Examining the Planarity of Poly(3,4-ethylenedioxythiophene): Consideration of Self-Rigidification, Electronic, and Geometric Effects

Jordi Poater,[†] Jordi Casanovas,[‡] Miquel Solà,*,[†] and Carlos Alemán*,[§,||]

Institut de Química Computacional and Departament de Química, Universitat de Girona, Campus de Montilivi, Girona E-17071, Spain, Departament de Química, Escola Politècnica Superior, Universitat de Lleida, c/Jaume II no 69, Lleida E-25001, Spain, Departament d'Enginyeria Química, E. T. S. d'Enginyeria Industrial de Barcelona, Universitat Politècnica de Catalunya, Diagonal 647, Barcelona E-08028, Spain, and Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya, Campus Sud, Edifici C', C/Pasqual i Vila s/n, Barcelona E-08028, Spain

The intramolecular interactions responsible for the planarity observed in poly(3,4-ethylenedioxythiophene) and small 3,4-ethylenedioxythiophene-containing oligomers have been investigated using quantum mechanical methods. Specifically, the relative influence of electron-donating effects, π-conjugation, and geometric restrictions induced by the cyclic substituent and attractive S···O intramolecular noncovalent interactions, which were proposed to be the most relevant factor for such planarity on the self-rigidification observed in these compounds, have been examined considering a wide number of model compounds. Results evidenced that noncovalent S···O interactions, which were postulated on the basis that the nonbonded distances between sulfur and oxygen atoms belonging to neighboring repeating units are significantly shorter than the sum of the van der Waals radii of sulfur and oxygen, are slightly repulsive destabilizing the planar anti conformation. In contrast, the latter arrangement is favored by the π-conjugation produced by both geometric restrictions imposed by the cyclic substituent and the electron-donating effects provided by the oxygen atoms attached to positions three and four of each tiophene ring. Therefore, these factors produce gain in aromaticity and favorable electrostatic interactions when the planarity is reached, compensating the Pauli repulsions between the shared electron pairs of the sulfur and oxygen atoms.

Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is a commercial conducting polymer originally described by researchers at the Bayer Company. Because of a combination of properties, that is, moderate band gap, low oxidation potential, high conductivity, good optical transparency, and exceptional environmental stability,[1–3] PEDOT attracted considerable interest, and many applications based on these properties were rapidly developed, for example, antistatic coatings, electrode material in supercapacitors, hole injection layer in organic light-emitting diodes, and solar cells.[4–7] Recently, we have also proposed some potential biotechnological applications for this material, which are based on the following observations: (i) PEDOT is able to form specific interactions with DNA,[8,9] this clear preference toward specific nucleotide sequences being appropriate for the development of biosensors; and (ii) PEDOT is both a bio- and an electrocompatible material, living cells being able to adhere and proliferate on its surfaces without introducing any damage in its electrochemical properties.[10,11] These features suggested that PEDOT is a promising material for developing components for electric transmission in orthopedic devices, artificial muscles, and so on.

PEDOT
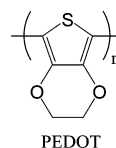
In addition to their strong electron-donating effects, the oxygen atoms attached at the β,β'-positions of the thiophene ring prevent the formation of parasitic $\alpha-\beta$ linkages during the polymerization of the 3,4-ethylenedioxythiophene (EDOT) monomers. Therefore, the excellent properties of PEDOT combined with the high reactivity conferred to the free α,α'-positions make EDOT a very attractive building block for the design of new classes of functional π-conjugated systems.[12] The properties and applications of PEDOT as well as of other EDOT-based molecular systems have been reviewed several times in the last years.[6,7,12]

The molecular and electronic properties of PEDOT and small EDOT-containing oligomers have been extensively studied using quantum mechanical methods.[13–20] The rotational energy profile calculated for the inter-ring dihedral angle (θ) defined by two adjacent EDOT units indicated that the most favored arrangement corresponds to the planar anti conformation ($\theta \approx 180°$) rather than to the antigauche conformations ($\theta \approx \pm150°$), as is frequently found for thiophene derivatives.[21,22] Indeed, the antigauche has been characterized as the lowest energy conformation for other thiophene derivatives that incorporate cyclic substituents at positions three and four, for example, isothianaphthene oligomers in which each unit is formed by the fusion of a benzene ring upon thiophene.[23] Moreover, early studies on

* Corresponding authors. E-mail: miquel.sola@udg.edu (M.S.); carlos.aleman@upc.edu (C.A.).
[†] Universitat de Girona.
[‡] Universitat de Lleida.
[§] E. T. S. d'Enginyeria Industrial de Barcelona, Universitat Politècnica de Catalunya.
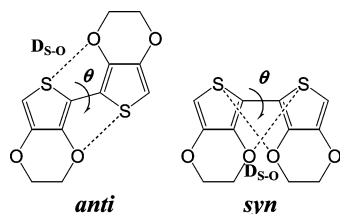[||] Center for Research in Nano-Engineering, Universitat Politècnica de Catalunya.

Figure 1. Geometric parameters used to identify the presence of S···O interactions for both the anti and syn conformations: D_{S-O} and θ refer to the S···O distance (dashed lines) and the inter-ring dihedral angle (arrow), respectively.

substituted thiophene oligomers showed that the incorporation of substituents at position three of each unit usually produces significant distortions from the planarity, which should be attributed to the strong repulsive interaction generated by the substituents of adjacent units.[24−26]

The preference of EDOT oligomers toward the planar anti conformation was traditionally attributed to the electron donation effects exerted by the oxygen atoms of the dioxane rings. Quantum mechanical calculations evidenced that the planar arrangement induced by this electronic phenomenon enhances the π-conjugation between adjacent units and reduces the lowest $\pi-\pi^*$ transition energy (ε_g).[13−20] In addition, analysis of the crystallographic structure of a single crystal of the EDOT dimer[27,28] (**1**) showed that the nonbonded distances (Figure 1) between sulfur and oxygen atoms belonging to different units (2.92 Å) are significantly shorter than the sum of the van der Waals radii of sulfur and oxygen (3.25 Å). A similar feature was observed from the X-ray structure of the tricyclic system based on thieno[3,4-*c*]-pyrazine (**2**).[29] These short distances led to postulate the occurrence of strong S···O intramolecular noncovalent interactions, which rigidify the π-conjugated structure in a fully planar anti conformation. However, these interactions were restricted at the intramolecular level because intermolecular S···O distances were considerably larger than 3.25 Å. Indeed, self-rigidification was used to explain the fact that electron-transmitting properties are better in **1** than in 2,2′-bithiophene (**3**).[29] Moreover, self-rigidification by means of S···O (or other heteroatoms) intramolecular noncovalent interactions was assumed to be responsible, in addition to the electron donor effect, for the optimization of the (opto)electronic properties of various classes of molecular functional π-conjugated systems.[29,30]
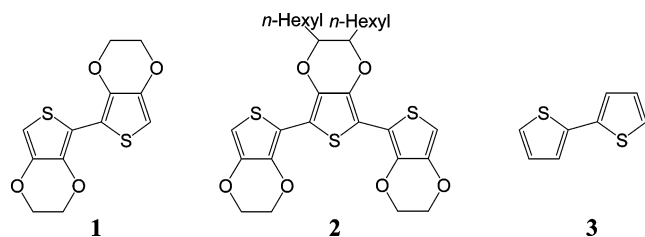
In this work, we use quantum mechanical methods to discuss the contribution of the postulated S···O intramolecular noncovalent interactions to the planar structure of EDOT-containing oligomers/polymers and their derivatives. Therefore, the participation of such interactions in the planarity of these compounds has been compared with those of the electron-donating effects induced by the oxygen atoms and the geometric restraints imposed by the cyclic substituent.

Methods

All calculations were done by means of the Gaussian 03 computer program.[31] Density functional theory (DFT) calcula-

tions were carried out using the B3LYP method[32,33] combined with the 6-311++G(d,p) basis set,[34] whereas ab initio calculations were performed at the MP2 level[35] using the 6-31+G(d,p) basis set.[36] For simplicity, hereafter these theoretical levels will be denoted B3LYP and MP2, respectively. Calculations were performed in a number of model compounds that will be explicitly described in the next section.

The existence and importance of attractive S···O interactions in oligomers formed by EDOT derivatives were examined using three different criteria. First, we compared the minimum energy conformations predicted for each calculated compound. Specifically, we analyzed the S···O distances (D_{S-O}), the inter-ring dihedral angle (θ), and the energy difference between the minima (ΔE_{s-a}). These parameters allow us to estimate the relative importance of the S···O interaction with respect to other effects that also contribute to the planarity of PEDOT, that is, electron donation and restrictions imposed by the dioxane ring. The values of D_{S-O} are very sensible to the anti (or antigauche) or syn (or syn-gauche) arrangement of the minima (Figure 1). Second, the inter-ring rotational profile of **1** was compared with that obtained for some selected model compounds to determine the attractive or repulsive character of the S···O interaction. Finally, the electronic structures of some model molecules, and some simple complexes were analyzed and compared.

Full Geometry Optimizations. Complete geometry optimizations were carried out at the B3LYP level using the two planar conformations, anti ($\theta = 180°$) and syn ($\theta = 0°$), as starting points. However, early studies showed the tendency of the B3LYP functional to overestimate π-conjugation effects,[22,37,38] which may lead to an exaggeration of the planarity of the compounds under study. For example, the inter-ring dihedral angle of **3** predicted using B3LYP/6-31G(d) calculations ($\theta = 157°$) was 9° larger than that obtained at the MP2/6-31G(d) level.[22] Similarly, the energetic of gauche−gauche barrier was slightly underestimated (1.2 kcal/mol) by the former method.[22] To estimate the importance of this limitation in each case, the anti conformations of all the investigated compounds were also fully optimized at the MP2 level.

Rotational Profiles and Simple Model Complexes. Rotational profiles representing the conformational energy as a function of the inter-ring dihedral angle, $E = E(\theta)$, were calculated for **1** and some selected derivatives. The internal rotation of these compounds was studied by scanning θ in steps of 10° between 90 (gauche−gauche barrier) and 180° (planar anti). The angle θ was held fixed for each point of the potential energy surface, whereas all other geometrical parameters were fully relaxed at the B3LYP level. The strength of the S···O interaction was studied using small model complexes formed by H_2S and H_2O molecule/s, which depending on the case, were submitted to full or partial geometry optimizations at the B3LYP level.

Electronic Structure. Full natural bond orbital (NBO) analyses were carried out for selected compounds using the NBO program (version 3.1) developed by Weinhold and coworkers,[39,40] which was implemented in Gaussian 98. NBO analysis is based on the transformation of a given wave function into localized two-center bonds and lone pairs (one-center) resembling the localized picture of Lewis models. Additionally, nucleus-independent chemical shift (NICS)[41,42] calculations were performed to determine the aromaticity of the thiophene ring of the different investigated compounds. The GIAO method[43] was used to perform calculations of NICS at ring centers (NICS(0)) determined by the nonweighted mean of the heavy atoms coordinates and at 1 Å above the ring taken into study

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TABLE 1: Results Obtained at the B3LYP and MP2 Levels of Theory for the Model Compounds Investigated in This Work (See Text)[a]

no.	B3LYP/6-311++G(d,p)					MP2/6-31+G(d,p)	
	D_{S-O}	θ	D_{S-O}	θ	ΔE_{s-a}	D_{S-O}	θ
1	2.925	180.0	4.486	52.4	1.9	2.925	180.0
3		152.9		36.6	0.7		134.2
4	2.916	180.0	4.384	57.1	1.9	2.937	162.0
5		71.6					81.6
6		76.3					81.2
7	2.948	180.0	4.475	53.4	1.8	3.033	153.6
8	2.901	178.5	4.378	58.0	1.8	3.008	149.6
9		150.9		36.4	0.9		135.9
10		150.0		45.9	0.7		130.0
11		148.4		44.5	0.8		153.6
12	3.278	155.8	3.883	93.7	−0.1	2.947	155.8
13	3.087	180.0	4.507	47.7	2.5	3.065	180.0
14	3.144	180.0	4.593	44.7	2.6	3.124	180.0
15		179.9		47.1	3.3		179.5
16		180.0		41.6	2.9		179.6
17	3.116	180.0	4.548	45.2	2.1	3.174	146.7
18	3.124	167.9	4.564	45.4	0.9	3.244	145.2
19		85.9					100.9
20		64.4					100.8
21		167.9		36.6	1.5		144.5
22	3.280	179.9	4.852	39.0	0.6	3.393	155.1

[a] Geometric parameters θ (in degrees) and D_{S-O} (in angstroms) are described in Figure 1. ΔE_{s-a} (in kilocalories per mole) corresponds to the energy difference between the two minima.

(NICS(1)), and, in addition, the corresponding out-of-plane component (NICS(1)$_{zz}$) was also analyzed.[44]

Results and Discussion

Full Geometry Optimizations. For all model compounds investigated in this work, Table 1 lists: the values of D_{S-O} and θ (Figure 1) for the minima derived from geometry optimization at the B3LYP level, the relative energy between such minima (ΔE_{s-a}), and the values of D_{S-O} and θ obtained after geometry optimization of the anti conformation at the MP2 level.

If they exist, then attractive S···O intramolecular nonconvalent interactions are expected to stabilize the planar anti conformation ($\theta \approx 180°$) of the investigated dimers with respect to the syn or syn-gauche conformation ($\theta \approx 0$ or $50°$, respectively), the value of D_{S-O} being significantly shorter in the former arrangement than in the latter ones (Figure 1). Accordingly, full-geometry optimizations on **1** at the B3LYP level led to minima with $\theta = 180.0$ and $52.4°$ (syn-gauche$^+$), the latter minimum being less stable than the former one by 1.9 kcal/mol. The values of D_{S-O}, 2.925 and 4.486 Å, respectively, suggest that the planarity of **1** is partially due to the existence of attractive S···O interactions. Indeed, the value of D_{S-O} determined at the B3LYP level for this compound is in excellent agreement with those determined by X-ray crystallography ($D_{S-O} = 2.92$ Å)[27,28] and MP2 geometry optimization ($D_{S-O} = 2.925$ Å).

To provide a better description of the influence of the S···O inter-ring interactions in EDOT-containing oligomers and polymers, calculations were performed on three dimers constructed by replacing partially (**4** and **5**) or totally (**6**) the oxygen atoms of **1** by methylene units. Results, which are provided in Table 1, seem to corroborate the conclusions extracted from the parent compound **1**. Therefore, an ideal planar anti conformation is the lowest energy minimum for **4** at the B3LYP level, the syn-gauche$^+$ being destabilized by 1.9 kcal/mol. However,
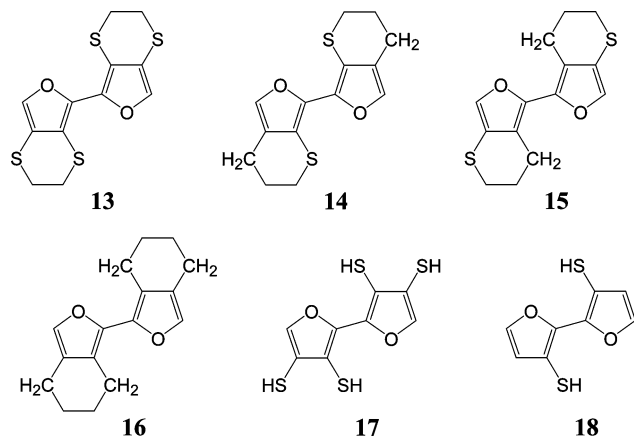
MP2 calculations predict a distortion of 18° for the anti minimum, even though the resulting θ value is significantly higher than that obtained for **3** (Table 1). In contrast, the replacement of the oxygen atom closest to the sulfur by a methylene unit (**5** and **6**) produces a very significant deformation of the planar arrangement, and the only minimum obtained at both the B3LYP and MP2 levels is a gauche−gauche arrangement with $\theta \approx 90°$. Therefore, as expected, the conformational preferences of these compounds, which cannot form S···O interactions, are determined by unfavorable steric repulsions.
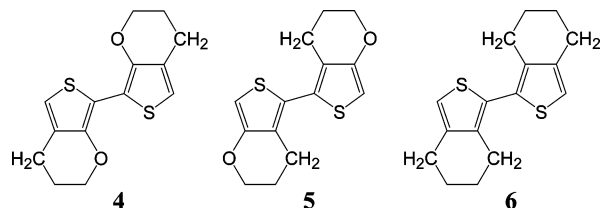
The influence of the cyclic nature of the substituent as well as the strength of the electron donation effects, which is related to the position of the oxygen atoms, on the planarity of **1** were examined by calculating dimers **7−12**. In these compounds, the geometric strain induced by the dioxane ring has been eliminated, even though oxygen atoms able to form S···O interactions are still present in some of them (**7**, **8**, and **12**). Results obtained for **7** and **8** at the B3LYP level (Table 1) are fully coincident with those provided for **1** and **4**, whereas distortions from the planarity are obtained for **9−12**. In contrast, MP2 calculations provide significant deviations from the planarity for all of these compounds, including **7** and **8**. Indeed, although both S···O interactions and electron-donating effects may be present, the distortions predicted for the three latter dimers are 26.4 and 30.4°, respectively. From the results obtained, especially by comparing **8**, **9**, and **10** with **3**, it can be concluded that a hydroxyl group in position three of the thiophene ring favors planarity, whereas that at positions four and five disfavors it.
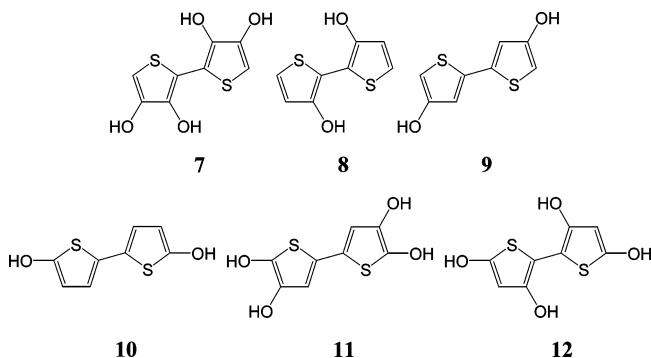
The role and strength of the electron donation exerted by the oxygen atoms in **1**, **4**, **5**, **7**, and **8** have been also investigated by determining the minimum energy conformations of **13−18**, which were constructed by interchanging the positions of sulfur and oxygen atoms. As can be seen, both B3LYP and MP2 calculations predict that the planar anti conformation is the lowest energy minimum in all cases (even for cases where S···O interactions are not possible, i.e., **15** and **16**) with the exception of **17** and **18**, where a distortion of 33.3 and 34.8° is obtained at the MP2 level.

Figure 2. Potential energy curves for the internal rotation of **1**, **3**, and **7**−**11** as a function of the inter-ring dihedral angle θ using B3LYP/6-311++G(d,p) geometry optimizations. In all cases energies (in kilocalories per mole) are relative to the anti conformation.

These furane derivatives present some significant differences with respect to the corresponding thiophene analogues, which can be summarized as follows: (i) the distance D_{S-O} measured for the minimum with anti conformation is slightly larger ($\sim$0.2 and $\sim$0.1 Å at the B3LYP and MP2 levels, respectively) for the former than for the latter compounds; (ii) in the syn-gauche local minimum, the deviation of θ with respect to the planarity is larger for the thiophene derivatives than for the furane derivatives (compare **1**, **7**, and **8** with respect to **13**, **17**, and **18**, respectively), with the difference between the two sets of compounds ranging from 4.7 to 12.6°; and (iii) dimers **15** and **16**, in which at least one heteroatom of the six-membered ring substituent has been replaced by a methylene group, show two minima at the anti and syn-gauche arrangements, whereas the only minimum found for **5** and **6** was the gauche−gauche conformation. Overall, these results suggest that, although attractive S$\cdots$O interactions are also possible in **13**−**18**, the particular conformational properties calculated for these compounds should be mainly attributed to the interfurane π-conjugation and the electron-donating effects of the sulfur atoms. Therefore, it seems that the planarity of **1** should be mainly attributed to both the electron-donating effects of the oxygen atoms, which are larger than those induced by sulfur atoms, and the geometric restraints imposed by the dioxane ring rather than to attractive S$\cdots$O inter-ring interactions.

Substitution of the four oxygen atoms of **1** by sulfur atoms (compound **19**) led to a minimum energy conformation with $\theta \approx 90-100°$ (Table 1). This result is evidence of repulsive character of the S$\cdots$S interactions, which are strong enough to distort the planar anti minimum of **1** by $\sim$90°. This feature is in opposition to the self-rigidification concept proposed for PEDOT, which was based on attractive S$\cdots$O interactions.[27−29] Therefore, the origin of such noncovalent intramolecular interactions was based on the fact that the S$\cdots$O distance was shorter than the sum of the van der Waals radii of sulfur and oxygen. However, in **19**, the S$\cdots$S distance is significantly larger in the gauche−gauche minimum (4.146 Å) than in the planar anti conformation (2.853 Å), which is not a minimum in the potential energy surface of this compound, reflecting the repulsive character of the interaction.
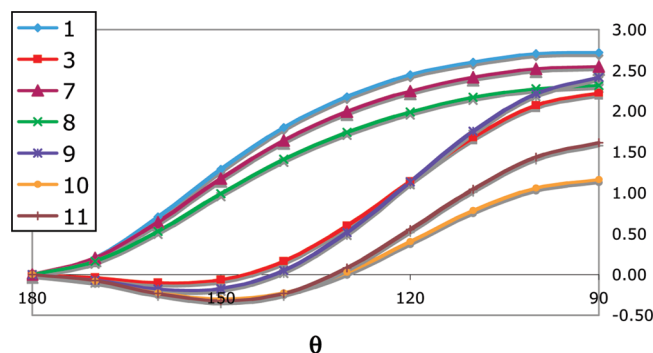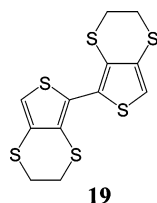
Compounds **20** and **21** have been calculated to evaluate the strength of the inter-ring π-conjugation in the absence of both the electron-donation effects induced by the heteroatoms and the conformational restraints imposed by the six-membered ring. Results (Table 1) are fully consistent with the conclusions derived from **13**−**18**. Therefore, the syn-gauche and gauche−gauche minima predicted for **20** at the B3LYP and MP2 levels, respectively, clearly indicate that π-conjugation effects are significantly stronger in **21**, which shows an antigauche minimum at the two theoretical levels. Moreover, the θ values obtained at the B3LYP and MP2 levels for the latter compound again reflect the overestimation of π-conjugation effects by the DFT method.
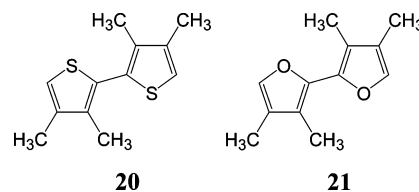

We examined the influence of the strain of the fused ring by considering **22**. Comparison of the results obtained for **1** and **22** reveals that the anti conformation is destabilized upon decreasing the size of the dioxane ring. This is evidenced not only by the reduction of the relative energy of the syn-gauche conformation but also by the distortion from the planarity predicted at the MP2 level for **22**. The geometrical restraints imposed by the 1,3-dioxolane ring increases the values of D_{S-O} with respect to those obtained for **1** by 0.355 and 0.468 Å at the B3LYP and MP2 levels.
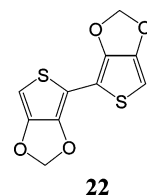
Rotational Profiles and Simple Model Complexes. The rotational profile calculated for **1** at the B3LYP level is displayed in Figure 2. The global minimum at $\theta = 180.0°$ is stabilized by $\sim$3 kcal/mol with respect to the gauche−gauche barrier at $\theta = 90°$. This energy difference indicates that, if attractive, the contribution of each of the two S$\cdots$O interactions to the stability

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of the planar anti conformation is <1.5 kcal/mol. This is because the π-conjugation is broken when the planar arrangement transforms into the perpendicular one, ensuring an unfavorable energy contribution. We estimated a more precise description of the role of the latter contribution by calculating the $H_2S\cdots OH_2$ complex (**23**), which should be considered to be a simple model system of **1** but without π-conjugation. Complete geometry optimization at the B3LYP level led to a minimum (not shown) stabilized by a S−H⋯O hydrogen bond (the H⋯O distance and <S−H⋯O angle are 2.157 Å and 178.3°, respectively), the sulfur and oxygen atoms being separated by $D_{S-O} = 3.510$ Å. In contrast, a partial geometry optimization in which the relative positions of the sulfur and oxygen atoms located at adjacent rings were kept identical to those obtained in the lowest energy minimum of **1**, that is, $D_{S-O} = 2.925$ Å, led to a repulsive complex that is destabilized by 1.8 kcal/mol with respect to separated reactants. However, optimization allowing the variation of D_{S-O} but fixing the relative disposition of the two heteroatoms, as was determined in **1**, converged in a complex with $D_{S-O} = 3.200$ Å, which is stabilized by −1.3 kcal/mol.

23
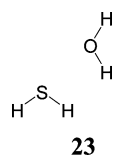
To analyze the S⋯O interaction, NBO analyses were performed for the planar anti conformation of **1** and complex **23**. For the former model compound, no hyperconjugation was detected between the lone pairs of the sulfur atom and the $\sigma_{OC}*$, whereas the lone pairs of the oxygen atom contribute 0.87 kcal/mol to the $\sigma_{SC}*$. Results for complex **23**, which were calculated considering the relative positions of the sulfur and oxygen atoms identical to those obtained in the planar anti conformation of **1**, indicated a stabilizing contribution of 0.40 kcal/mol from the electron lone pairs of the sulfur atom to the $\sigma_{OH}*$ and of 1.89 kcal/mol from the electron lone pairs of the oxygen atom to the $\sigma_{SH}*$. These results show small hyperconjugation effects for the two systems, although slightly higher for model **23** despite the fact that the interaction is repulsive. This result indicates that hyperconjugation is not an important factor for explaining the planarity of species **1**.

The rotational profiles $E = E(\theta)$ calculated for **3** and **7−11** at the B3LYP level, which are included in Figure 2, confirm the results provided in the previous section. Therefore, the potential surface obtained for **8** fits that of **1**. The most remarkable difference corresponds to the energy barrier, which is 0.40 kcal/mol higher for the latter than for the former. In contrast, the minimum predicted for **3**, **9**, and **10** deviates from the planarity by 27.1, 29.1, and 30.0°, respectively. Although these features may suggest the existence of stabilizing S⋯O interactions in **1** and **8**, it should be noted that the DFT method used in this work overestimates the planarity of **8**, as was evidenced above (Table 1). Furthermore, the energy barriers predicted for **3** and **9** (2.32 and 2.59 kcal/mol, respectively) are almost identical to that of **8**, allowing us to either discard the possible existence of such interactions or assume that they are very weak. Similarly, the rotational profile of **11** (Figure 2), in which hydroxyl groups are attached to positions four and five of each thiophene ring, shows an energy barrier (1.94 kcal/mol) that is halfway between those of **9** and **10**. In contrast, when the hydroxyl groups are attached to positions three and four of
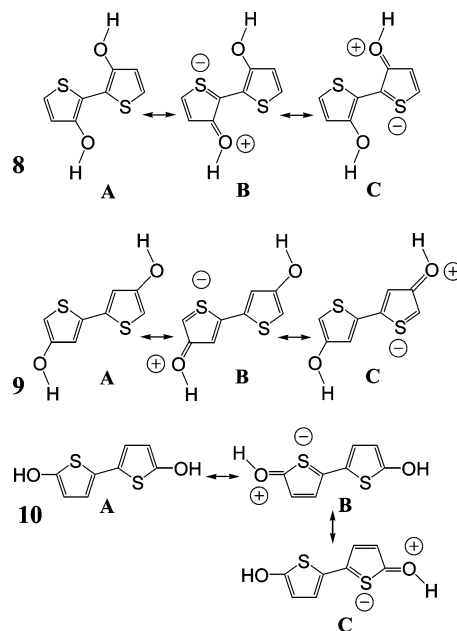

Figure 3. Representative canonical forms for **8**, **9**, and **10**.

the thiophene ring, as in **7**, the whole profile almost matches that calculated for **1**.

The electron donation effects induced by the oxygen atoms are expected to promote the participation of different canonical forms in the description of each of the hydroxylated model compounds. However, comparison of the dihedrals obtained at the B3LYP and MP2 for the lowest minimum energy conformation (Table 1) indicates that the contribution of these charged forms, which are displayed in Figure 3 for **8**, **9**, and **10**, is significantly overestimated by the former method. Despite this, results displayed in Figure 2 and Table 1 provide evidence of the participation of the charged canonical forms B and C depending on the position of the hydroxyl substituent. Therefore, this contribution is small for **9** and **10**, as reflected by the fact that the θ predicted at the MP2 level for the global minimum of these compounds is very similar to that obtained for **3**. In contrast, for **8**, the dihedral angle θ increases 15.4° with respect to that of **3**, and this behavior is partially attributed to the electrostatic attraction between the charges on the oxygen and sulfur atoms that are relatively close (Figure 3). Finally, the $NICS(1)_{zz}$ values calculated for the thiophene ring of the different hydroxylated derivatives indicate aromaticity for compounds **1** (−19.18 ppm), **7** (−18.91 ppm), and **8** (−20.02 ppm), all of them presenting both the S⋯O interaction and a planar conformation. NICS indicates lower aromatic character for **9**, **10**, and **11** (−16.97, −15.76, and −13.66 ppm, respectively), all of them nonplanar and without an OR substituent in position three. For comparison, compound **3** (−20.34 ppm) presents the highest aromaticity, thus proving that the OH groups cause a decrease in aromaticity in all positions; however, when the OR group is in position three, this reduction is smaller, and the systems prefer the planar conformation.

Our conclusion is that the final θ angle in **1** and related species depends on the interplay of two main factors. First, Pauli repulsions between electron pairs of the S and O atoms promote nonplanar structures. Second, conjugation along the two thiophene rings tends to form planar species. Because these two factors are, from an energetic point of view, relatively small and they compensate each other, flat θ energy profiles are, in general, obtained for these species. Conjugation effects are more important than Pauli repulsions in species having an OR group

in position three of the thiophene ring because, in these cases, there is almost no reduction of aromaticity of the thiophene ring due to the OR substituent, and there is some $S^{\delta+}\cdots O^{\delta-}$ charge separation that helps to reduce the $S\cdots O$ repulsion. As a consequence, the planar conformation is the most stable for these systems. Finally, as we have discussed before, hyperconjugation does not seem to play a key role in determining the θ angle.

Conclusions

The results presented in this work indicate that the planarity of **1** and by extension the rigidification of PEDOT are mainly due to the restrictions imposed by the fused dioxane ring and to the electron-donating effects provided by the oxygen atoms contained in such cyclic substituent. Calculations on model molecules and complexes did not detect the previously proposed attractive intramolecular noncovalent $S\cdots O$ interaction.[27−30] Indeed, calculations on model complex **23** suggest that the $S\cdots O$ interaction is somewhat destabilizing for **1**, that is, about 2 kcal/mol, which should be attributed to Pauli repulsions between the shared electron pairs of these heteroatoms. However, the π-conjugation of the planar anti conformation induced by the cyclic substituent and the electron-donating effects provided by the oxygen atoms attached to positions three and four (especially the former) of each thiophene ring allows the compensation of such unfavorable energy contribution because of some gain in aromaticity and more electrostatic favorable interactions. It is worth noting that the potential energy surfaces of the systems under study are extremely flat, and the energy differences between the planar anti and both of the partially folded antigauche$^+$ conformations are very small, that is, <0.5 kcal/mol. Moreover, the energy barrier and the syn-gauche local minimum are also very energetically close. Accordingly, the inter-ring π-conjugation is drastically affected by small variations in the electronic effects induced by the substituents.

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