

# A theoretical study on the interaction between *N*-methylpyrrole and 3,4-ethylenedioxythiophene units in copolymer molecules

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## Abstract

Quantum mechanical calculations at the density functional theory level have been used to examine the interaction between 3,4-ethylenedioxythiophene and *N*-methylpyrrole units when they are directly linked in copolymer chains. Specifically, in this study, which was motivated by experimental observations of electrochemically synthesized copolymers, the conformation and electronic properties of co-oligomers formed by two, three and four units have been examined in both neutral and radical cation states. Results reveal significant differences, especially in the radical cation state, between the co-oligomers and the corresponding individual homo-oligomers, which have also been explored considering the same theoretical method. Furthermore, electronic properties of oligomers have been used to estimate those of poly(3,4-ethylenedioxythiophene), poly(*N*-methylpyrrole) and the copolymer with alternated structure, which have been compared among them. The overall results allowed to understand the anomalous features detected in copolymers prepared by electrochemical techniques from 3,4-ethylenedioxythiophene and *N*-methylpyrrole mixtures, which were initially attributed to some type of *unfavourable* interaction between the two types of monomeric units. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Polythiophene; Poly(*N*-methylpyrrole); Conducting polymer

## 1. Introduction

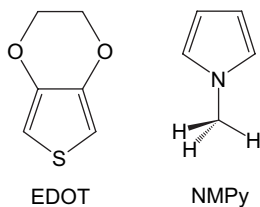
Poly(3,4-ethylenedioxythiophene), abbreviated as PEDOT, is the most successful polythiophene derivative because of its interesting properties [1–8]. Thus, its high conductivity and excellent environmental stability in the oxidized state have promoted the use of PEDOT in a number of applications, *e.g.* antistatic coatings for photographic films, electrode material in inorganic electroluminescent lamps, material for through-hole plating of printed circuit boards, etc. [1–3]. Furthermore, PEDOT was found to be a very promising material for biomedical applications since it can be successfully used as

support for cell attachment and proliferation [9], its electroactivity being significantly enhanced when contact with the cells. In addition, we recently reported that PEDOT is also able to form specific interactions with DNA [10], which were determined using restriction enzymes.

Electrochemical synthesis of PEDOT has been studied in detail considering different conditions and/or substrates [2,4–10]. Furthermore, copolymers of 3,4-ethylenedioxythiophene (EDOT, see Scheme 1) with other simple heterocyclic monomers, *i.e.* thiophene or pyrrole derivatives, have been successfully prepared by direct electrochemical oxidation of the corresponding mixtures [6,10–15]. Within this context, we recently reported on the electrochemical, structural and physical properties of copolymers electrochemically synthesized from EDOT and *N*-methylpyrrole (NMPy, see Scheme 1) on steel electrodes [14,15]. Copolymers of EDOT and NMPy, hereafter denoted poly(EDOT-*co*-NMPy), were prepared by

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Scheme 1.

chronoamperometry under a constant potential of 1.4 V using monomer mixtures with different concentration ratios [14]. Elemental analyses of the generated films showed that the molar ratio of EDOT in the organic phase of the copolymers was considerably smaller than in the generation media, while the molar proportion of NMPy was higher in the copolymer than in the generation media. This feature was fully consistent with the diffusion coefficients ( $D$ ) determined for EDOT and NMPy, *i.e.*  $D(\text{NMPy}) > D(\text{EDOT})$ .

On the other hand, comparison of the chronoamperograms obtained for the oxidation of different mixtures of EDOT and NMPy with those obtained for pure monomer solutions (the total concentration of monomers was kept identical in all cases) revealed that the current density stabilizes at lower values for poly(EDOT-*co*-NMPy) than for the individual polymers. This suggests the existence of some type of unfavourable interaction between EDOT and NMPy monomers that hinders the growing of copolymer chain reducing the success in the formation of poly(EDOT-*co*-NMPy) [14]. This unfavourable interaction was also evidenced by the doping level that, in general, was lower for the copolymers than for both PEDOT and poly(*N*-methylpyrrole) (PNMPy). Furthermore, cyclic voltammetry experiments indicated that the electroactivity of the copolymers decreases when the concentration of NMPy increases and the electrochemical stability of poly(EDOT-*co*-NMPy) is significantly smaller than that of the two homopolymers.

The overall results suggest that the interaction between EDOT and NMPy monomers in the copolymer should be examined by using theoretical methods able to explain at the atomistic level the anomalous observations previously described. It should be noted that the electronic properties of PNMPy [16,17] and, especially, PEDOT [18–22] were previously examined by applying Density Functional Theory (DFT) and *ab initio* quantum mechanical methods to model oligomers. In this work we present DFT calculations on model co-oligomers formed by EDOT and NMPy that allow to explain some experimental observations for poly(EDOT-*co*-NMPy) previously described [14,15]. More specifically, the following systems have been analyzed in both neutral and radical cation states: EDOT–NMPy (**1** and **1**<sup>+</sup>), NMPy–EDOT–NMPy (**2** and **2**<sup>+</sup>), EDOT–NMPy–EDOT (**3** and **3**<sup>+</sup>) and NMPy–EDOT–NMPy–EDOT (**4** and **4**<sup>+</sup>).

## 2. Computational methods

All calculations were done with the PC-Gamess program [23] and Gaussian 03 package of programs [24]. The Becke's

three-parameter hybrid functional (B3) [25], combined with the non-local correlation provided by Perdew and Wang's (PW91) [26], and the 6-31 + G(d,p) [27] basis set were employed for the calculations. In all cases, quantum-chemical calculations on the neutral state (closed-shell system) and the radical cation (open-shell system) were performed considering the restricted (B3PW91) and unrestricted (UB3PW91) formalisms. It should be noted that the B3PW91 functional provides a very satisfactory description of the molecular and electronic structures of heterocyclic derivatives of pyrrole and thiophene in both neutral and radical cation states [17,18,22].

The conformational space of all the investigated compounds with exception of **4**<sup>+</sup> was rigorously sampled by applying a multidimensional conformational analysis (MDCA) method. For this purpose, all the *theoretical minima* of each compound were constructed by considering that each interring dihedral angle, hereafter denoted  $\theta_i$  (where  $i$  ranges from 1 to  $n-1$ ,  $n$  being the number of monomeric units in the co-oligomer), can adopt the following four arrangements described below:  $ag^+$ ,  $ag^-$ ,  $sg^+$  and  $sg^-$ . Accordingly, the number of *theoretical minima* was 4 for **1** and **1**<sup>+</sup>;  $4 \times 4 = 16$  for **2**, **2**<sup>+</sup>, **3** and **3**<sup>+</sup>; and  $4 \times 4 \times 4 = 64$  for **4**. All these *theoretical minima* were used as starting structures for full geometry optimizations at the (U)B3PW91/6-31 + G(d,p) level. All geometry optimizations were performed with the Berny algorithm using redundant internal coordinates and the default convergence criteria. Unfortunately, a complete conformational search of **4**<sup>+</sup> was not possible since calculations at the UB3PW91/6-31 + G(d,p) level on radical cation tetramers require a huge amount of computational resources. In order to overcome this limitation, calculations on **4**<sup>+</sup> were restricted to more important conformations (see Section 4). On the other hand, calculations on homo-oligomers of EDOT and NMPy were performed at the (U)B3PW91/6-31 + G(d,p) level to calculate their structural and electronic properties at this computational level. In some cases, the coordinates reported in previous studies [17–19,22], which were obtained by applying other theoretical methods were used as starting geometries.

The minimum energy conformations of the compounds studied in this work have been denoted using a label code that specifies the arrangement of each inter-ring dihedral angle. These arrangements are: *anti* (*a*) with  $\theta = 180^\circ$ , *anti-gauche*<sup>+</sup> ( $ag^+$ ) with  $\theta \approx +150^\circ$ , *anti-gauche*<sup>-</sup> ( $ag^-$ ) with  $\theta \approx -150^\circ$ , *syn-gauche*<sup>+</sup> ( $sg^+$ ) with  $\theta \approx +30^\circ$ , *syn-gauche*<sup>-</sup> ( $sg^-$ ) with  $\theta \approx -30^\circ$  and *syn* (*s*) with  $\theta = 0^\circ$ . For example, the minima of **4** and **4**<sup>+</sup> are described by the label codes of the three consecutive inter-ring dihedral angles. On the other hand, it should be noted that the  $ag^+$  and  $ag^-$  are degenerated and equivalent minima in homo-dimers of EDOT and NMPy, these structures being described together by using the label code  $ag^\pm$ . Similarly,  $sg^\pm$  refers to the equivalent and degenerated  $sg^+$  and  $sg^-$  minima. In all cases the inter-ring angles  $\theta_i$  were calculated using the sequence X–C–C–Y, where X and Y correspond to the heteroatoms of adjacent cycles.

Formally, Koopman's theorem (KT) does not apply to DFT since the Kohn–Sham orbital energies do not carry any physical meaning. However, using Janak's theorem [28,29], which provides a meaning for the eigenvalues of the Kohn–Sham equation, Perdew [30] showed a connection between ionization potentials (IPs) and electron affinities (EAs) to the HOMO and LUMO energies, respectively, in DFT, *i.e.*  $IP = -\varepsilon_{\text{HOMO}}$  and  $EA = -\varepsilon_{\text{LUMO}}$ . On this basis, B3PW91 calculations have been shown to provide  $\pi$ – $\pi^*$  transition energies ( $\varepsilon_g$ ), which were calculated as the difference between the HOMO and LUMO energies, *i.e.*  $\varepsilon_g = \varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}}$ , lying between pure density functionals and Hartree–Fock results [29,31–33]. On the other hand, more accurate IP values were obtained using the energies of the fully relaxed neutral and ionized species. This approach, usually denoted by  $\Delta\text{SCF}$ , takes into account the relaxation energy of the ionized state, which can be calculated as the difference between the KT and  $\Delta\text{SCF}$  IPs [34,35].

### 3. Theoretical background on homo-oligomers of EDOT and NMPy

Although the conformational properties of homo-oligomers formed by EDOT and NMPy were previously reported [16–22], some of such compounds have been re-investigated in this work at the (U)B3PW91/6-31 + G(d,p) computational level. The results provided by these additional calculations are very similar to those previously reported and, therefore, they will not be detailed in Section 4. In spite of this, the main characteristics of homo-oligomers are summarized in this section to facilitate the comparison with co-oligomers.

The all-*anti*, in which all the inter-ring dihedral angles are arranged at  $180^\circ$ , is the most favourable conformation of neutral homo-oligomers formed by EDOT. This is an important difference with respect to the *ag* arrangements typically found in both simple thiophene derivatives [36–38] and polycyclic systems formed by units with fused rings [39,40]. Thus, in EDOT-containing homo-oligomers the oxygen atoms attached at the 3- and 4-positions exert an electron-donating effect that stabilizes the planar *anti* arrangement by increasing the interannular  $\pi$ -conjugation. A conformational analysis of EDOT–EDOT dimer showed two degenerated local minima at  $\theta = +50^\circ$  and  $-50^\circ$  ( $sg^\pm$ ), which were about 2 kcal/mol less stable than the *anti* one. On the other hand, the all-*anti* is also the most stable arrangement of charged homo-oligomers formed by EDOT, the *sg* conformations with  $\theta \approx \pm 23^\circ$  being slightly less stable in the radical cation state than in the neutral one. This must be attributed to the reduction of the inter-ring bond length upon oxidation, which produces an enhancement of the repulsive interactions between heteroatoms of neighboring rings.

On the other hand, the inter-ring dihedral angles of NMPy-containing homo-oligomers prefer the *ag* arrangements, even though they are significantly different from those found for unsubstituted pyrrole-containing compounds. Specifically,  $\theta$  is about  $\pm 128^\circ$  for NMPy derivatives, the resulting conformers being about  $\sim 23^\circ$  less planar than those typically determined for pyrrole homo-oligomers. Furthermore, calculations on the

NMPy–NMPy dimer indicated that the *sg* is not local minima. The reason for these conformational preferences has to be found in the repulsive steric interactions generated by the methyl groups. Thus, the high degree of folding produced by the *N*-methyl substitution, *i.e.* loss of planarity, was used to explain the small conductivity of PNMPy [15,41]. Oxidation of homo-oligomers formed by NMPy leads towards structures with significant quinoid character, in which the inter-ring bond lengths present a certain degree of double bond character. Consequently, the  $ag^+$  and  $ag^-$  conformations, which are the most favored ones, become less folded, even though positively charged NMPy-containing homo-oligomers are not able to adopt the planar all-*anti* conformation. Furthermore, the partial double bond character of the inter-ring bond lengths stabilizes the  $sg^+$  and  $sg^-$  arrangements as local minima. Thus, calculations on NMPy–NMPy $^{+\bullet}$  allowed to characterize the *ag* ( $\theta = \pm 162.4^\circ$ ) and *sg* ( $\theta = \pm 30.5^\circ$ ) minima, the latter being less stable than the former by 3.9 kcal/mol.

## 4. Results

### 4.1. EDOT–NMPy

Table 1 lists the inter-ring dihedral angle, relative energy and  $\varepsilon_g$  for the minimum energy conformations obtained for **1** and **1** $^{+\bullet}$ . As can be seen, the conformational characteristics of the neutral and positively charged dimers differ significantly, even though three minima were characterized in each case.

The lowest energy arrangement of **1** corresponds to the  $ag^-$  conformation. In the  $ag^+$  minimum the sign of  $\theta$  is changed with respect to that of  $ag^-$  while the twist conformation of the dioxane ring is identical in the two cases. The interaction between the methyl substituent and the dioxane ring is slightly worse in the  $ag^+$  than in the  $ag^-$ , the former being unfavored by 0.2 kcal/mol. This small difference, which is consequence of the non-planar conformation of the dioxane ring, is non-significant and has a negligible effect on the  $\varepsilon_g$  value. The third minimum of the neutral state, which is destabilized by 1.2 kcal/mol, corresponds to the  $sg^-$  conformation. This is an expected result since the *sg* arrangements are typically unfavored with respect to *ag* ones in dimers of both thiophene and pyrrole derivatives. Furthermore, the data of Table 1 indicate that the destabilization of the  $sg^-$  conformation with respect to the other two minima is accompanied by a loss of the  $\pi$ -conjugation, which is reflected by a small increase of the  $\varepsilon_g$  value, *i.e.* about 0.2 eV [1,2]. It is worth noting that

Table 1  
Inter-ring dihedral angle ( $\theta$ , in degrees), relative energy ( $\Delta E$ , in kcal/mol) and energy gap ( $\varepsilon_g$ , in eV) of the minimum energy conformations calculated for the EDOT–NMPy in both neutral and charged states (**1** and **1** $^{+\bullet}$ , respectively)

Neutral state				Charged state (+1)			
Conf.#	$\theta$	$\Delta E$	$\varepsilon_g$	Conf.#	$\theta$	$\Delta E$	$\varepsilon_g$
$ag^-$	-127.1	0.0	4.71	<i>s</i>	0.8	0.0	1.84
$ag^+$	127.1	0.2	4.72	$ag^-$	-158.0	2.8	1.81
$sg^-$	-68.3	1.2	4.90	$ag^+$	158.6	3.4	1.81

no minima with  $sg^+$  conformation were detected because of the repulsive interactions between the methyl group and the closest oxygen atom of the dioxane ring.

On the other hand, calculations on  $\mathbf{1}^{\bullet+}$  revealed significant conformational differences with respect to the charged homodimers EDOT–EDOT $^{\bullet+}$  and NMPy–NMPy $^{\bullet+}$  (see above). Thus, the planar  $s$  conformation was identified as the lowest energy minimum of  $\mathbf{1}^{\bullet+}$ , the  $ag^-$  and  $ag^+$  arrangements being significantly destabilized, *i.e.* 2.8 and 3.4 kcal/mol, respectively. It is worth noting that the tendency of the  $ag^-$  and  $ag^+$  minima to adopt a planar arrangement after oxidation of  $\mathbf{1}$  is significantly smaller than that of the  $sg^-$ . Thus, the inter-ring dihedral angle  $\theta$  decreases almost 70° in the latter conformation. This is fully consistent with the inter-ring bond lengths calculated for the three minima of  $\mathbf{1}^{\bullet+}$ , *i.e.* 1.411, 1.412 and 1.406 Å for the  $ag^-$ ,  $ag^+$  and  $s$ , respectively, which indicate that the global minimum presents the highest degree of quinoid structure. Thus, the inter-ring bond length of the  $ag^-$  and  $ag^+$  minima decreases by about 0.043 Å after oxidation of  $\mathbf{1}$  while a reduction of 0.051 Å is observed when the  $sg^-$  transforms into the  $s$  minimum. It is worth noting that the  $\epsilon_g$  value of  $\mathbf{1}^{\bullet+}$  is almost independent of the molecular conformation. Within this context, comparison between the neutral and charged dimer indicates that, as expected,  $\epsilon_g$  is significantly lower for the latter. Thus, DFT calculations predict that oxidation reduces the gap by more than a half, *i.e.*  $\epsilon_g$  decreases by about 3 eV.

#### 4.2. NMPy–EDOT–NMPy

Geometry optimizations of the starting structures considered for  $\mathbf{2}$  and  $\mathbf{2}^{\bullet+}$  led to six minima, which are described in Table 2. Regarding the neutral state, the three conformations with the two inter-ring dihedral angles arranged in  $ag^+$  and/or  $ag^-$  are separated by less than 0.5 kcal/mol, the most stable being the  $ag^-–ag^-$  one. The remaining three minima, which are destabilized by about 1 kcal/mol with respect to the global minimum, show at least one inter-ring dihedral angle arranged in  $sg^+$  or  $sg^-$ . According to these results, the six minima listed in Table 2 participate in the Boltzmann distribution that describes the conformational preferences of  $\mathbf{2}$ . Thus, the population of conformations with the two inter-ring dihedral angles arranged in  $ag$  is 81% (the largest contribution, 38%, corresponds to the global minimum), while the population of conformations with at least one inter-ring dihedral angle

arranged in  $sg$  is 19%, which is not a negligible value. Inspection to the gap energies reveals that  $\epsilon_g$  ranges from 4.05 to 4.35 eV. Amazingly, the  $ag^+–ag^+$  and  $ag^-–ag^-$  minima, which were expected to present the higher degree of interannular  $\pi$ -conjugation, show the higher values of  $\epsilon_g$  (4.35 and 4.34 eV, respectively). On the other hand, no correlation between  $\epsilon_g$  and either the relative energy or the degree of planarity predicted for the different minima was detected.

However, the most striking results are those obtained for the radical cation state. Thus, inspection of Table 2 reveals that the global minimum of  $\mathbf{2}^{\bullet+}$  corresponds to a planar structure with the two inter-ring dihedral angles arranged in  $s$ , the next minimum,  $ag^-–s$ , being unfavored by 1.5 kcal/mol. The relative energies of the four remaining minima range from 2.0 to 5.6 kcal/mol. Interestingly, the less stable conformations are those with the two inter-ring dihedral angles arranged in  $ag$ . According to the Boltzmann distribution of minima, the conformation of  $\mathbf{2}^{\bullet+}$  is described by only three states: 90% of  $s–s$ , 7% of  $ag^-–s$  and 3% of  $ag^+–s$ . On the other hand, it is worth noting that the  $\epsilon_g$  gap, which ranges from 1.41 to 1.44 eV, does not depend on the conformation. Oxidation of  $\mathbf{2}$  to  $\mathbf{2}^{\bullet+}$  produces a gap reduction of about 2.8 eV, this value being very close to that calculated for the oxidation of  $\mathbf{1}$ .

#### 4.3. EDOT–NMPy–EDOT

Table 3 lists the inter-ring dihedral angles and energy gaps calculated for the six minimum energy conformations of  $\mathbf{3}$  and  $\mathbf{3}^{\bullet+}$ . The lowest energy minimum of  $\mathbf{3}$ , with a population of 49%, corresponds to the  $ag^+–ag^-$ , the relative energies of the  $ag^+–ag^+$  and  $ag^-–ag^-$  conformations being 0.4 and 0.9 kcal/mol, respectively. The  $ag^-–sg^-$  is unfavored by only 0.8 kcal/mol, while the other two minima with inter-ring dihedral angles arranged in  $sg$  are destabilized by 2.0 kcal/mol. Accordingly, the population of the conformations with at least one dihedral angle arranged in  $sg$  amounts to 17%, which is very close to the value found for  $\mathbf{2}$ . The  $\epsilon_g$  values range from 4.18 to 4.59 eV, this range of variation being also similar to that predicted for  $\mathbf{2}$ . Again, no correlation between the conformational and gap energies was detected.

Inspection of results obtained for the radical cation state reveals a remarkable difference between  $\mathbf{3}^{\bullet+}$  and the two charged compounds described above. It is worth noting that, in this case, the inter-ring dihedral angles associated to the  $s$  arrangement deviate by about 12°–17° from planarity. Thus,

Table 2

Inter-ring dihedral angle ( $\theta$ , in degrees), relative energy ( $\Delta E$ , in kcal/mol) and energy gap ( $\epsilon_g$ , in eV) of the minimum energy conformations calculated for the NMPy–EDOT–NMPy in both neutral and charged states ( $\mathbf{2}$  and  $\mathbf{2}^{\bullet+}$ , respectively)

Neutral state					Charged state (+1)				
Conf.#	$\theta_1$	$\theta_2$	$\Delta E$	$\epsilon_g$	Conf.#	$\theta_1$	$\theta_2$	$\Delta E$	$\epsilon_g$
$ag^-–ag^-$	–127.4	–127.4	0.0	4.34	$s–s$	1.8	1.8	0.0	1.44
$ag^+–ag^-$	129.4	–129.2	0.2	4.08	$ag^-–s$	–152.0	–5.2	1.5	1.43
$ag^+–ag^+$	–127.8	127.9	0.5	4.35	$ag^+–s$	151.7	7.2	2.0	1.43
$ag^-–sg^+$	–127.9	43.0	1.0	4.12	$ag^+–ag^-$	150.5	–150.9	3.7	1.42
$ag^+–sg^+$	128.3	48.3	1.1	4.05	$ag^-–ag^-$	–155.2	–155.2	4.6	1.41
$ag^-–sg^-$	–128.3	–55.1	1.1	4.17	$ag^+–ag^+$	155.6	155.6	5.6	1.42

Table 3  
Inter-ring dihedral angle ( $\theta$ , in degrees), relative energy ( $\Delta E$ , in kcal/mol) and energy gap ( $\epsilon_g$ , in eV) of the minimum energy conformations calculated for the EDOT–NMPy–EDOT in both neutral and charged states (**3** and **3**<sup>+</sup>, respectively)

Neutral state					Charged state (+1)				
Conf.#	$\theta_1$	$\theta_2$	$\Delta E$	$\epsilon_g$	Conf.#	$\theta_1$	$\theta_2$	$\Delta E$	$\epsilon_g$
$ag^+ - ag^-$	131.0	−131.6	0.0	4.14	$sg^+ - sg^-$	16.8	−15.8	0.0	1.48
$ag^- - ag^-$	−125.7	−123.3	0.4	4.43	$ag^- - sg^-$	−152.7	−12.9	0.5	1.47
$ag^- - sg^-$	−131.2	−57.5	0.8	4.18	$ag^+ - sg^+$	152.0	14.2	1.0	1.47
$ag^+ - ag^+$	123.7	124.9	0.9	4.46	$ag^+ - ag^-$	153.2	−152.8	2.5	1.46
$ag^+ - sg^-$	124.4	−69.5	2.0	4.59	$ag^- - ag^-$	148.9	−148.0	4.9	1.46
$sg^+ - sg^-$	55.9	−63.3	2.0	4.27	$ag^+ - ag^+$	147.8	148.2	6.2	1.46

in spite of its quinoid structure,  $sg^+$  and  $sg^-$  are clearly identified in the lower energy arrangements of **3**<sup>+</sup>, which should be attributed to the strong steric interactions between the methyl group of the NMPy unit and the neighboring dioxane rings. The lowest energy conformation is the  $sg^+ - sg^-$ , the  $ag^- - sg^-$  and  $ag^+ - sg^+$  being destabilized by 0.5 and 1.0 kcal/mol. Furthermore, again the conformations with the two inter-ring dihedral angles arranged in  $ag$  are significantly unfavored with respect to the global minimum, *i.e.* more than 2.5 kcal/mol. On the other hand, the  $\epsilon_g$  gap is similar to that predicted for **2**<sup>+</sup>, the variation of this electronic property with the conformation being almost negligible.

#### 4.4. NMPy–EDOT–NMPy–EDOT

Geometry optimization of the 64 starting structures constructed for **4** using the MDCA method led to 37 different minimum energy conformations. Table 4 lists the inter-ring dihedral angles and  $\epsilon_g$  of all the minima with a relative energy smaller than 1.0 kcal/mol. In terms of the Boltzmann distribution, the minima displayed in Table 4 are more representative, *i.e.* they show a population higher than 3.1%. As can be seen, the three inter-ring dihedral angles are arranged in  $ag$  in the two conformations of lower energy, which are almost isoenergetic. Indeed, the 12 conformations with a relative energy lower than 1 kcal/mol show at least two inter-ring dihedral angles arranged in  $ag$ , which is in full agreement with the results

Table 4  
Inter-ring dihedral angle ( $\theta$ , in degrees), relative energy ( $\Delta E$ , in kcal/mol) and energy gap ( $\epsilon_g$ , in eV) of selected minimum energy conformations<sup>a</sup> calculated for the NMPy–EDOT–NMPy–EDOT in the neutral state (**4**)

Conf.#	$\theta_1$	$\theta_2$	$\theta_3$	$\Delta E$	$\epsilon_g$
$ag^+ - ag^- - ag^-$	−128.6	132.2	−132.2	0.0	3.85
$ag^- - ag^- - ag^-$	−127.7	−131.9	−131.0	0.1	3.96
$sg^- - ag^- - ag^+$	−48.5	−132.5	130.9	0.2	3.85
$ag^+ - ag^- - ag^+$	128.8	−132.5	130.9	0.2	3.85
$ag^+ - ag^+ - ag^-$	128.2	132.1	−131.2	0.4	3.96
$ag^+ - ag^- - sg^+$	128.8	−126.4	54.6	0.7	4.09
$ag^- - sg^- - ag^-$	−129.1	−52.2	−132.6	0.7	3.83
$ag^- - ag^+ - sg^-$	−129.1	132.2	48.5	0.8	3.78
$ag^- - sg^+ - ag^+$	−128.2	44.7	132.2	0.8	3.82
$ag^- - ag^- - sg^-$	−127.5	−131.6	−56.4	0.8	3.98
$ag^+ - sg^+ - ag^+$	129.1	45.6	132.6	0.9	3.76
$sg^+ - ag^+ - ag^-$	44.7	132.3	−131.3	0.9	3.76

<sup>a</sup> Only the minima with a relative energy smaller than 1 kcal/mol have been listed.

obtained for **1–3**. Inspection of Table 3 reveals that  $\epsilon_g$ , which ranges from 3.76 to 4.09 eV, is about 0.3 eV smaller for **4** than for **2** and **3**. Similar to the other neutral molecules, no correlation with the dihedral angles and relative energies was consistent with the range of variation of  $\epsilon_g$ .

Regarding **4**<sup>+</sup>, six starting conformations were constructed considering the *anti* (*a*) and *syn* (*s*) arrangements for the inter-ring dihedral angles, *i.e.*  $\theta = 180^\circ$  and  $0^\circ$ , respectively. These conformations were *a–a–a*, *a–a–s*, *a–s–a*, *s–s–a*, *s–a–s* and *s–s–s*. Geometry optimization of these structures at the UB3PW91/6-31 + G(d,p) led to the six minima listed in Table 5. It should be mentioned that each calculation took more than 280 h on a computer using relatively fast Altix SGI processors. As expected from the results presented above for **1**<sup>+</sup>, **2**<sup>+</sup> and **3**<sup>+</sup>, the values of three inter-ring dihedral angles are closer to  $0^\circ$  than to  $180^\circ$  in the lowest energy conformation ( $sg^- - sg^+ - s$ ). Thus, the  $ag^- - ag^+ - ag^-$  is unfavored by 2.5 kcal/mol. Again, the dependence of the energy gap  $\epsilon_g$  on the conformation is practically negligible, the resulting values being about 0.2 eV smaller than those predicted for **2**<sup>+</sup> and **3**<sup>+</sup>.

## 5. Discussion

The DFT calculations presented in this work show significant structural differences between homo-oligomers and co-oligomers, especially in the radical cation state. Thus, the inter-ring dihedral angles  $\theta$  tend to adopt *a* and *ag* arrangements in charged homo-oligomers of EDOT and NMPy, respectively. In these situations, particularly in the planar structure of the former, the inter-ring  $\pi$ -conjugation is maximum [19–21]. On the contrary, calculations on charged co-oligomers formed by EDOT and NMPy units located alternatively evidence that the most stable conformation corresponds to that with all the inter-ring dihedral angles arranged in *sg*. Moreover, the energy of the conformations with all the inter-ring dihedral angles arranged in *ag* are notably destabilized indicating that their contribution to the model of this system is very small. This destabilization results from a conflict of interests. Charged co-oligomers tend to adopt a quinoid structure, which is characterized by the partial double bond character of the inter-ring bond [18,42], *i.e.* the partial double bond tends to impose a planar *a* structure. In opposition, the steric interactions induced by the methyl attached to the *N*-position of NMPy precludes the formation of planar *a* arrangements in charged homo- and co-oligomers inducing large distortions

Table 5  
Inter-ring dihedral angle ( $\theta$ , in degrees), relative energy ( $\Delta E$ , in kcal/mol) and energy gap ( $\epsilon_g$ , in eV) of selected minimum energy conformations calculated for the NMPy–EDOT–NMPy–EDOT in the radical cation state ( $4^+$ )

Conf.#	$\theta_1$	$\theta_2$	$\theta_3$	$\Delta E$	$\epsilon_g$
$sg^- - sg^+ - s$	-21.2	14.8	-1.3	0.0	1.22
$s - sg^- - ag^-$	3.1	-11.8	-147.1	0.1	1.25
$ag^- - sg^+ - ag^-$	-148.5	15.7	-148.0	0.8	1.24
$ag^- - ag^+ - ag^-$	-149.0	151.4	-147.0	2.5	1.23
$ag^- - ag^- - sg^-$	-149.8	-156.0	-17.6	2.5	1.22

in the inter-ring dihedral angles  $\theta$ . Accordingly, the preferences established by electronic and steric interactions are in opposition. As a consequence of this conflict, the  $sg$  conformation is stabilized with respect to the  $ag$  in charged systems with NMPy directly attached to EDOT.

These features are fully consistent with the experimental data reported about electrochemically prepared poly(EDOT-*co*-NMPy) [14,15]. The polycondensation mechanism associated to the electrogeneration process involves the addition of monomeric units to a positively charged molecular chain. Accordingly, charged co-oligomers are excellent model systems to evaluate the characteristics of the interaction between NMPy and EDOT units when they are directly linked in the molecular chain. Within this context, our recent experimental results suggested that the unfavourable interaction between NMPy and EDOT units is responsible of the poor properties of poly(EDOT-*co*-NMPy) [14]. Specifically, we found that this unfavourable interaction reduces the success in the formation of copolymer chains. The present calculations indicate that these observations are explained by the steric interactions found in the  $alag$  arrangements of charged co-oligomers. Thus, in this particular sequence the  $s/sg$  arrangements are clearly the most stable. Moreover, the unique conformation of the charged co-oligomers is also consistent with the poor electroactivity and electrochemical stability of the copolymers with respect to the two homopolymers. It should be noted that  $a$  and  $ag$  are the most stable arrangements in EDOT and

NMPy-containing homo-oligomers, respectively. Accordingly, the extension of the  $\pi$ -conjugation effects along the molecular chain is significantly lower in copolymers than in homopolymers.

In opposition, the conformational preferences of neutral co-oligomers correspond to those typically found in homo-oligomers made of substituted pyrrole and thiophene derivatives [38,43,44]. Thus, neutral co- and homo-oligomers formed by EDOT and NMPy clearly prefer the  $ag$  arrangement, the population of  $sg$  being small or even negligible. These results suggest that the properties of poly(EDOT-*co*-NMPy) prepared by chemical polymerization would be different from those of the material produced electrochemically. Accordingly, the largest distortion found in neutral co-oligomers corresponds to the values of  $\theta$  that are closer to  $120^\circ$  than to  $150^\circ$ , the latter value being that typically found in neutral heterocyclic systems. Obviously, this deviation should be attributed to the steric interaction induced by the methyl group of the NMPy units.

In order to evaluate how the interaction between NMPy and EDOT units within the molecular chain affects the electronic properties, the IP, EA and  $\epsilon_g$  of homo- and co-oligomers formed by two, three and four units of NMPy and/or EDOT have been calculated. Regarding co-oligomers, properties were estimated by averaging according to a Boltzmann distribution the values calculated for all the minima provided by the MDCA (Tables 1–5). Furthermore, the electronic properties of PNMPy, PEDOT and poly(EDOT-*co*-NMPy) have been estimated by representing the IPs, EAs and  $\epsilon_g$ s calculated for the different oligomers under study against their inverse chain length ( $1/n$ , where  $n$  is the number of NMPy and/or EDOT units) [22,43]. The extrapolation of these plots, which show a perfect linearity, to infinite chain lengths provides the electronic properties of the polymers. It should be noted that due to the chemical composition of the calculated co-oligomers, the properties predicted for poly(EDOT-*co*-NMPy) are for an alternated architecture. The overall of these results are displayed in Table 6. In addition, the IP of all neutral systems

Table 6  
Ionization potentials (IP, in eV), electron affinities (EA, in eV) and energy gap ( $\epsilon_g$ , in eV) for homo- and co-oligomers of NMPy or/and EDOT, and for poly(EDOT-*co*-NMPy), PEDOT and PNMPy

	Neutral state				Charged state (+1)		
	IP <sub>KT</sub>	IP <sub><math>\Delta</math>SCF</sub>	EA	$\epsilon_g$	IP	EA	$\epsilon_g$
EDOT–NMPy	5.38	6.53	0.66	4.73	9.73	7.89	1.84
EDOT–EDOT	5.15	6.49	1.11	4.04	9.61	7.83	1.98
NMPy–NMPy	5.26	6.60	0.28	5.24	9.92	8.06	1.85
NMPy–EDOT–NMPy	5.04	5.03	0.81	4.22	8.44	7.00	1.44
EDOT–NMPy–EDOT	5.13	6.02	0.87	4.25	8.55	7.07	1.48
EDOT–EDOT–EDOT	4.71	5.83	1.41	3.30	8.35	6.94	1.41
NMPy–NMPy–NMPy	4.95	6.01	0.34	4.55	8.65	7.23	1.42
NMPy–EDOT–NMPy–EDOT	4.93	5.66	1.02	3.91	7.77	6.59	1.17
EDOT–EDOT–EDOT–EDOT	4.46	5.34	1.56	2.90	7.59	6.39	1.20
NMPy–NMPy–NMPy–NMPy	4.80	5.73	0.37	4.22	8.10	6.86	1.24
Poly(EDOT- <i>co</i> -NMPy)	4.48	4.79	1.34	3.13	5.87	5.31	0.54
PEDOT	3.79	4.27	2.01	1.78	5.64	5.01	0.39
PNMPy	4.35	4.86	0.46	3.22	6.26	5.65	0.62

The IP of neutral systems has been calculated using both the Koopman's theorem (IP<sub>KT</sub>) and  $\Delta$ SCF approach (IP <sub>$\Delta$ SCF</sub>).

has been calculated using both the Koopman theorem (KT) and the  $\Delta$ SCF approach (see Section 2), both the  $IP_{KT}$  and  $IP_{\Delta SCF}$  being listed in Table 6.

As can be seen, the electronic properties of neutral co-oligomers are, in general, closer to those homo-oligomers formed by NMPy than by EDOT. This is not a surprising feature because the steric interactions produced by the methyl group of the NMPy units arranged in *ag* are not expected to be significantly altered by the neighboring EDOT units with respect to those found in the NMPy-containing homo-oligomers. Accordingly, the  $\pi$ -conjugation of neutral co-oligomers is not so high like that of homo-oligomers formed by EDOT but it is not worse than that of NMPy homo-oligomers. As a result, the electronic properties of neutral co-oligomers are intermediate between those of homo-oligomers, even though in general they are notably closer to those of homo-oligomers formed by NMPy. An exception to this behavior corresponds to the EA, which is remarkably low for homo-oligomers formed by NMPy. However, as a consequence of the incorporation of EDOT units, the EAs predicted for co-oligomers are actually intermediate between those of individual homo-oligomers. On the other hand, these general trends are also identified when the electronic properties predicted for infinite chains of poly(EDOT-*co*-NMPy), PEDOT and PNMPy are examined.

The electronic properties of charged oligomers are significantly different from those of their corresponding neutral analogues. As was expected, both the IP and EA are significantly higher in the radical cation state, while the gap  $\epsilon_g$  is considerably lower. In addition, in this case the IP and EA of co-oligomers are, in general, closer to those of homo-oligomers formed by EDOT than to those of NMPy homo-oligomers. This should be attributed to the unique interaction between NMPy and EDOT units within the charged co-oligomer chains. Thus, the tendency to adopt the planar conformation characteristic of the quinoid-like structure typically found in charged systems is partially satisfied in co-oligomers through the stabilized *s* and *sg*<sup>±</sup> arrangements. Analysis of the inter-ring bond lengths indicated that, in average, such distance is 0.035 Å shorter for charged co-oligomers (average value: 1.420 Å) supporting the enhancement of the quinoid-like structure. Interestingly, the  $\epsilon_g$  values calculated for charged co-oligomers are slightly lower than those obtained for EDOT homo-oligomers. However, it is worth noting that the evolution of the gap with the number of units contained in the chain is very different for these two systems, *i.e.* the slope of  $1/n$  vs  $\epsilon_g$  is more pronounced for EDOT homo-oligomers. Thus, extrapolation to an infinite chain system allows to predict that the  $\epsilon_g$  of oxidized poly(EDOT-*co*-NMPy) is significantly higher than that of oxidized PEDOT.

## 6. Conclusions

Calculations reported in this work evidence that in charged molecules the inter-ring dihedral angles connecting NMPy and EDOT units prefer the *sg* conformations ( $\theta \approx \pm 30^\circ$ ) rather than the *a* conformation ( $\theta \approx 180^\circ$ ), as is typically found in quinoid-like structures. This unique conformational behavior,

which explains experimental features obtained for oxidized poly(EDOT-*co*-NMPy), is due to the steric interactions induced by the methyl group of the NMPy units. In contrast, in neutral compounds these dihedral angles prefer the same conformation than other substituted pyrrole and thiophene derivatives. It should be noted that in neutral compounds the two rings are connected by a single-bond, steric interactions being alleviated by increasing the distortion of the inter-ring bond dihedral angle. In contrast, the partial double character of the inter-ring bond in charged compounds forces the system towards a planar conformation, which is severely unfavored in the *a* or *ag* ( $\theta \approx \pm 150^\circ$ ) conformation.

Prediction of the electronic properties indicated that  $\epsilon_g$  is practically independent of the conformation for both neutral and charged co-oligomers. For small charged co-oligomers the gap was found to be smaller than those of homo-oligomers with the same number of rings. However, the  $\epsilon_g$  values predicted for poly(EDOT-*co*-NMPy) by extrapolation to infinite chains were found to be closer to those of PNMPy than to those of PEDOT independent of the ionization state.

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