

# Solvent effects on electronic properties, geometries and internal rotation barriers of bithiophenes. An ab initio self-consistent reaction field theoretical study

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## Abstract

A self-consistent reaction field (SCRF) theoretical model has been used to simulate the average solvent effects on some  $\pi$ -conjugated organic thiophene dimers. Restricted Hartree–Fock molecular orbital calculations, using ab initio basis sets up to 6-31 + G\*, are reported on geometries, total energies and rotational barriers of 2,2'-bithiophene, and its 3,3'- and 3,4'-dimethyl derivatives.

**Keywords:** Solvent effects; Electronic properties; Bithiophene; Internal rotation barriers; Theoretical study

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## 1. Introduction

Oligothiophenes usually show enhanced optical and electrical properties compared to those of polythiophene; their use for molecular electronics applications and optical devices has been recently suggested [1,2]. The better structural organization (typically in layers) of the oligomers may be the reason for this improvement. Alkyl-oligothiophenes are soluble if the alkyl side chains are sufficiently long; i.e., longer than the butyl group. This property makes alkyl-oligothiophenes easily processable from solution and particularly interesting for various applications.

Intramolecular delocalization of  $\pi$  electrons in oligothiophenes depends on the extent of the overlapping of the  $p_z$  orbitals of the carbon atoms in the  $\alpha$  positions. Such overlapping is in turn modulated by the molecular conformation. It would be important to obtain information on the influence of the solvent on molecular properties of oligothiophenes (such as geometry, total energy and internal torsional potential) when they are dissolved.

We present here a theoretical analysis of the modulation by the solvent of conformational and geometrical properties of 2,2'-bithiophene, and its 3,3'- and 3,4'-methyl derivatives, which are models for unsubstituted oligothiophenes and 3-alkyl-oligothiophenes in solution.

The self-consistent continuum approach (SCRF) simulates the solvent effect on the solute by means of the solvent

reaction field induced by the solute molecule [3,4]. In this model, the solute is placed in a cavity (usually spherical, with radius  $a_0$ ) immersed in a continuous medium with a dielectric constant,  $\epsilon$ . The molecular charge distribution of the solute polarizes the solvent generating a dipole in the medium, and the electric field applied to the solute by the solvent (reaction) dipole will in turn interact with the solute charge distribution to lead to stabilization.

## 2. Experimental and computational methods

The calculations were carried out with the Gaussian 92 series of programs [5] and were run on a Convex 240 at the CICA Computer Center of Sevilla, (Spain). This ab initio molecular orbital theory system of programs allows for the computation of molecular properties in solution, using the Hartree–Fock and the Onsager reaction field approximations [6–9]. Throughout this paper, we have chosen the 6-31 + G\* and 6-31G\*\* (or 3-21G\*) basis sets for our highest level SCRF calculations.

## 3. Results and discussion

The atom numbering used in this work for 2,2'-bithiophene (2Th), 3,3'-dimethylbithiophene (2Th33) and 3,4'-dimethylbithiophene (2Th34) are plotted in Fig. 1. The cavity radii of 2Th ( $a_0 = 5.32$  Å), 2Th33 ( $a_0 = 5.35$  Å) and 2Th34

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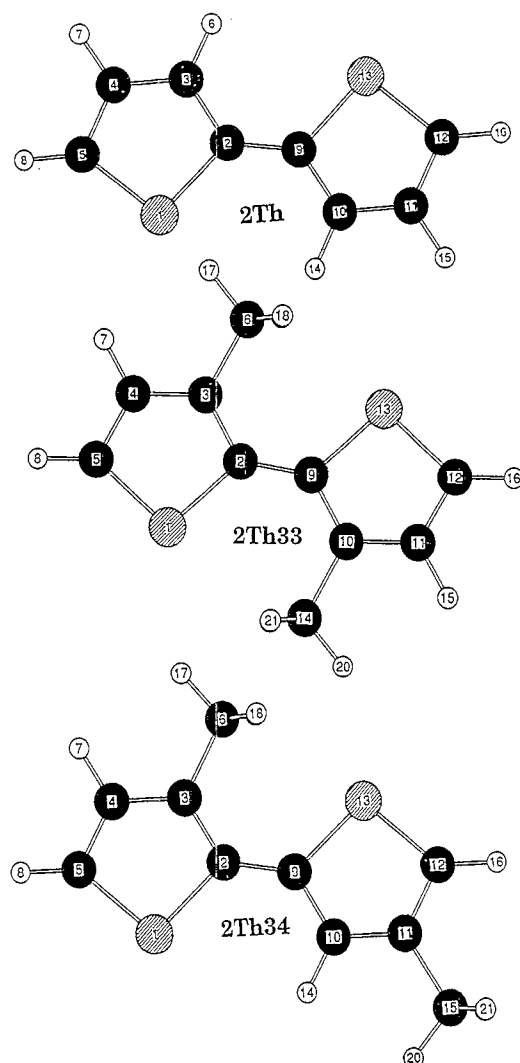


Fig. 1. Atom numbering for the molecules studied in this work.

( $a_0 = 5.84 \text{ \AA}$ ) were estimated from the greatest internuclear distance of the theoretical gas phase [10] and by adding the van der Waals radii of the two hydrogen atoms involved.

To analyse the geometry dependence on the dielectric constant of the medium, 6-31G\*\* full geometry optimizations for the equilibrium and *syn* conformers of 2Th and 2Th33 were carried out with  $\epsilon = 1.0$  (corresponding to the gas phase),  $\epsilon = 6.0$  (ethyl acetate) and  $\epsilon = 35.9$  (acetonitrile). A 3-21G\* basis set has been used in the full geometry optimizations of the equilibrium and *syn* conformers of 2Th34, since the absence of symmetry and the required computer time precluded us performing high level calculations. The dipole moment reaches its largest value for the *syn* conformer, thus making this arrangement of the thiophene rings particularly sensitive to solvent effects (namely:  $\mu_{6-31G^{**}} = 1.64 \text{ D}$  for 2Th,  $\mu_{6-31G^{**}} = 2.16 \text{ D}$  for 2Th33,  $\mu_{3-21G^{*}} = 2.11 \text{ D}$  for 2Th34, values for  $\epsilon = 1.0$ ). Results for 2Th and 2Th34 are displayed in Tables 1 and 2, respectively. The optimized geometry with a polar medium ( $\epsilon = 35.9$ ) is essentially the same as that with a nonpolar medium ( $\epsilon = 6.0$ ). From these data we can conclude that the molecular geometry is rather insensitive to the dielectric property of the medium.

Next, we consider the internal rotational potentials in solutions of different polarity. Calculations on 2Th and 2Th33 were performed assuming that the molecules belong to the  $C_{2h}$  and  $C_{2v}$  symmetry point groups in the *anti* and *syn* conformations, respectively. A  $C_2$  symmetry was imposed otherwise. No symmetry constraints were imposed for 2Th34, apart from planarity of the ring. The torsional dihedral angle  $\theta$  ( $C_3C_2C_9C_{10}$  in Fig. 1) was fixed at selected values of  $0$  (*syn*),  $40$ ,  $90$ ,  $145$ ,  $180^\circ$  (*anti*). Since the geometry is rather insensitive to the dielectric property of the medium, we shall use the optimized gas phase geometry of each conformer [10] to perform single-point SCRF energy calculations with slightly larger basis sets: 6-31+G\* (2Th) and 6-31G\*\* (2Th33 and 2Th34) as a function of the dielectric constant. Table 3 summarizes the calculated HF/6-31+G\* total and relative energies of several conformations of 2Th in different media. The theoretical data for 2Th33 and 2Th34 are displayed in Tables 4 and 5, respectively.

Theoretically, all conformational equilibria are found to be almost independent of the dielectric constant. The introduction of a polar medium seems to have little effect on the gas phase internal torsional potential (columns  $\epsilon = 1.0$  in Tables 3–5). For 2Th, the ‘solution’ calculations ( $\epsilon = 6.0$  and  $\epsilon = 35.9$ ) indicate that the *anti*-like  $C_2$  minimum conformation (about  $145^\circ$ ) lies about  $0.40$ – $0.41 \text{ kcal/mol}$  below the *anti*  $C_{2h}$  conformer. Another stable *syn*-like conformer is also calculated at torsional angles of about  $40^\circ$ . The *anti*-like minimum conformer is more stable by  $0.61$ – $0.63 \text{ kcal/mol}$  than the *syn*-like one. The barrier height we calculate at the perpendicular conformation is  $1.28$ – $1.29 \text{ kcal/mol}$ . The total energy of the *syn* conformer in solution is  $1.44$ – $1.48 \text{ kcal/mol}$  higher than the *anti* conformer. This energy difference is slightly lower than in the gas phase (about  $1.58 \text{ kcal/mol}$ ).

Table 1  
Calculated geometrical parameters of 2,2'-bithiophene (2Th) <sup>a,b</sup>

Parameter	Minimum			<i>syn</i>		
	$\epsilon = 1.0$	$\epsilon = 6.0$	$\epsilon = 35.9$	$\epsilon = 1.0$	$\epsilon = 6.0$	$\epsilon = 35.9$
C2–S1	1.739	1.739	1.739	1.740	1.740	1.740
C3–C2	1.351	1.351	1.351	1.354	1.353	1.353
C4–C3	1.433	1.433	1.433	1.431	1.431	1.431
C5–C4	1.344	1.344	1.344	1.344	1.344	1.344
C9–C2	1.465	1.465	1.465	1.467	1.467	1.467
H6–C3	1.074	1.074	1.074	1.073	1.073	1.073
H7–C4	1.074	1.074	1.074	1.074	1.074	1.074
H8–C5	1.071	1.071	1.071	1.071	1.071	1.071
C3–C2–S1	110.77	110.78	110.78	110.41	110.41	110.41
C4–C3–C2	113.17	113.17	113.16	113.38	113.38	113.39
C5–C4–C3	112.65	112.65	112.65	112.67	112.68	112.69
C9–C2–C3	128.29	128.29	128.29	127.32	127.31	127.30
H6–C3–C4	123.60	123.60	123.61	123.12	123.11	123.11
H7–C4–C3	123.63	123.62	123.62	123.60	123.57	123.57
H8–C5–C4	127.88	127.87	127.87	128.06	128.05	128.05
$\theta$	147.9	147.7	147.6	0.0	0.0	0.0

<sup>a</sup> HF/6-31G\*\* ( $a_0 = 5.32 \text{ \AA}$ ) values.

<sup>b</sup> Bond lengths are given in angstroms and bond angles in degrees.

Table 2

Calculated geometrical parameters of 3,4'-dimethyl-2,2'-bithiophene (2Th34)<sup>a,b</sup>

Parameter	Minimum			<i>syn</i>			Parameter	Minimum			<i>syn</i>		
	$\epsilon=1.0$	$\epsilon=6.0$	$\epsilon=35.9$	$\epsilon=1.0$	$\epsilon=6.0$	$\epsilon=35.9$		$\epsilon=1.0$	$\epsilon=6.0$	$\epsilon=35.9$	$\epsilon=1.0$	$\epsilon=6.0$	$\epsilon=35.9$
C2–S1	1.735	1.735	1.735	1.744	1.745	1.745	C9–S13	1.735	1.735	1.735	1.744	1.744	1.744
C3–C2	1.354	1.354	1.354	1.362	1.362	1.362	C10–C9	1.349	1.349	1.349	1.356	1.356	1.356
C4–C3	1.439	1.439	1.439	1.438	1.438	1.438	C11–C10	1.441	1.441	1.441	1.439	1.439	1.439
C5–C4	1.347	1.347	1.347	1.345	1.344	1.344	C12–C11	1.348	1.348	1.348	1.346	1.346	1.346
C9–C2	1.468	1.468	1.468	1.462	1.462	1.462	H14–C10	1.070	1.070	1.070	1.065	1.065	1.065
C6–C3	1.511	1.511	1.511	1.509	1.509	1.509	C15–H11	1.508	1.508	1.508	1.508	1.508	1.508
H7–C4	1.070	1.070	1.070	1.070	1.070	1.070	H16–C12	1.068	1.068	1.068	1.068	1.068	1.068
H8–C5	1.068	1.068	1.068	1.067	1.067	1.067	H20–C15	1.083	1.083	1.083	1.083	1.083	1.083
H17–C6	1.083	1.083	1.083	1.083	1.083	1.083	H21–C15	1.084	1.084	1.084	1.084	1.084	1.084
H18–C6	1.084	1.084	1.084	1.084	1.084	1.084							
$\theta$	108.61	106.99	106.57	0.0	0.0	0.0	C10–C9–S13	110.98	110.99	110.99	110.07	110.05	110.04
C3–C2–S1	111.79	111.79	111.80	110.86	110.85	110.85	C11–C10–C9	113.55	113.55	113.55	113.88	113.91	113.91
C4–C3–C2	111.76	111.77	111.77	112.00	112.02	112.02	C12–C11–C10	111.49	111.49	111.49	111.84	111.84	111.84
C5–C4–C3	113.14	113.13	113.13	113.55	113.55	113.55	H14–C10–C11	123.48	123.48	123.48	121.82	121.81	121.80
C9–C2–C3	127.70	127.58	127.55	129.20	129.23	129.23	C15–C11–C10	123.13	123.13	123.12	122.82	122.80	122.80
C6–C3–C4	123.37	123.42	123.44	121.21	121.16	121.16	H16–C12–C11	126.50	126.49	126.48	126.91	126.89	126.89
H7–C4–C3	122.94	122.94	122.95	122.58	122.56	122.55	H20–C15–C11	110.48	110.48	110.48	110.48	110.48	110.48
H8–C5–C4	126.91	126.91	126.91	127.26	127.25	127.25	H21–C15–C11	110.83	110.83	110.83	110.83	110.83	110.83
H17–C6–C3	110.48	110.48	110.48	110.48	110.48	110.48	C10–C9–C2	127.26	127.28	127.29	129.16	129.19	129.19
H18–C6–C3	110.83	110.83	110.83	110.83	110.83	110.83							

<sup>a</sup> HF/3-21G\* ( $\alpha_0=5.84$  Å) values.<sup>b</sup> Bond lengths are given in angstroms and bond angles in degrees.

Table 3

Calculated <sup>a</sup> total and relative energies of several conformations of 2,2'-bithiophene (2Th) in different media <sup>b</sup>

$\theta$	$\epsilon=1.0$	$\epsilon=6.0$	$\epsilon=35.9$
0.0	–1101.43695 (1.973)	–1101.43711 (1.880)	–1101.43716 (1.854)
40.0	–1101.43895 (0.717)	–1101.43910 (0.632)	–1101.43914 (0.612)
90.0	–1101.43796 (1.336)	–1101.43805 (1.292)	–1101.43807 (1.280)
145.0	–1101.44009 (0.000)	–1101.44011 (0.000)	–1101.44011 (0.000)
180.0	–1101.43946 (0.394)	–1101.43946 (0.404)	–1101.43946 (0.406)

<sup>a</sup> HF/6-31+G\* || HF/6-31G\*\* ( $\alpha_0=5.32$  Å) values.<sup>b</sup> Total energies in hartrees and relative energies in kcal/mol.

Table 4

Calculated <sup>a</sup> total and relative energies of several conformations of 3,3'-dimethyl-2,2'-bithiophene (2Th33) in different media <sup>b</sup>

Conf. ( $\theta$ )	$\epsilon=1.0$	$\epsilon=6.0$	$\epsilon=35.9$
<i>syn</i> (0)	–1179.49911 (12.738)	–1179.49941 (12.653)	–1179.49950 (12.628)
Minimum ( $\sim 90$ )	–1179.51941 (0.000)	–1179.51958 (0.000)	–1179.51962 (0.000)
<i>anti</i> (180)	–1179.51228 (4.474)	–1179.51228 (4.581)	–1179.51228 (4.606)

<sup>a</sup> HF/6-31G\*\* ( $\alpha_0=5.35$  Å) values.<sup>b</sup> Total energies in hartrees and relative energies in kcal/mol.

As the *anti* rotamer has no dipole moment, the reaction field has no effect on its structure and energy. However, in polar media, the *syn* form with a larger dipole moment is preferentially stabilized.

In 2Th33 and 2Th34, the steric hindrance causes significant changes on rotation. Both torsional potentials differ too much from that of 2Th. The gas phase and 'solution' calculations give a largely tilted equilibrium conformation for both mol-

ecules: about 90° (2Th33) and about 110° (2Th34). No other stable minimum was found outside the nearly orthogonal arrangement of the rings. Nevertheless, the overall torsional potential in 2Th34 is rather flat (energy differences between conformers are less than 1.75 kcal/mol). From the shape of the torsional potential of 2Th33 we learn that backbone flattening is only reachable from an *anti*-like twisting, even when the energy is not too low (about 4.60 kcal/mol).

Table 5

Calculated <sup>a</sup> total and relative energies of several conformations of 3,4'-dimethyl-2,2'-bithiophene (2Th34) in different media <sup>b</sup>

Conf. ( $\theta$ )	$\epsilon = 1.0$	$\epsilon = 35.9$
<i>syn</i> (0)	–1179.51794 (1.864)	–1179.51825 (1.745)
Minimum ( $\sim 110$ )	–1179.52091 (0.000)	–1179.52103 (0.000)
<i>anti</i> (180)	–1179.51965 (0.790)	–1179.51965 (0.862)

<sup>a</sup> 6-31G\*\* || 3-21G\* ( $a_0 = 5.84$  Å) values.

<sup>b</sup> Total energies in hartrees and relative energies in kcal/mol.

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