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 π-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

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 π electrons in oligothiophenes depends on the extent of the overlapping of the p₂ orbitals of the carbon atoms in the α 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 a₀) immersed in a continuous medium with a dielectric constant, ε. 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 (a₀ = 5.32 Å), 2Th33 (a₀ = 5.35 Å) and 2Th34

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(a₀ = 5.84 Å) 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 ϵ = 1.0 (corresponding to the gas phase), ϵ = 6.0 (ethyl acetate) and ϵ = 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: μ₆-31G* = 1.64 D for 2Th, μ₆-31G* = 2.16 D for 2Th33, μ₃-21G* = 2.11 D for 2Th34, values for ϵ = 1.0). Results for 2Th and 2Th33 are displayed in Tables 1 and 2, respectively. The optimized geometry with a polar medium (ϵ = 35.9) is essentially the same as that with a nonpolar medium (ϵ = 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 solvents of different polarity. Calculations on 2Th and 2Th33 were performed assuming that the molecules belong to the C₂ᵥ and C₂ᵥ symmetry point groups in the anti and syn conformations, respectively. A C₂ᵥ symmetry was imposed otherwise. No symmetry constraints were imposed for 2Th34, apart from planarity of the ring. The torsional dihedral angle θ (C₃C₄C₉C₁₀ in Fig. 1) was fixed at selected values of 0 (syn), 40, 90, 145, 180° (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 ϵ = 1.0 in Tables 3–5). For 2Th, the ‘solution’ calculations (ϵ = 6.0 and ϵ = 35.9) indicate that the anti-like C₂ minimum conformation (about 145°) lies about 0.40–0.41 kcal/mol below the anti C₂α conformer. Another stable syn-like conformer is also calculated at torsional angles of about 40°. The anti-like minimum conformer is more stable by 0.61–0.63 kcal/mol than the syn-like one. The barrier height we calculate at the perpendicular conformation is 1.28–1.29 kcal/mol. The total energy of the syn conformer in solution is 1.44–1.48 kcal/mol higher than the anti conformer. This energy difference is slightly lower than in the gas phase (about 1.58 kcal/mol).

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Table 1
Calculated geometrical parameters of 2,2'-bithiophene (2Th) ab

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>Syn</th>
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</thead>
<tbody>
<tr>
<td>e = 1.0</td>
<td>1.739</td>
<td>1.740</td>
</tr>
<tr>
<td>e = 6.0</td>
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<tr>
<td>e = 35.9</td>
<td>1.465</td>
<td>1.470</td>
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<tr>
<td>C2-S1</td>
<td>1.371</td>
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</tr>
<tr>
<td>C3-C2</td>
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<tr>
<td>C4-C3</td>
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<td>1.465</td>
</tr>
<tr>
<td>C5-C4</td>
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<td>1.074</td>
</tr>
<tr>
<td>H6-C3</td>
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<td>1.071</td>
</tr>
<tr>
<td>H7-C4</td>
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</tr>
<tr>
<td>H8-C5</td>
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</tr>
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</table>

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ab HF/6-31G** (a₀ = 5.32 Å) values.
Bond lengths are given in angstroms and bond angles in degrees.
Table 2
Calculated geometrical parameters of 3,4'-dimethyl-2,2'-bithiophene (2Th34) \(^a,b\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
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<th>Minimum</th>
<th>syn</th>
<th>Minimum</th>
<th>syn</th>
</tr>
</thead>
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<tr>
<td></td>
<td>(\varepsilon = 1.0)</td>
<td>(\varepsilon = 6.0)</td>
<td>(\varepsilon = 35.9)</td>
<td>(\varepsilon = 1.0)</td>
<td>(\varepsilon = 6.0)</td>
<td>(\varepsilon = 35.9)</td>
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<tr>
<td>C2–C1</td>
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<tr>
<td>C3–C2</td>
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<tr>
<td>C4–C3</td>
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<tr>
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<td>C9–C2</td>
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<tr>
<td>H15–C6</td>
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<td>H18–C6</td>
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<td>1.070</td>
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</tbody>
</table>

\(^a\) HF/3-21G* \((\alpha_s = 5.84 \text{ Å})\) values.
\(^b\) Bond lengths are given in angstroms and bond angles in degrees.

Table 3
Calculated \(^a\) total and relative energies of several conformations of 2,2'-bithiophene (2Th) in different media \(^b\)

<table>
<thead>
<tr>
<th>(\theta)</th>
<th>(\varepsilon = 1.0)</th>
<th>(\varepsilon = 6.0)</th>
<th>(\varepsilon = 35.9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-1101.43965 (1.973)</td>
<td>-1101.43711 (1.880)</td>
<td>-1101.43716 (1.854)</td>
</tr>
<tr>
<td>40.0</td>
<td>-1101.43895 (0.717)</td>
<td>-1101.43910 (0.632)</td>
<td>-1101.43914 (0.612)</td>
</tr>
<tr>
<td>90.0</td>
<td>-1101.43796 (1.336)</td>
<td>-1101.43805 (1.292)</td>
<td>-1101.43807 (1.280)</td>
</tr>
<tr>
<td>145.0</td>
<td>-1101.44009 (0.000)</td>
<td>-1101.44011 (0.000)</td>
<td>-1101.44011 (0.000)</td>
</tr>
<tr>
<td>180.0</td>
<td>-1101.43946 (0.394)</td>
<td>-1101.43946 (0.404)</td>
<td>-1101.43946 (0.406)</td>
</tr>
</tbody>
</table>

\(^a\) HF/6-31 +G* \[HF/6-31G** \((\alpha_s = 5.32 \text{ Å})\) values.
\(^b\) 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 molecules: 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 a total and relative energies of several conformations of 3,4'-dimethyl-2,2'-bithiophene (2Th34) in different media b

<table>
<thead>
<tr>
<th>Conf. (0)</th>
<th>$\epsilon = 1.0$</th>
<th>$\epsilon = 35.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>syn (0)</td>
<td>$-1179.51794 (1.864)$</td>
<td>$-1179.51825 (1.745)$</td>
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<tr>
<td>Minimum (~110)</td>
<td>$-1179.52091 (0.000)$</td>
<td>$-1179.52103 (0.000)$</td>
</tr>
<tr>
<td>anti (180)</td>
<td>$-1179.51965 (0.790)$</td>
<td>$-1179.51965 (0.862)$</td>
</tr>
</tbody>
</table>

a 6-31G** | 3-21G* ($\alpha_0 = 5.84 \AA$) values.
b Total energies in hartrees and relative energies in kcal/mol.

Acknowledgements

The present studies are financially supported by Dirección General de Investigación Científica y Técnica (DGICYT, Spain) through the Research Project PB93-1244. We are also indebted to Junta de Andalucía (Spain) for funding our research group (No. 6072).

References