties of bridged bithiophene S-oxide (BTO-X) with bridge X = S, S=O, O, SiH_2 and BH_2. The results will be compared to un-bridged thiophene S-oxide dimmer (2TO).

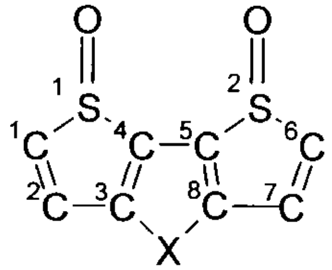

Fig.1 The structure and atomic numbering of bithiophene S-oxide (BTO); X=S, for BTO-S, X= S=O for BTO-SO, X=O for BTO-O, X=SiH_2 for BTO-Si and X=BH_2 for BTO-B.

2. COMPUTATIONAL METHODS

All calculations to study the un-bridged and bridged bithiophene-S-oxide (BTO) derivatives were performed by Spartan 06 program [20] implemented on an Intel Pentium M 1.7GHz Computer. The geometries of 2TO and bridged bithiophene S-oxide (BTO) derivatives have been full optimized at Semi-empirical methods (AM1 and PM3), ab initio (Hatree Fock and Density Functional Theory (Beckes's Three Parameter Hybrid [21] Functional) using the Lee, Yang and Parr correlation Functional B3LYP [22]). The basis set 6-31G(d) was used for all atoms in ab initio methods. We have also examined HOMO and LUMO levels; the energy gap is evaluated as the difference between the HOMO and LUMO energies. All optimizations were without symmetry restrictions.

3. RESULTS AND DISCUSSION

3.1 Geometries and Stabilities

The optimization of the geometrical structures of the bithiophene S-oxide derivatives was carried out with both semi-empirical and DFT quantum mechanical methods. Generally, the bond lengths calculated by B3LYP/6-31G(d) are slightly different from those calculated by PM3. For instance, the value of C_4-C_5 calculated by PM3 and DFT are 1.445 and 1.422Å for BTO-B, 1.442 and 1.445Å for BTO-Si, 1.411 and 1.408Å for BTO-S, 1.435 and 1.431Å for BTO-SO, 1.418 and 1.419Å for BTO-O and 1.440 and 1.433 for 2TO respectively. The overall mean deviations of bond lengths calculated by PM3 as compared DFT are 0.014, 0.032 and 0.018Å for BTO-S, BTO-SO and BTO-O respectively, but both BTO-B and BTO-Si is deviated by 0.015Å. However, the bridge X has profound effect on the geometries on the bridged bithiophene S-oxide derivatives as compared to 2TO (Table 1). The mean deviation with respect to bond angles in bridged BTO derivatives calculated by PM3 are 1.00°, 1.18°, 1.27°, 1.02° and 0.57° for BTO-B, BTO-Si, BTO-S, BTO-SO and BTO-O respectively. The largest difference in bond angles between PM3 and B3LYP/6-31G(d) is in $C_1C_2C_3$ ($C_6C_7C_8$) for BTO-B, BTO-S, BTO-SO and BTO-O and $C_3C_4C_5$ ($C_7C_5C_4$) for BTO-Si and 2TO.

Generally, the dihedral angles of bridged BTO-X derivatives with X= BH_2, SiH_2, S, S=O and O bridge show distortion from planarity, although insertion of X to 2TO increase the planarity. There are differences in dihedral angles calculated by both theoretical methods. For instance, the dihedral angles $C_1S_1C_4C_5$ ($C_2C_3C_4C_5$) calculated by PM3 are -178.29° (178.37°), -178.52° (179.82°), -178.53° (179.48°), 178.64° (-179.06°), 178.37° (179.88°) and -175.04° (176.69°) for BTO-B, BTO-Si, BTO-S, BTO-SO, BTO-O and 2TO respectively, while those calculated by B3LYP/6-31G(d) for the same dihedral angles are -177.68° (177.57°), 177.86° (-177.20°), 175.40° (-176.93°), 173.55° (-176.25°), 164.63° (-172.70°) and -175.15° (178.91°) for BTO-B, BTO-Si, BTO-S, BTO-SO and BTO-O respectively.

In the process of calculation of energies, both HF/6-31G(d) and B3LYP/6-31G(d) are employed. However, the energies calculated show that the predictive order of stability by HF/6-31G(d) and B3LYP/6-31G(d) are the same, although DFT predicted lower energies. For instance, the energies calculated by B3LYP/6-31G(d) method for BTO-SO, BTO-S, BTO-Si, BTO-O and BTO-B are -1727.23au, -1652.09au, -1544.59au, -1329.10au and -1279.91au respectively as compared to -1255.10au for 2TO.

Table 1. Calculated geometries of bridged BTO-X derivatives with BH_2, SiH_2, S, S=O and O by means of PM3 and B3LYP/6-31G(d) methods: Bond lengths are in Å, bond angles and Dihedral angles in degree.

	2TO		BTO-B		BTO-Si		BTO-S		BTO-SO		BTO-O	
	PM3	B3LYP/6-31G(d)	PM3	B3LYP/6-31G(d)	PM3	B3LYP/6-31G(d)	PM3	B3LYP/6-31G(d)	PM3	B3LYP/6-31G(d)	PM3	B3LYP/6-31G(d)
C_1-S_1 (C_6-S_2)	1.783	1.784	1.803	1.816	1.788	1.794	1.795	1.814	1.788	1.801	1.813	1.822
C_4-S_1 (C_5-S_2)	1.812	1.826	1.793	1.808	1.796	1.805	1.787	1.812	1.789	1.811	1.774	1.807
C_1-C_2 (C_6-C_7)	1.346	1.352	1.369	1.364	1.350	1.353	1.348	1.349	1.351	1.354	1.351	1.350
C_2-C_3 (C_7-C_8)	1.461	1.449	1.431	1.435	1.446	1.452	1.452	1.450	1.448	1.442	1.448	1.440
C_3-C_4 (C_5-C_8)	1.355	1.363	1.374	1.386	1.371	1.372	1.398	1.382	1.378	1.365	1.401	1.337
C_4-C_5	1.440	1.433	1.445	1.422	1.442	1.445	1.411	1.408	1.435	1.431	1.418	1.419
C_3-X (C_8-X)	-	-	1.574	1.607	1.835	1.888	1.717	1.747	1.787	1.822	1.374	1.366
$C_1S_1C_4$ ($C_5S_2C_6$)	89.17	90.18	88.29	86.85	88.89	89.15	88.87	88.67	88.79	89.06	88.76	88.72
$C_1C_2C_3$ ($C_6C_7C_8$)	113.28	114.04	113.11	114.21	112.59	113.76	111.88	111.83	111.98	111.67	109.57	110.01
$C_2C_3C_4$ ($C_7C_8C_5$)	113.08	114.15	111.70	110.38	113.42	112.66	111.33	114.94	113.45	115.66	115.78	117.49
$C_3C_4C_5$ ($C_7C_5C_4$)	124.64	128.99	110.49	111.49	115.45	117.52	111.44	112.66	112.40	113.68	105.42	105.51
$C_1S_1C_4C_5$ ($C_6S_2C_5C_4$)	-175.04	-175.15	-178.29	-177.68	-179.52	177.86	-179.53	175.40	178.63	173.55	178.37	164.63
$C_2C_1S_1C_4$ ($C_7C_6S_2C_5$)	-7.25	-13.12	-7.07	-9.89	-6.77	-11.81	-6.34	-10.31	-7.03	-11.24	-6.68	-11.59
$C_1C_2C_3X$ ($C_6C_7C_8X$)	-	-	178.60	176.78	178.53	179.75	178.81	-178.75	172.83	171.02	179.83	-174.82
$C_2C_3C_4C_5$ ($C_7C_8C_5C_4$)	176.69	178.91	178.37	177.57	179.82	-177.20	179.48	-176.93	-179.06	-176.25	179.88	-172.70
$C_1C_2C_3C_4$ ($C_6C_7C_8C_5$)	0.07	0.22	-0.12	0.78	0-03	0.22	-0.23	0.01	-0.13	1.95	-0.29	0.47
$C_4C_3XC_8$ ($C_3C_8XC_3$)	-	-	0.26	0.04	-0.37	-0.89	-0.09	-0.76	-8.09	-12.06	0.03	-1.39

3.2. Opto-Electronic Properties

The HOMO, LUMO and energy band gaps (ΔE_g) calculated by semi-empirical (AM1 and PM3) and ab initio (HF/6-31G(d) and B3LYP/6-31G(d)) methods are displaced in Tables 2.. To further understand the properties of bridged BTO derivatives, some frontier molecular orbitals levels obtained from B3LYP/6-31G(d) are shown in Figure. 2. In BTO-B structure, the HOMO-1 and HOMO-3, and LUMO+2 and LUMO+3 are doubly degenerate respectively. In the case of BTO-S, HOMO and HOMO-3 are doubly degenerates, whereas in BTO-SO, HOMO-1 and HOMO-3 are doubly degenerate. However, in BTO-O and BTO-Si electronic orbitals levels are HOMO-1 degenerate; HOMO-1, LUMO+2 and LUMO+3 are degenerate in 2TO (Figure 2).

There is a systematic change of the HOMO and LUMO energies as X (X= BH_2, SiH_2, S, S=O and O) are introduced to bridge thiophene S-oxide dimmer. The ΔE_g of bridged BTO derivatives containing X (X =S and O) are less than that of 2TO, hence there is a more localization of π-electrons in BTO-S and BTO-O. However, BTO-BH_2, BTO-Si and BTO-SO are lower in ΔE_g than 2TO. The ΔE_g calculated by B3LYP/6-31G(d) ranged from 3.94eV (BTO-O) – 3.16eV (BTO-BH_2) as compared to 3.45eV for 2TO. The order of decrease in ΔE_g is BTO-BH_2 < BTO-SO < BTO-Si < 2TO < BTO-S < BTO-O.

Table 2. Calculated HOMO(eV), LUMO(eV), Band gap (ΔE_g), λ_{max} (nm) and Oscillator strength (OS) BTO derivatives by various methods.

Compound	Calculation method	HOMO	LUMO	ΔE_g	*Shift in ΔE_g	λ_{max} (OS)
2TO	AM1	-9.29	-1.45	7.84	-	-
	PM3	-9.51	-.1.43	8.08	-	-
	HF/6-31G(d)	-9.05	1.30	10.35	-	-
	B3LYP/6-31G(d)	-6.12	-2.67	3.45	-	360.95 (0.26)
BH_2	AM1	-9.49	-2.34	7.15	-0.69	-
	PM3	-9.60	-2.64	6.96	-1.12	-
	HF/6-31G(d)	-9.62	0.32	9.94	-0.41	-
	B3LYP/6-31G(d)	-6.55	-3.39	3.16	-0.29	536.21 (0.05)
SiH_2	AM1	-9.26	-1.71	7.55	-0.23	-
	PM3	-9.26	-1.60	7.66	-0.42	-
	HF/6-31G(d)	-8.67	0.56	9.23	-1.12	-
	B3LYP/6-31G(d)	-6.24	-3.00	3.24	-0.21	411.97 (0.20)
S	AM1	-9.21	-1.48	7.73	-0.11	-
	PM3	-9.36	-1.89	7.47	-0.62	-
	HF/6-31G(d)	-8.78	1.06	9.84	-0.54	-
	B3LYP/6-31G(d)	-6.36	-2.55	3.81	+0.36	341.79 (0.23)
S=O	AM1	-9.62	-2.20	7.42	-0.42	-
	PM3	-9.66	-2.35	7.31	-0.77	-
	HF/6-31G(d)	-9.32	0.07	9.39	-0.96	-
	B3LYP/6-31G(d)	-6.66	-3.39	3.27	-0.18	478.60 (0.04)
O	AM1	-9.25	-1.42	7.83	-0.01	-
	PM3	-9.49	-1.58	7.91	-0.17	-
	HF/6-31G(d)	-8.71	1.38	10.09	-0.26	-
	B3LYP/6-31G(d)	-6.34	-2.40	3.94	+0.48	328.53 (0.30)

*The shift in band gap (eV) is the differences in the bridged BTO-X and 2TO

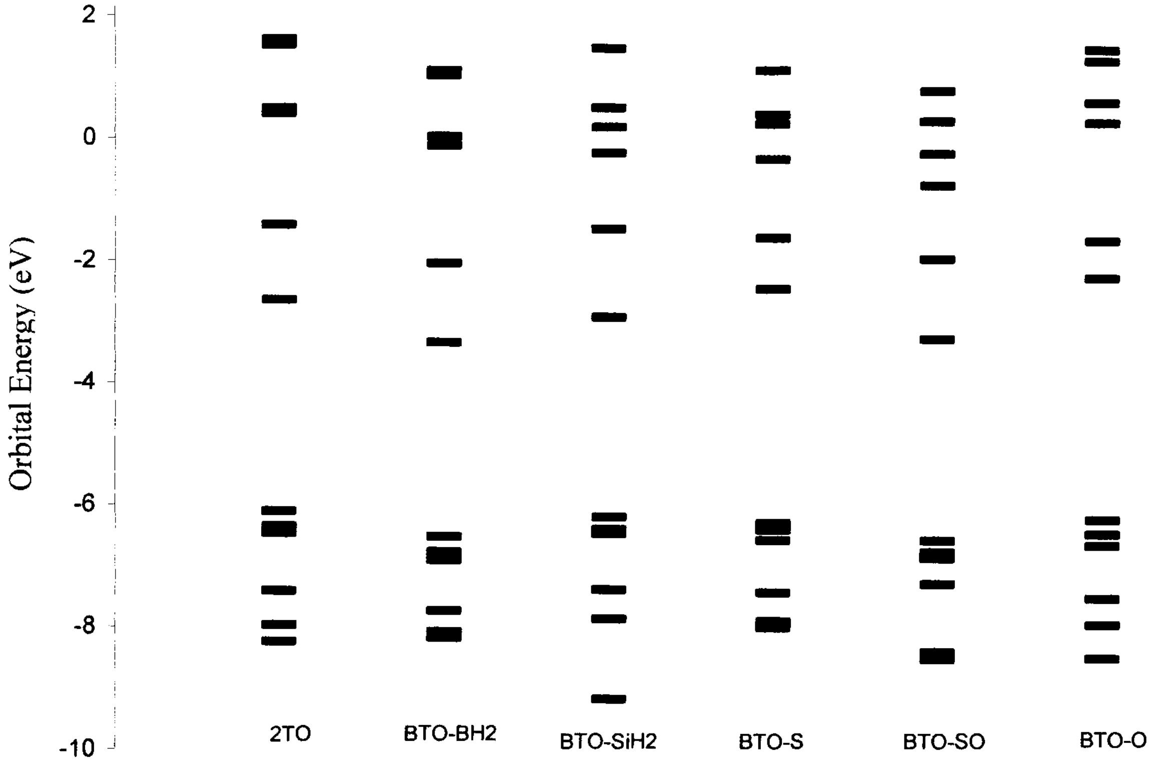

Fig. 2. Partial molecular orbital energy diagram for bridged BTO-X and 2TO calculated by B3LYP/6-31G(d) method.

The electronic spectra involving transition of valence electrons that occur in the UV-visible absorption was studied theoretically in order to investigate the effect of 2TO and the X bridged derivatives (X= BH_2, SiH_2, S, S=O and O) are shown in Table 2. It is found that with X= BH_2, SiH_2 and S=O, the λ_{max} shifted to a longer wavelength due to enhancement of π-conjugated system whereas, BTO-S and BTO-O shifted to shorter wave lengths as compared to BTO-CH_2 analogue. For example, the calculated λ_{max} for BTO-BH_2 and BTO-O are 536.21 and 328.53nm respectively as compared to 360.95nm for 2TO, there is in accordance with calculated Shift in band gaps by DFT method.

33. The Thermodynamic Properties

The standard thermodynamic properties at 298K calculated from all methods used are listed in Table 3 to determine the thermodynamic of insertion of X to bridged 2TO. It is observed that the results obtained from PM3 are in good agreement with that of DFT calculation [23] except in BTO-B and BTO-Si, this may be due to poor parameterization of boron and Silicon in PM3 method. For instances, the values of G° calculated by PM3

(DFT) for 2TO, BTO-S, BTO-SO and BTO-O are 217.48 (218.64), 167.82 (166.45), 170.90 (167.70) and 167.82 (175.74) respectively. The heat of formation for 2TO, BTO-B, BTO-Si, BTO-S and BTO-SO are higher than that of AM1 (Table 3).

Table 3. Standard enthalpy (H°), Standard entropy (S°) and Standard Gibb's free energy (G°) calculated by various methods at 298K.

Cdp	Calculation method	H° (kJ/mol)	S° (J/mol)	G° (kJ/mol)	H_f (kJ/mol)
2TO	AM1	355.94	419.73	230.80	119.07
	PM3	345.66	429.92	217.48	144.58
	HF/6-31G(d)	373.24	424.65	246.57	-
	B3LYP/6-31G(d)	346.63	429.26	218.64	-
BH_2	AM1	363.96	429.91	225.78	343.50
	PM3	342.83	439.76	211.72	346.38
	HF/6-31G(d)	366.81	423.89	240.43	-
	B3LYP/6-31G(d)	346.74	444.52	214.43	-
SiH_2	AM1	347.84	441.36	216.25	128.10
	PM3	336.15	448.89	202.31	169.38
	HF/6-31G(d)	365.56	431.28	236.97	-
	B3LYP/6-31G(d)	340.35	452.86	205.33	-
S	AM1	305.66	422.00	179.84	130.50
	PM3	296.96	433.13	167.82	186.53
	HF/6-31G(d)	318.92	417.68	194.39	-
	B3LYP/6-31G(d)	296.13	434.98	166.45	-
S=O	AM1	316.74	448.13	186.55	84.05
	PM3	307.46	457.90	170.94	125.77
	HF/6-31G(d)	331.81	448.32	198.14	-
	B3LYP/6-31G(d)	307.40	468.55	167.70	-
O	AM1	313.16	414.47	189.58	106.20
	PM3	304.61	421.81	178.85	82.08
	HF/6-31G(d)	326.57	405.90	205.55	-
	B3LYP/6-31G(d)	302.87	427.09	175.54	-

4. CONCLUSION

The geometrical and electronic structure, UV-visible absorption band, change in thermodynamic parameters of standard enthalpy, standard entropy and standard Gibb's free energy of bridged bithiophene S-oxide (BTO-X) derivatives have been investigated through quantum chemistry calculations using semi-empirical (AM1 and PM3), Hatree Fock (6-31G(d)) and B3LYP/6-31G(d) methods. The mean deviations of bond lengths calculated by PM3 as compared DFT are 0.014, 0.032 and 0.018Å for BTO-S, BTO-SO and BTO-O respectively, but both BTO-B and BTO-Si is deviated by 0.015Å. However, the bridge X has profound effect on the geometries on the bridged bithiophene S-oxide derivatives as compared 2TO. The values of thermodynamics parameters calculated by

PM3 and B3LYP/6-31G(d) are in good agreement except in BTO-B and BTO-Si due to poor parameterization of boron and silicon in PM3 method. The UV-visible absorption λ_{max} shifted to longer wavelength in BTO-B, BTO-Si and BTO-SO whereas in BTO-S and BTO-O the λ_{max} shifted to short wavelength.

5. REFERENCES

[1] (a) H.S. Nalwa, *Handbook of Organic Conductive Molecules and Polymer*, John Wiley, New York, 1997. (b) R. L. Elsenbaumer, T.Skotheim, and J. R. Reynolds *Handbook of Conductive Polymers*, Dekker, New York, 1998. (c) K. Mullen and G. Wegner, *Electronic Materials: The Oligomer Approach*,Wiley-VCH, Weinheim, 1997. (d) D. Fichou, *Handbook of Oligo- and Polythiophenes*, Wiley-VCH, Weinheim, 1999.

[2] V.C. Nguyen and K. Potje-Kamloth, *Thin Solid Films*. 1999, 338, p. 142-149.

[3] R.E. Gill, G.G. Malliaras, J. Wildeman and G. Hadziioannou, *Adv. Mater.* 1994, 6, p. 132-142,

[4] F. Garnier, G. Horowitz, X. Peng and D. Fichou, *Adv. Mater.* 1990, 2, p.562-572.

[5] G. Wang, S. Qian, J. Xu, W. Wang, X. Liu, X. Lu and F. Li, *Physica*, Part B. 2000, 279, p.116-123.

[6] J.L. Bredas, *J. Chem. Phys.* 1985, 82, p.3808-3812.

[7] J. Roncali, *Chem. Rev.* 1992, 92, p.711. (b) J. Roncali, *Chem. Rev.* 1997, 97, p. 173-178.

[9] J. A. E. H. van Haare, E. E. Havinga, J. L. J. van Dongen, R. A. J. Janssen, J. Cornil, and J. L. Bredas, *Chem. Eng. J.* 1998, 4, p.1509-1517.

[8] J. A. E H. van Haare, M. van Boxtel, and R. A. J. Janssen, *Chem. Mater.* 1998, 10, p.1166-1172.

[10] A . Dobadalapur, L. Torsi, and H. E. Katz, *Science*, 1995, 28, p.270-279.

[11] A. Dobadalapur, H. E. Katz, L. Torsi, and R. C. Haddon, *Science*, 1995, 269, p.1560-1568. (b) G. Horowitz, *Adv. Mater.* 1998, 10, p. 365-370. (c) D. Fichou, *J. Mater. Chem.* 2000, 10, p.571-578.

[12] T. Noda and Y. Shirota, *J. Am. Chem. Soc.* 1998, 120, p.9714-9721. (b) N. Noma, T. Tsuzuki, and Y. Shirota, *Adv. Mater.* 1995, 7, p.647-653.

[13] E. Lukevics, P. Arsenyan, S. Belyakov, O. Pudova, J. *Hetero. Compd.* 2002, 38, p.632-639.

[14] T. Thiemann, D.J. Walton, A. O. Brett, J. Iniesta, F. Marken, Y –Q. Li, "Thiophene *S*-oxides and related compounds". *Issue 5th Eurasian Conference on Heterocyclic Chemistry* ARKIVOC, 6, (2009), p.96-99.

[15] T. Thiemann, D. Ohira, K. Arima, T. Sawada, S. Mataka, F. Marken, R.G. Compton , S.D. Bull, S.G. Davies, *J. Phys. Org. Chem.*, 2000, 13(10), p.648-655.

[16] A. Bongini, G. Barbarella, M. Zambainchi, C. Arbizzani, M. Mastragostino, *Chem. Commun.* 2000, p.439-451.

[17] S.M. Bouzzine, S. Bouzakraoui, M.Bouachrine, M. Hamidi. *J. Mol. Struct.* [THEOCHEM], 2005, 726, p.271-275.

[18] S. M. Bouzzinea, M. Hamidia, M. Bouachrine, *Orbital*, 2009 1 (2), p. 203-208.

[19] H.A. Aouchiche, S. Djennane, A. Boucekkine, *Synth. Met.* 2004, 140, p.127-110

[20] Spartan 06, *Wavefunction*, Irvine, U.S.A, 2007.

[21] A.D. Becke, *J. Chem. Phys.* 1993, 98, 5p.648-5655.

[22] C.Lee, W.Yang, R.G. Parr, *Phys. Rev*.B. 1988, 37, p.785-791.

[23] G.Liu, J.Yu, *J. Mol. Struct.* [THEOCHEM], 2005, 717, p.15-22.

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