LETTER

Evidence for the contribution of sulfur–bromine intramolecular interactions to the self-rigidification of thiophene-based π-conjugated systems†

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Bithiophene associating 3,4-ethylenedioxythiophene and 3-bromothiophene, and the corresponding polymer exhibit self-rigidified structures of the conjugated backbones resulting from the association of S–Br and S–O non-bonded intramolecular interactions.

The considerable research activity developed around functional polymeric π-conjugated systems is motivated by the high current interest in these materials in the field of plastic electronics.[1] Polythiophenes have been particularly investigated as the most significant class of conjugated polymers[2] and in particular poly(3,4-ethylenedioxythiophene) (PEDOT), which has become one of the most popular polythiophene derivatives.[3,4] PEDOT presents a unique combination of stability, moderate band gap, low oxidation potential and optical transparency in the visible spectral region. These properties result from the synergistic associations of the strong donor effect of the ethylenedioxy groups with the propensity of EDOT to develop noncovalent intramolecular S–O interactions.[5] The self-rigidification resulting from these intramolecular interactions makes EDOT an interesting building block to develop copolymers promoting the planarization of the π-conjugated systems. Even if in 3,4-ethylenedisulfanylthiophene (EDST), the sulfur analogue of EDOT, S–S steric repulsions induce torsions between the cycles in dimer bis-EDST and polymer poly-EDST,[6] it has been recently demonstrated that the combination of EDOT and EDST moieties leads to a quasi-planar conformation in bithiophene[6] or terthiophene[7] systems. The planar conformations are associated with both S–O and S–S intramolecular interactions. Therefore, the balance between the S–S steric repulsions and non-bonding interactions can be favorably oriented for strengthening the self-rigidification by the combination of S–O and S–S interactions.

Chalcogen–halogen interactions represent another type of non-bonding interaction potentially useful for stabilizing the planar conformation of π-conjugated systems. It has been reported that sulfur–fluorine interactions contribute to rigidify

oligomers in which the thiophene ring is associated with 3,4-difluorothiophene[8,9] or fluorophenylene units.[8,10,11] Replacing fluorine by a bulkier halogen atom, such as chlorine and bromine, can be expected to induce steric repulsions and thus to twist the conjugated system. Indeed, the crystal structures of bithiophenes substituted by bromine at the 3 and 3′ positions revealed a large torsion between the thiophene cycles.[12] Nevertheless, planar conformations have been observed for bithiophenes bearing only one bromine atom at the 3-position,[13,14] indicating that the steric hindrance can be counterbalanced by weak non-bonding interactions and by the deformability of the thiophene ring.[15] Recently, it has been demonstrated that an electrodeposited film of poly(3-bromo-4-methoxythiophene) presented spectroscopic data characteristic of a rigid planar structure without pointing out the origin of this result.[16] In order to analyze the structuring effect resulting from the combination of bromine and oxygen atoms in conjugated systems, we compare here the structural and electronic properties of bithiophenes EDOT-3-bromothiophene **1** and EDOT-thiophene **2** and their corresponding polymers (Chart 1).

Compounds **1** and **2** were synthesized by Stille coupling between the stannyl derivative of EDOT with 2-bromothiophene or 2,3-dibromothiophene in the presence of Pd(PPh₃)₄ (Scheme 1). By using 1 equivalent of stannyl derivative, the coupling of EDOT on the 2-position of 2,3-dibromothiophene was favored and led exclusively to compound **1** in 57% yield. With 2-bromothiophene an excess of stannyl EDOT was used to obtain compound **2** in 69% yield.[17] Bithiophene **1** was obtained as a crystalline solid while **2** was an oil.

Single crystals of **1**, obtained by slow evaporation of CHCl₃–EtOH solution, have been analyzed by X-ray diffraction.† The structure of compound **1** shown in Fig. 1, reveals a good planarity of the conjugated system with the two thiophene cycles in an *anti* conformation. The dihedral angle
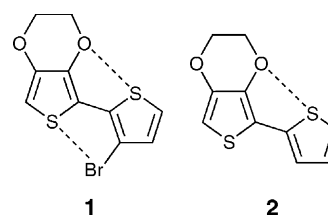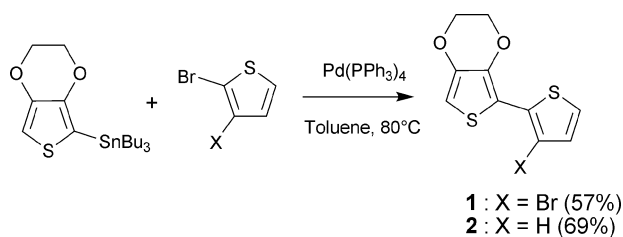
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Chart 1

Scheme 1 Synthesis of bithiophenes **1** and **2**.

Fig. 2 Electronic absorption spectra of **1** and **2** in CH_2Cl_2.

between thienyl rings is less than 1°. The observed d_{S1O1} = 2.834(3) Å and d_{S2Br} = 3.220(1) Å distances are considerably shorter than the sum of the van der Waals radii of sulfur and oxygen (3.25 Å) or sulfur and bromine (3.80 Å), thus indicating that both S–O and S–Br intramolecular interactions contribute to the self-rigidification of the π-conjugated system of **1**.

Fig. 2 shows the UV-Vis absorption spectra of compounds **1** and **2** in methylene chloride. The spectrum of **2** presents a discernible vibronic fine structure with an absorption maximum (λ_{max}) at 318 nm and shoulders at 300 nm and 330 nm consistent with the establishment of a self-rigidified structure due to intramolecular S–O interaction. In spite of the bulky Br atom, compound **1** displays a better resolved fine structure with the appearance of three distinct maxima at 303 nm, 316 nm and 331 nm. The three maxima are equally spaced in energy by 1300–1400 cm^{-1}, which is consistent with a C=C stretching mode in the heteroaromatic moieties, strongly coupled to the electronic structure. Such behavior is indicative of a more rigidified π-conjugated system for compound **1** than for compound **2**. Thus, in addition to the S–O interaction, the non-bonding S–Br intramolecular interaction observed in the solid state persists in solution and contributes to strengthening the self-rigidification of the molecule.

Theoretical calculations have been performed at the *ab initio* density functional level with the Gaussian 03 package. Becke's three parameter gradient corrected functional (B3LYP) with a polarized 6-31G(d,p) basis was used for all full geometry optimization of the bithiophenes. The most stable optimized conformations for the two compounds correspond to the planar *anti* structures with dihedral angles between the thiophene cycles of less than 2°.[18,19] In order to study the influence of the internal rotation between the two cycles, the evolution

of the energy as a function of the dihedral angle θ has been calculated from $\theta = 0°$ (*anti* conformer) to $\theta = 180°$ (*syn* conformer). The comparison of the profile of the curves in Fig. 3 for compounds **1** and **2** shows an analogous evolution between 0° and 90° and a strong difference after 90°. For compound **2**, a nearly planar *cis* conformer is stabilized at 166°, only 0.6 kcal mol^{-1} higher in energy than the planar *trans* conformation. On the other hand, a minimum appears for **1** at $\theta = 130°$ corresponding to a *cis* distorted conformation at 1.73 kcal mol^{-1} higher in energy that the planar *trans* conformation. Due to strong steric Br–O repulsion the planar *cis* conformer is strongly destabilized by about 7.3 kcal mol^{-1}. For both compounds, minima are separated by a barrier at $\theta = 90°$ with a maximum energy around 3.0–3.3 kcal mol^{-1} with respect to the *trans* planar conformation. The planar conformation adopted by compound **1**, completely agrees with the geometry obtained from the X-ray structure, with short S–O (2.85 Å) and S–Br (3.26 Å) distances as expected for intramolecular interactions. For compound **2** the S–O distance is slightly longer than for **1**, thus suggesting weaker S–O intramolecular interactions. As indicated in Table 1, the slight decrease in energy of the HOMO and LUMO levels of compound **1** compared to **2** corresponds to a weak electron-withdrawing effect of the bromine atom.

The cyclic voltammograms (CV) of compounds **1** and **2** present irreversible anodic peaks at 1.2 V and 1.1 V,
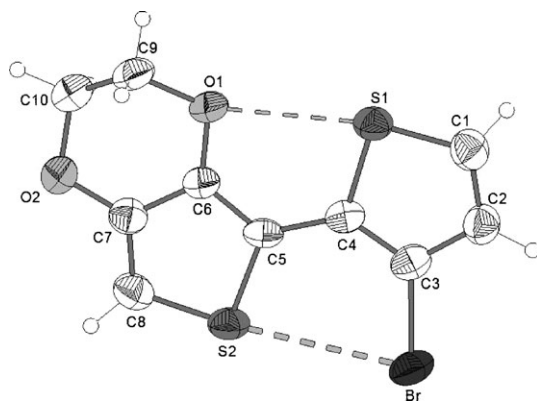

Fig. 1 Molecular structure of compound **1**; ellipsoids drawn at the 50% probability level. The intramolecular interactions are presented by dotted lines.
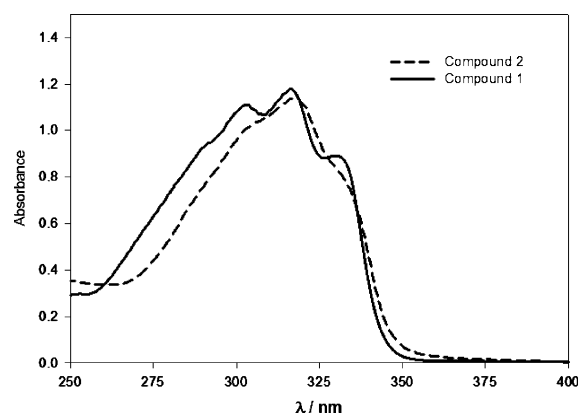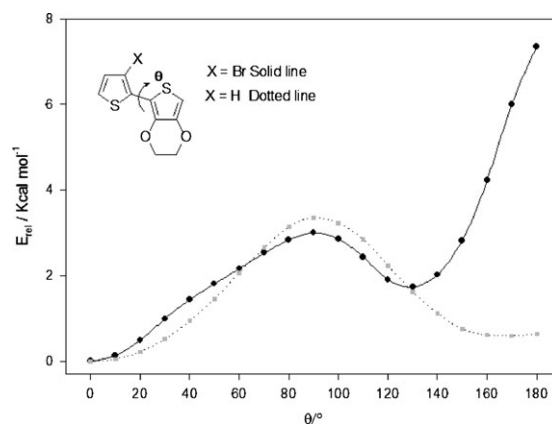

Fig. 3 Relative energy curves for the internal torsion of compounds **1** (black) and **2** (grey).

Table 1 UV-Vis[a], electrochemical data[b] and calculated HOMO/LUMO energy levels and gap[c] of compounds **1** and **2**

Compound	λ_{max}	λ_{0-0}	E_{ox}	HOMO	LUMO	ΔE
1	316 nm	331 nm	1.22 V	−5.3 eV	−1.2 eV	4.10 eV
2	318 nm	330 nm	1.11 V	−5.1 eV	−1.0 eV	4.10 eV

[a] 5.10^{-5} M in CH_2Cl_2. [b] 10^{-3} M in 0.1 M Bu_4NPF_6 in CH_3CN, reference Ag/AgCl, $v = 100$ mV s^{-1}. [c] HOMO/LUMO energy levels and gap are calculated by DFT methods (B3LYP/6-31g(d,p)).

respectively, corresponding to the oxidation of the compounds into the corresponding radical cations. For compound **1** the weakly electron-withdrawing bromine atom on the 3 position leads to a slight increase of the oxidation potential corresponding to a decrease of the HOMO level, in agreement with theoretical calculations.

Application of recurrent potential scans to acetonitrile solutions of compounds **1** and **2** in the presence of Bu_4NPF_6 as supporting electrolyte leads to the progressive development of a new redox system at lower potential associated with the electrodeposition of the polymers. The dissymmetry introduced in the electronic structure of radical cations **1**[+•] and **2**[+•] should result in a different reactivity of the two free α-positions. Thus, both polymers have probably a regularly alternated polymeric structure, but the very low solubility of the electrodeposited films did not allow characterization of their structures.

The CV trace of poly(**2**) (Fig. 4 right) recorded in a monomer-free electrolytic medium presents a broad reversible oxidation wave with a maximum at *ca.* 0.78 V and a shoulder at 0.30 V which corresponds with the p-doping of the polymer. The CV of poly(**1**) (Fig. 4 left) shows two anodic waves peaking at 0.40 V and 0.95 V which can be attributed to the oxidation to the polaron and bipolaron states. After a hundred charging–discharging cycles, the CV of the polymers does not present any decrease in the amount of exchanged charge, thus indicating that the polymers are stable upon cycling.

The optical properties of the polymers have been analyzed on a thin film electrodeposited on indium tin oxide (ITO)

electrodes. Fig. 5 shows the spectral series for polymers at various potentials from the neutral to the fully oxidized states. The spectrum of the neutral poly(**2**) presents a λ_{max} at 505 nm and a band gap of 1.82 eV estimated from the low energy absorption onset. The spectrum of poly(**1**) shows a larger absorption band with a λ_{max} at 500 nm, a shoulder at 580 nm and a band gap of 1.72 eV. The absorption band displays a discernible fine structure consistent with a more rigid structure due to synergistic effects of the intramolecular S–Br and S–O interactions. Oxidation of the two polymers leads to a similar change in the optical spectra. When the applied potential reaches the first oxidation wave, two bands appear around 800 nm and 1400 nm which can be attributed to the polaron state while at the second oxidation potential, a large band with a maximum around 1000 nm appears which should correspond to the formation of bipolaronic species.

In summary, the comparison of the electronic properties of hybrid bithiophenes **1** and **2** shows that the presence of a bromine atom at the 3-position of the thiophene ring leads to the development of noncovalent intramolecular sulfur–bromine interactions. Combined with the already well-established sulfur–oxygen interactions observed in many EDOT-containing compounds, bromine–sulfur interactions contribute to strengthening the self-rigidification of the conjugated system. The electropolymerization of the two precursors leads to polymers with similar electronic properties which confirms that the self-structuring effects persist in the films of polymers.

Experimental

General

NMR spectra were recorded with a Bruker Advance DRX 500 (^{1}H, 500.13 MHz and ^{13}C, 125.75 MHz) instrument. Chemical shifts are given in ppm relative to TMS. Cyclic voltammetry was performed in CH_3CN solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte was purchased from Acros and used without purification. Solutions were de-aerated by
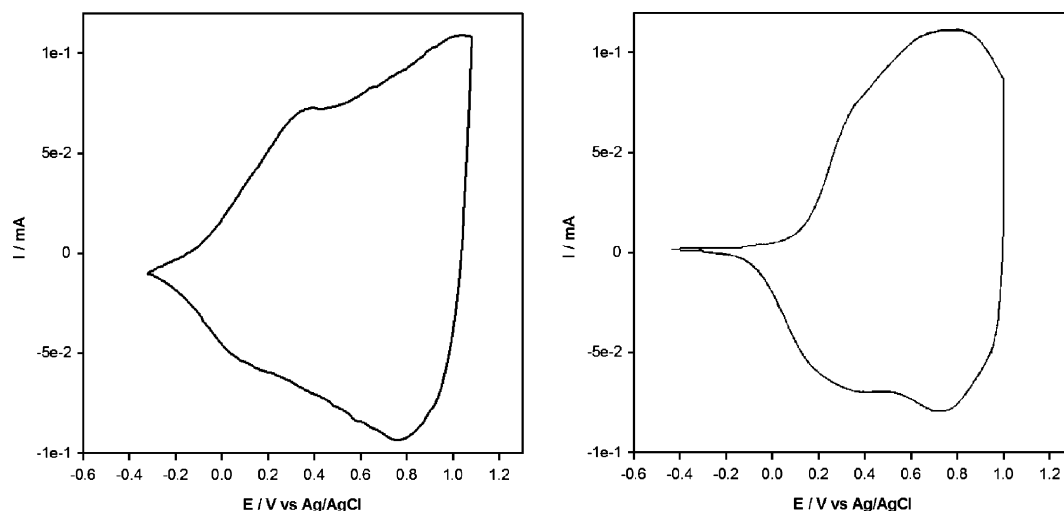
Fig. 4 CV traces of film of poly(**1**) (left) and poly(**2**) (right) deposited on a Pt disk ($d = 1$ mm) in 0.10 M Bu_4NPF_6 in CH_3CN, scan rate 100 mV s^{-1}.
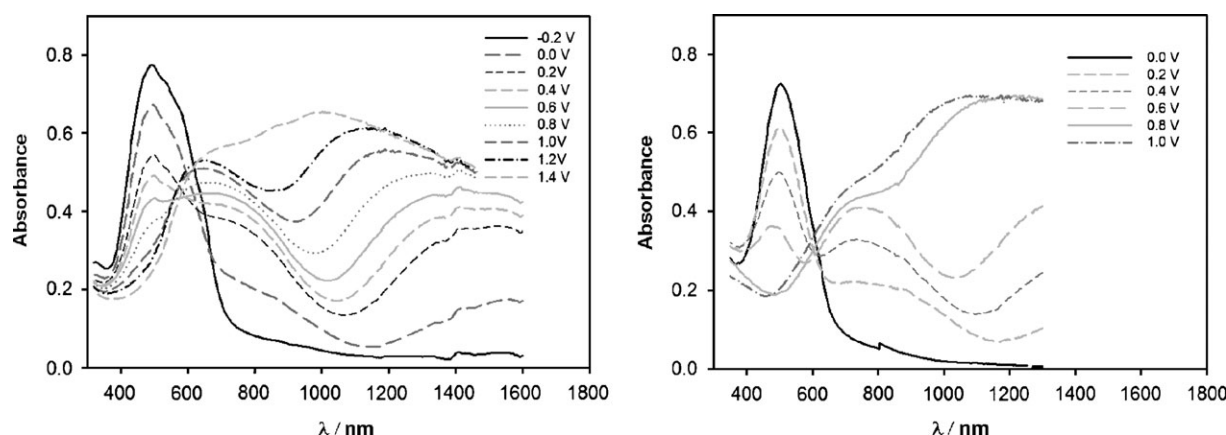
Fig. 5 Electronic absorption spectra of films of poly(**1**) (left) and poly(**2**) (right) electrodeposited on ITO.

nitrogen bubbling prior to each experiment, each of which was run under a nitrogen atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\Phi = 1$ mm) and a platinum wire counter electrode. An Ag/AgCl electrode checked against the ferrocene/ferricinium couple (Fc/Fc$^+$) before and after each experiment was used as reference. Electrochemical experiments were carried out with a PAR 273 potentiostat with positive feedback.

Procedure for Stille coupling

Preparation of the stannyl derivative of EDOT. To a solution containing EDOT dissolved in dry THF at -78 °C under an inert atmosphere (N$_2$), an equivalent of n-BuLi (2.5 M or 1.6 M in hexane) was added dropwise. The mixture was stirred for 1 h at the addition temperature. Then, tributyltin chloride was added dropwise and the mixture was stirred at the same temperature for $\frac{1}{2}$ h before allowing to warm at room temperature. After dilution with diethyl ether, the organic phase was successively washed using a saturated solution of NaHCO$_3$ then water. After drying over MgSO$_4$, the solvent was evaporated and the stannic derivative was used without other purification in the Stille coupling reactions.

EDOT-3-bromothiophene 1. A mixture of stannyl derivative (3.56 g, 8.2 mmol) and 2,3-dibromothiophene (1.98 g, 8.2 mmol) and Pd(PPh$_3$)$_4$ (5% mol) was heated in anhydrous toluene at 80 °C for 16 h under an inert atmosphere. After concentration, the residue was dissolved in CH$_2$Cl$_2$. The organic phase was washed twice with a saturated solution of NaHCO$_3$ and then with water. After drying over MgSO$_4$ and evaporating the solvent, the product was purified by chromatography on silica gel (CH$_2$Cl$_2$–petroleum ether (PE) 1 : 1) to give **1** as a pale yellow solid (1.41 g, 57%).

1: mp 72 °C; ^{1}H NMR (CDCl$_3$): $\delta = 4.25$ (m, 2H), 4.33 (m, 2H), 6.41 (s, 1H), 7.00 (d, $^3J = 5.4$ Hz, 1H), 7.23 (d, $^3J = 5.4$ Hz, 1H); ^{13}C NMR (CDCl$_3$): $\delta = 64.4$, 64.9, 99.5, 107.6, 109.3, 124.9, 129.3, 130.8, 139.1, 141.3; HRMS (EI$^+$) C$_{10}$H$_7$BrO$_2$S$_2$ calculated 301.907, found 301.9067; elemental analysis calculated (%) for C$_{10}$H$_7$BrO$_2$S$_2$: C 39.61, H 2.33; found: C 40.02, H 2.36.

EDOT-thiophene 2. Stille coupling was done with the above procedure by using 2-bromothiophene (0.81 g, 5 mmol) and the stannic derivative (7.5 mmol, 1.5 equivalents), and Pd(PPh$_3$)$_4$ (5% mol). The product was purified by chromatography on silica gel (CH$_2$Cl$_2$–PE 1 : 1) to give **2** as a colourless oil (770 mg, 69%).

2: ^{1}H NMR (CDCl$_3$): $\delta = 4.24$ (m, 2H), 4.33 (m, 2H), 6.21 (s, 1H), 7.01 (dd, $^3J = 5.1$ Hz, $^3J = 3.7$ Hz, 1H), 7.20 (d, $^3J = 5.1$ Hz, 1H), 7.22 (d, $^3J = 3.7$ Hz, 1H); elemental analysis calculated (%) for C$_{10}$H$_8$O$_2$S$_2$: C 53.55, H 3.60; found: C 53.82, H 3.49.

Crystal data and structure refinement for compound 1†

Data collections were performed at 293 K on a STOE IPDS diffractometer equipped with a graphite monochromator utilizing MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SIR92[20] and refined on F^2 by a full-matrix least-squares method, using SHELXL97[21]. Non-hydrogen atoms were refined anisotropically and absorption was corrected by a Gaussian technique. The H atoms were found by Fourier difference synthesis.

C$_{10}$H$_7$BrO$_2$S$_2$, $M_w = 303.19$, crystal size $0.77 \times 0.19 \times 0.14$ mm^3, orthorhombic, $P2_12_12_1$ $a = 4.1115(4)$ Å, $b = 14.688(1)$ Å, $c = 17.247(2)$ Å, $V = 1041.6(2)$ Å^3, $Z = 4$, $\rho_{calc} = 1.933$ g cm^{-3}, 6104 reflections collected in the 2.4–26° θ range, 1988 independent reflections ($R_{int} = 0.04$) from which 1738 with $I > 2\sigma(I)$ converged to $R = 0.0292$ and wR_2 (all data) $= 0.0721$ with 164 parameters, GOF $= 0.975$, $-0.417 < \Delta\rho < 0.478$ e Å^{-3}.

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