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Thiophene *S*-oxides: orbital energies and electrochemical properties

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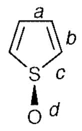
***Ab initio* calculations and experimental oxidation and reduction potentials show that the functionalization of thiophene to the corresponding *S*-oxide leads to only a minor change in ionization potential but to a dramatic increase in the electron affinity.**

Owing to their electrical and optical properties, α-conjugated oligo- and poly-thiophenes are currently the subject of intense research activity in the field of organic materials. There is great interest in finding functionalization capable of decreasing the energy of the LUMO orbital of these compounds. Indeed, easily reducible compounds are useful for application in a variety of electrochemical and electrooptical devices.[1]

Unsubstituted thiophene *S*-oxide has not yet been isolated; however, new oxidation methods have recently been developed that make it possible to obtain stable substituted thiophene *S*-oxides.[2] Thus, following our research line on thiophene *S,S*-dioxides,[3] we have commenced a study aimed at elucidating how the functionalization of the thienyl sulfur of thiophene-based materials to the corresponding *S*-oxide affects the orbital energies and the electrochemical properties of these compounds.

Here, we report *ab initio* theoretical calculations performed on the thiophene *S*-oxide and compare the results with related physical properties for 2,5- and 3,4-disubstituted counterparts. The results on thiophene and thiophene *S,S*-dioxide analogues are also reported for comparison.

MP2/6-31G* *ab initio* calculations[4] indicate a non-planar structure for thiophene *S*-oxide with the sulfur atom lying outside the plane formed by the other four atoms by 0.26 Å (Scheme 1).



	I	**II**
a	1.455	1.404
b	1.356	1.397
c	1.768	1.676
d	1.512	1.500
>*ab*	113.0	113.9
>*bc*	110.6	106.9
>*cc'*	90.7	98.3
>*cd*	116.3	130.8
>*bab'*	0.0	0.0
>*abc*	9.8	0.0
>*bcd*	-132.9	180.0

Scheme 1 Selected bond lengths (Å) and angles (°) of the MP2/6-31G* ground state (**I**) and transition state (**II**) structures of thiophene *S*-oxide.

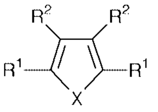
The results are in agreement with previous *ab initio* calculations at a lower level of theory[5] and with the X-ray structure reported for 2,5-diphenyl[2a] and 3,4-di-*tert*-butyl[2c] derivatives.

The non-planar geometry implies that thiophene *S*-oxide should be less aromatic than unmodified thiophene. Indeed, using this geometry, we calculated the aromaticity Bird index[6a] to be 37.4, which is much lower than that reported for thiophene (66)[6a] and similar to that of phosphole (35.5).[6b]

MP2/6-31G* calculations also show that inversion at the pyramidal sulfur proceeds through a fully planar transition state (Scheme 1) with a calculated energy barrier of 13.5 kcal mol^{-1}, in good agreement with the experimental value of 14.8 kcal mol^{-1} reported for 2,5-di-*tert*-octylthiophene *S*-oxide,[7] but much lower than the energy inversion barriers reported for sulfoxides (37–42 kcal mol^{-1}).[8] Clearly, in thiophene *S*-oxide the increased π-conjugation makes the planar transition state more aromatic than the ground state (the Bird index calculated for this planar geometry is 90.8) and furnishes extra stabilization that accounts for the lower value of the inversion barrier.

Table 1 reports the *ab initio* calculated frontier orbital energies of thiophene, thiophene *S*-oxide and thiophene *S,S*-dioxide (**1**–**3**) together with the oxidation and reduction potentials of the corresponding 2,5-disilylated derivatives (**4**–**6**) and of 3,4-di-*tert*-butylthiophene *S*-oxide **7**, measured by cyclic voltammetry (CV); UV maxima and optical edges for **4**–**7** are also reported.†

Table 1 MP2/6-31G* frontier orbital energies (E_{HOMO}, E_{LUMO}/eV) of thiophene **1**, thiophene *S*-oxide **2** and thiophene *S,S*-dioxide (**3**), along with oxidation and reduction potentials [I_p (A) I_p (C)/V *vs.* SCE], λ_{max} (CHCl$_3$/nm) and optical edge values (ΔE/eV) of the substituted derivatives **4**–**7**



1 X = S, $R^1 = R^2 = H$
2 X = SO, $R^1 = R^2 = H$
3 X = SO_2, $R^1 = R^2 = H$
4 X = S, $R^1 = SiMe_3$, $R^2 = H$
5 X = SO, $R^1 = SiMe_3$, $R^2 = H$
6 X = SO_2, $R^1 = SiMe_3$, $R^2 = H$
7 X = SO, $R^1 = H$, $R^2 = Bu^t$

	E_{HOMO}	E_{LUMO}	I_p (A)[a]	I_p (C)[b]	λ_{max}	ΔE_{edge}
1	−8.71	3.57				
2	−9.58	1.84				
3	−10.09	1.27				
4			1.98	< −2.60	248	4.43
5			2.02	−1.70	256 324	2.95
6			2.74	−1.46	230 314	3.39
7			2.06	−1.90	227 329	3.14

[a] CV in MeCN–NEt$_4$BF$_4$ 0.2 M at 100 mV s^{-1}. [b] CV in propylene carbonate–NEt$_4$BF$_4$ 0.2 M at 100 mV s^{-1}.

The calculations show that the frontier orbitals of **1**–**3** are all π in character. The LUMO orbital of thiophene is spread over all five atoms of the ring, while the LUMO orbitals of **2** and **3** and the HOMO orbitals of **1**–**3** are essentially confined to the four carbon atoms. This indicates that it is the LUMO orbital that is most affected by the functionalization of thienyl sulfur to the *S*-oxide and that it is the first oxidation step that mostly affects the frontier orbitals. The trend of the electrochemical potentials of **4**–**7** is in agreement with the trend shown by the calculated frontier orbital energies. It appears that the functionalization of the thienyl sulfur to *S*-oxide affects the reduction potential to a greater extent than the oxidation potential strongly

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increasing the electroaffinity and bringing about much greater variation than the functionalization of the *S*-oxide to the corresponding *S*,*S*-dioxide. It is interesting that the potential values of sulfoxides **5** and **7** indicate that these compounds are both oxidizable and reducible at moderate potential values, in contrast to thiophene (which is easily oxidized and difficult to reduce) and thiophene *S*,*S*-dioxide (which is easily reduced but difficult to oxidize).

Examining the optical data, it is seen that the first functionalization to *S*-oxide leads to two distinct maxima, at 256 and 324 nm, the latter showing a strong bathochromic shift with respect to the parent thiophene **4**, and to a substantially smaller optical edge. Literature data for to 2,5-di-*tert*-butylthiophene and the corresponding *S*-oxide and *S*,*S*-dioxide show an analogous trend.[7] Similar λ_{max} and ΔE_{edge} values were found for compounds **5** and **7** which have different substituents and substitution pattern. Taking into account also the similarity of the oxidation and reduction potentials of **5** and **7**, it appears that it is the type of functionalization of the sulfur atom which is the main factor affecting the frontier orbitals energies.

A 4 × 4 singly excited CI ZINDO/S//PM3 analysis[9] performed on **1**–**3** shows that the low wavelength absorption in thiophene *S*-oxide and in thiophene *S*,*S*-dioxide is due to the mixing of transitions involving both S–O and π orbitals, while in all the compounds the highest wavelength absorption is due to the HOMO–LUMO π–π^* transition. It is of note that in both **2** and **3** the lone pairs of the oxygen atoms are not involved in the HOMO–LUMO transition.

In conclusion, theoretical calculations and electrochemical data show that the functionalization of thiophene to the corresponding *S*-oxide produces a dramatic increase in the electron affinity, without requiring complete de-aromatization of the molecule as in the case of the *S*,*S*-dioxide. In addition, there is only a minor variation in the oxidation potential. Therefore, this type of functionalization of thiophene-based compounds could lead to a novel class of materials with new and interesting properties.

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Notes and references

† Compounds **4**,[2b] **5**,[2b] **6**[3a] and **7**[2c] were synthesized according to the literature

1 J. Roncali, *Chem. Rev.*, 1997, **97**, 173.
2 (*a*) P. Pouzet, I. Erdelmeier, D. Ginderow, J.-P. Mornon, P. Dansette and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, 1995, 473; (*b*) N. Furukawa, S. Zang, S. Sato and M. Higaki, *Heterocycles*, 1997, **44**, 61; (*c*) J. Nakayama, T. Yu, Y. Sugihara and A. Ishii, *Chem. Lett.*, 1997, 499.
3 (*a*) G. Barbarella, O. Pudova, C. Arbizzani, M. Mastragostino and A. Bongini, *J. Org. Chem.*, 1998, **63**, 1742; (*b*) G. Barbarella, L. Favaretto, M. Zambianchi, O. Pudova, C. Arbizzani, A. Bongini and M. Mastragostino, *Adv. Mater.*, 1998, **10**, 551; (*c*) G. Barbarella, L. Favaretto, G. Sotgiu, M. Zambianchi, L. Antolini, O. Pudova and A. Bongini, *J. Org. Chem.*, 1998, **63**, 5497.
4 GAUSSIAN 94, Revision E.2, M. J. Frisch *et al.*, Gaussian Inc., Pittsburgh, PA, 1995.
5 I. Rozas, *J. Org. Phys. Chem.*, 1992, **5**, 74.
6 C. W. Bird, *Tetrahedron*, (*a*) 1985, **41**, 1409; (*b*) 1990, **46**, 5697.
7 W. L. Mock, *J. Am. Chem. Soc.*, 1970, **92**, 7610.
8 D. R. Rayner, A. J. Gordon and K. Mislow, *J. Am. Chem. Soc.*, 1968, **90**, 4854.
9 *HyperChem.*, release 4.5 from Hypercube, Inc. Waterloo, Ontario, Canada.

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