

# Structural and Electronic Properties of Poly[*N*-(2-cyanoalkyl)pyrrole]s Bearing Small Alkyl Groups

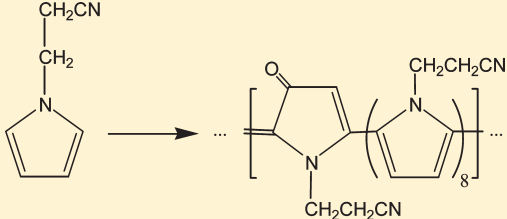
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**ABSTRACT:** The electronic and structural properties of poly[*N*-(2-cyanoalkyl)pyrrole]s bearing short alkyl groups have been investigated using different methodologies. Specifically, the electronic properties of poly[*N*-(2-cyanoethyl)pyrrole], which was prepared by anodic polymerization, have been determined using both electrochemical and spectroscopic techniques. On the other hand, quantum mechanical calculations on model oligomers of poly[*N*-(2-cyanomethyl)pyrrole] have been used to propose the conformation of an idealized polymer chain and to examine the influence of the conformation on the predicted electronic properties. Results indicated that the electronic properties of poly[*N*-(2-cyanoalkyl)pyrrole]s are not only influenced by effect of the conformation in the conjugation of the  $\pi$ -system but also by the existence of secondary oxidative processes on the pyrrole ring of selected repeating units. In this case, the combination of experimental information and quantum mechanical calculations proved to be essential to propose a structural model. This consists of a cross-linked structure formed by small branches of around nine repeating units in each one, with a carbonyl group at the last repeating unit of each branch.



## INTRODUCTION

Among organic conducting polymers (CPs), polypyrrole (PPy) is the most extensively applied due to its interesting properties: redox activity,<sup>1</sup> the ability to form supercapacitors in combination with multiwalled carbon nanotubes,<sup>2</sup> ion-exchange and ion discrimination capacities,<sup>3,4</sup> strong absorptive properties toward gases,<sup>5</sup> proteins,<sup>6</sup> DNA,<sup>7</sup> catalytic activity,<sup>8,9</sup> ability to protect against corrosion,<sup>10,11</sup> and so forth. Besides such a large spectrum of applications, PPy is easy to prepare using either electrochemical or chemical polymerization techniques.<sup>12–15</sup>

PPy derivatives can be obtained by incorporating the substituent at the nitrogen or the carbon (3-position) atoms.<sup>16,17</sup> The polymers produced by polymerizing *N*-substituted pyrrole (Py) monomers usually present a regular structure because of the molecular symmetry, while irregular polymeric structures are typically derived from 3-substituted Py monomers. In addition, the substitution at the nitrogen atom is also more versatile because of the characteristics of the synthetic process.<sup>17</sup> Specifically, among *N*-substituted PPy derivatives, we have been particularly interested in poly(*N*-hydroxypropylpyrrole) and poly(*N*-methylpyrrole) (abbreviated PNMPy) to prepare DNA sensors<sup>18</sup> (i.e., systems able to recognize specific DNA sequences) and micro/nanocondensers formed by alternated layers of two different CPs,<sup>19,20</sup> respectively.

On the other hand, the incorporation of a strong electron-withdrawing substituent, such as the cyano group, at the 3-position of the thiophene or Py ring induces interesting changes in properties of the corresponding CPs.<sup>21,22</sup> Thus, this substituent perturbs the  $\pi$ -conjugated system of the polyheterocycle reducing

the barrier for electron injection, increasing the oxidation potential, and improving the electron transport properties. Interestingly, an early study devoted to examine the ability of different PPy derivatives to detect vapor gases showed that the incorporation of the cyano group at the *N*-position of the Py repeating units improves the capabilities of these materials as selective gas sensors.<sup>23–25</sup> Specifically, poly[*N*-(2-cyanoethyl)pyrrole] (PNCEPy; Scheme 1) was found to be an excellent detector of molecules in the vapor phase.<sup>23–25</sup> More recently, PNCEPy has been used to develop impedimetric immunosensors,<sup>26</sup> ion-selective membranes,<sup>27</sup> and electrochemical nanocoatings of metallic medical devices.<sup>28</sup>

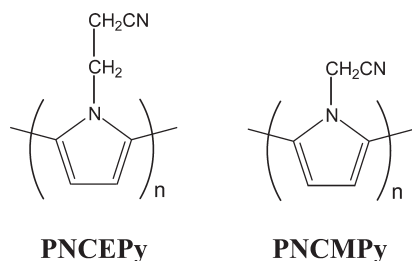
In spite of these potential applications, the knowledge about the chemical and physical properties of PNCEPy is, unfortunately, very scarce. Recently, some of the own authors<sup>29</sup> reported a comprehensive experimental study of PNCEPy, which provided an exhaustive characterization of the electrochemical, physical, electrical, structural, and morphological properties of the material in both the oxidized and the reduced states. Additionally, three-layered films formed by poly(3,4-ethylenedioxythiophene), abbreviated PEDOT (first and last layers), and PNCEPy (middle layer) were prepared, their ability to act as microcondenser being compared with that observed for multi-layered films of PEDOT and PNMPy.<sup>18,19</sup>

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Scheme 1



In this work we use quantum mechanical calculations to propose an atomistic model for poly[*N*-(2-cyanoalkyl)pyrrole]*s* bearing short alkyl groups. Results have provided not only a detailed structural model but also a way to determine the electronic properties of these materials, i.e.,  $\pi$ – $\pi^*$  lowest transition energy ( $\varepsilon_g$ ), ionization potential (IP), and electron affinity (EA), which remained totally unknown. Calculations have been performed considering model oligomers of poly[*N*-(2-cyanomethyl)pyrrole], abbreviated PNCMPy (Scheme 1), containing *n* chemical repeating units with *n* ranging from 2 to 15. Previous studies on oligomers of poly(*N*-hydroxyalkylpyrrole)*s* with alkyl = methyl, ethyl, and propyl evidenced that the length of the alkyl group has a negligible effect on the structural and electronic properties.<sup>30</sup> This characteristic is expected to be also valid for poly[*N*-(2-cyanoalkyl)pyrrole]*s* bearing short alkyl groups. On the other hand, the electronic properties, calculated for PNCMPy have been compared with those experimentally determined for PNCEPy using ultraviolet–visible (UV–vis) spectroscopy and cyclic voltammetry (CV).

## METHODS

**Experimental Methods.** *N*-(2-cyanoethyl)pyrrole (NCEPy) and acetonitrile of analytical reagent grade were purchased from Aldrich and used without further purifications. Anhydrous lithium perchlorate, analytical reagent grade, from Aldrich was stored in an oven at 80 °C before use in the electrochemical trials. PNCEPy films were prepared by chronoamperometry (CA) using a polymerization time of 300 s and, subsequently, studied by CV using a VersaStat II potentiostat-galvanostat connected to a PC computer controlled through a Power Suite Princeton Applied Research Program. All electrochemical experiments were conducted in a three-electrode two-compartment cell under nitrogen atmosphere (99.995% in purity) at 25 °C. The anodic and cathodic compartments were filled with 40 and 10 mL of a 0.01 M monomer solution in acetonitrile containing 0.1 M LiClO<sub>4</sub> as supporting electrolyte, respectively. Steel AISI 316 sheets of 4 cm<sup>2</sup> area were employed as working and counter electrodes. In order to avoid interferences during the electrochemical analyses, the working and counter electrodes were cleaned with acetone before each trial. The reference electrode of Ag|AgCl|sat-KCl was connected to the working compartment through a salt bridge containing a KCl-saturated aqueous solution ( $E_0 = 0.222$  V vs standard hydrogen electrode at 25 °C).

The electronic properties investigated at the electrochemical level were determined by CV using an acetonitrile solution with 0.1 M LiClO<sub>4</sub>. Specifically, the recorded cyclic voltammograms were used to estimate the electrochemical IP and EA through the empirical relationship previously proposed

by Brédas et al.<sup>31</sup>

$$\text{IP} = \Phi_{\text{ox}} + 4.4 \text{ eV}$$

$$\text{EA} = \Phi_{\text{red}} + 4.4 \text{ eV}$$

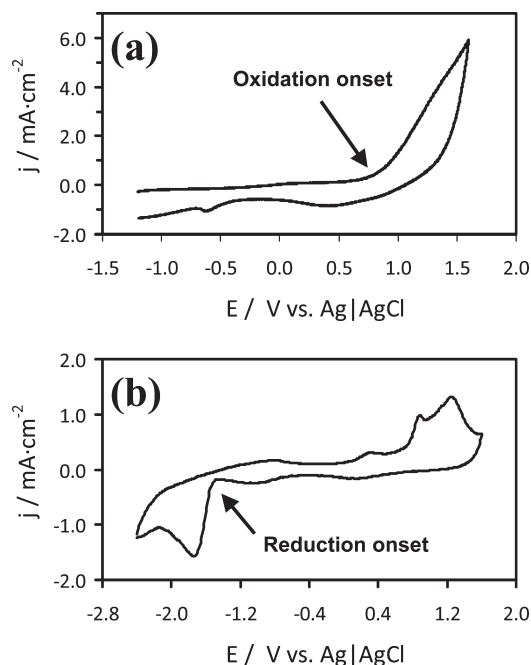
where  $\Phi_{\text{ox}}$  and  $\Phi_{\text{red}}$  are the onset potentials for oxidation and reduction, respectively, relative to the Ag|AgCl electrode. The electrochemical  $\varepsilon_g$  was determined as difference between the electrochemical IP and EA.

The optical  $\varepsilon_g$  was derived from the UV–vis spectra of reduced material. For this purpose, PNCEPy was deposited on indium–tin-oxide (ITO) electrodes by anodic polymerization of NCEPy (10 mM) in acetonitrile solution with 0.1 M LiClO<sub>4</sub> under a constant potential of 1.40 V. The resulting films were dedoped by chronopotentiometry applying a cathodic current density of  $-0.25 \text{ mA} \cdot \text{cm}^{-2}$ , i.e., a constant intensity of  $-1.0 \text{ mA}$  on the film of 4 cm<sup>2</sup> area, during 190 s.<sup>29</sup> Absorption spectra were recorded on a UV-3600 (Shimadzu) UV–vis–NIR spectrophotometer controlled by the UVProbe 2.31 software at room temperature, in the 200–900 nm range, with a bandwidth of 2 nm and a scan speed of  $600 \text{ nm} \cdot \text{min}^{-1}$ .

**Theoretical Methods.** The molecular model of poly[*N*-(2-cyanoalkyl)pyrrole] bearing short alkyl groups was derived from a conformational study on small oligomers formed by *n* *N*-(2-cyanomethyl)pyrrole units (*n*-NCMPy). Complete geometry optimizations in the gas phase of 2-NCMPy and 3-NCMPy were performed using the density functional theory (DFT) method. All DFT calculations were carried out using the Becke's three parameter hybrid functional (B3)<sup>32</sup> with the Lee, Yang, and Parr (LYP)<sup>33</sup> expression for the nonlocal correlation, combined with the 6-31G(d) basis set (B3LYP/6-31G(d)).<sup>34</sup> Previous studies indicated that this methodology is able to provide a very satisfactory description of the molecular geometry and relative energy for the minimum energy conformations of heterocyclic oligomers.<sup>35</sup>

The most stable conformation obtained from calculations on the dimer and the trimer was used as starting point for the modeling of larger oligomers. Specifically, the molecular geometries of *n*-NCMPy with *n* ranging from 6 to 15 were fully optimized using two different methods: (i) the B3LYP/6-31G(d) and (ii) the B3 functional with the Perdew and Wang's 1991<sup>36,37</sup> expression for the gradient-corrected correlation functional, combined with the 6-31+G(d,p)<sup>38,39</sup> basis set (B3PW91/6-31G+(d,p)). In addition, the molecular geometries of the positively charged oligomers, *n*-NCMPy<sup>+</sup>, were fully optimized using the unrestricted formalism of these two methods, i.e., UB3LYP/6-31G(d) and UB3PW91/6-31G+(d,p).

The IP of each calculated system was determined using two different methodologies. The first one was the Koopmans' theorem,<sup>40</sup> according to which the IPs were taken as the negative of the highest occupied molecular orbital (HOMO) energy (i.e.,  $\text{IP}^{\text{KT}} = -\varepsilon_{\text{HOMO}}$ ). More accurate values were obtained by calculating the IPs as the energy difference between optimized structures of the oxidized and neutral species ( $\text{IP}^{\text{ASCF}} = E_{\text{oxidized}} - E_{\text{neutral}}$ ). This approach takes into account the relaxation energy of the ionization state, which can be calculated as the difference between the  $\text{IP}^{\text{KT}}$  and  $\text{IP}^{\text{ASCF}}$ . The EAs were calculated using the Koopman's theorem:  $\text{EA} = -\varepsilon_{\text{LUMO}}$ , where  $\varepsilon_{\text{LUMO}}$  refers to the energy of the lowest unoccupied molecular orbital (LUMO). Although Koopman's theorem does not apply to DFT and the energies of Kohn–Sham orbitals do not involve any physical meaning, Janak's theorem<sup>41</sup> was used by Perdew<sup>42</sup> to show the



**Figure 1.** Cyclic voltammograms recorded at a scan rate of  $100 \text{ mV} \cdot \text{s}^{-1}$  for PNCEPy thin films deposited on steel electrodes. The onsets of (a) oxidation and (b) reduction were derived from the voltammogram recorded in the potential ranges from  $-1.20$  to  $1.60 \text{ V}$  and from  $-2.40$  to  $1.60 \text{ V}$ , respectively.

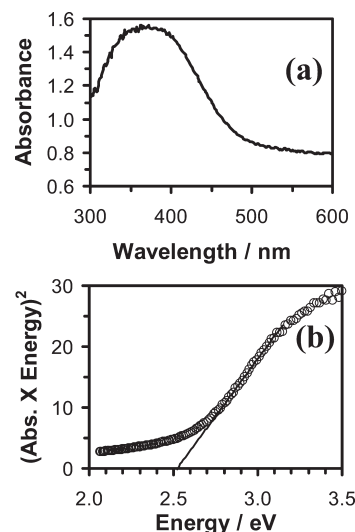
connection between these electronic properties (i.e., IPs and EAs) and the energies of the frontier orbitals (i.e.,  $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{LUMO}}$ ). The  $\epsilon_{\text{g}}$  was estimated using two different strategies. In the first,  $\epsilon_{\text{g}}$  was approximated as the difference between the energies of the frontier orbitals:  $\epsilon_{\text{g}} = \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$ . In an early work, Levy and Nagy showed that in DFT calculations  $\epsilon_{\text{g}}$  can be correctly estimated using this procedure.<sup>43</sup> The second estimation of  $\epsilon_{\text{g}}$  was derived from the excitation energies calculated with time-dependent density functional theory (TD-DFT). This method, which is widely applied to study the UV–vis spectra of conjugated organic compounds, provides a robust and efficient description of the low-lying molecular states.<sup>44–46</sup> Electronic excitations were evaluated with the B3P86<sup>32,47</sup> functional combined with the 6-31G(d) basis set.<sup>34</sup>

All the quantum mechanical calculations were performed with the Gaussian 03 computer program.<sup>48</sup>

## RESULTS AND DISCUSSION

### Electrochemical Estimation of the Electronic Properties.

PNCEPy films were generated by CA under a constant potential of  $1.40 \text{ V}$  and considering a polymerization time of  $300 \text{ s}$ . Films were rinsed several times with acetonitrile, dried in a nitrogen flow, and immersed in the electrolyte solution of the control cell for CV analysis. Figure 1a shows the cyclic voltammogram recorded in the potential range from  $-1.20$  to  $1.60 \text{ V}$ , which was used to determine the onset potential  $\Phi_{\text{ox}}$  of the dedoped (reduced) polymer. Using the procedure reported for other  $\pi$ -conjugated polymers,<sup>49,50</sup> taking the energy corresponding to the oxidation onset,  $\Phi_{\text{ox}} = 0.9 \pm 0.1 \text{ eV}$ , and making the conversion from the reference electrode to the vacuum level,<sup>31</sup> we estimate the IP of PNCEPy as  $(0.9 \pm 0.1) + 4.4 = 5.3 \pm 0.1 \text{ eV}$ . On the other hand, Figure 1b shows the voltammogram recorded in the



**Figure 2.** (a) UV–vis absorption spectrum of a PNCEPy thin film deposited on an ITO working electrode. (b) Absorption edge analysis to extract the band gap.

reduction potential range from  $-2.40$  to  $1.60 \text{ V}$ , the resulting onset potential  $\Phi_{\text{red}}$  being  $-1.5 \pm 0.1 \text{ eV}$ . This yields an EA value of  $(-1.5 \pm 0.1) + 4.4 = 2.9 \pm 0.1 \text{ eV}$ . Finally, the electrochemical  $\epsilon_{\text{g}}$ ,  $2.4 \pm 0.1 \text{ eV}$ , was derived from Koopman's theorem as the difference between the IP and EA.

### Spectroscopic Estimation of the Electronic Properties.

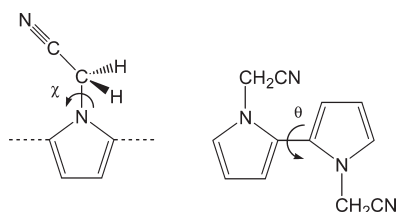
PNCEPy was electrochemically deposited on an ITO substrate using the same experimental conditions described in our previous work.<sup>29</sup> After reduction of the film by chronopotentiometry, the UV–vis absorption spectrum was recorded (Figure 2a). As it can be seen, a strong absorption, which corresponds to the  $\pi$ – $\pi^*$  transition, is detected at  $372 \text{ nm}$ . From analysis of the absorption edge and assuming direct transition, the optical  $\epsilon_{\text{g}}$  was calculated with the help of the  $(h\nu \times \alpha)^2$  versus  $h\nu$  plot (where  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant, and  $\nu$  is the frequency)<sup>51,52</sup> as presented in Figure 2b. The optical  $\epsilon_{\text{g}}$  of PNCEPy was estimated to be  $2.5 \text{ eV}$ , which is in excellent agreement with the electrochemical value.

**Conformational Analysis.** Previous studies considering small oligomers of poly(*N*-hydroxyalkylpyrrole)s with methyl, ethyl, and propyl groups evidenced that the alkyl group exerts a small influence on the conformational and electronic properties.<sup>30</sup> Furthermore, such difference decreases when the number of repeating units increases. According to this observation, the conformational properties of poly[*N*-(2-cyanoalkyl)pyrrole]s were investigated considering model oligomers of the polymer with the smallest alkyl group, PNCMPy (Scheme 1).

DFT calculations were performed to ascertain the conformational preferences of *n*-NCMPy oligomers, which have been expressed through the dihedral angles  $\theta$  and  $\chi$  (Scheme 2). These indicate the relative arrangement of two adjacent Py rings and the disposition of the *N*-cyanoalkyl substituents, respectively. Initially, all the possible initial conformations were constructed for 2-NCMPy and 3-NCMPy (i.e., those without steric clashes) and subsequently submitted to complete geometry optimization at the B3LYP/6-31G(d) level. Three different minimum energy conformations, which are described in Table 1, were identified for each compound. As it can be seen, the three minimum energy conformations of 2-NCMPy are within a



Scheme 2



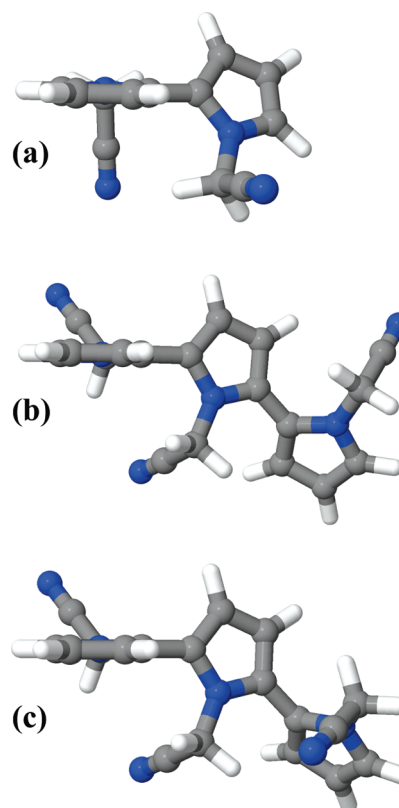
**Table 1. Structural and Electronic Properties of Selected Minimum Energy Conformations of 2-NCMPy and 3-NCMPy Calculated at the B3LYP/6-31G(d) Level.<sup>a</sup>**

#	$\theta_1$	$\theta_2$	$\chi_1$	$\chi_2$	$\chi_3$	$\Delta E$	IP	$\varepsilon_g$
2-NCMPy								
I-2	-114.9		80.1	-86.8		0.0	5.79	5.52
II-2	-131.6		-96.3	-96.3		0.1	5.59	5.16
III-2	122.7		-114.3	-114.3		1.3	5.77	5.55
3-NCMPy								
I-3	-92.7	-132.7	-129.2	-99.1	85.0	0.0	5.82	5.07
II-3	-96.1	-107.2	128.8	-97.2	-90.6	0.0	6.10	5.63
III-3	-104.4	-121.1	76.2	94.7	-52.2	1.6	5.80	5.35

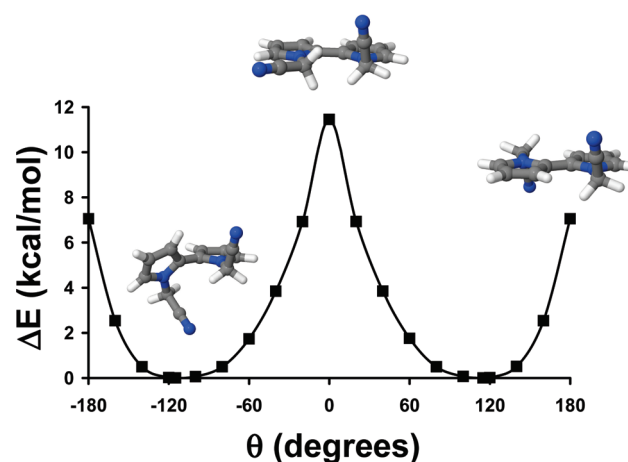
<sup>a</sup> Minima have been labeled considering a roman number followed by  $n$ , where  $n$  refers to the number of repeating units. Dihedral angles ( $\theta$ ,  $\chi$ ) in degrees; relative energy ( $\Delta E$ ) in kcal/mol, IP, and  $\pi$ - $\pi^*$  lowest transition energy ( $\varepsilon_g$ ) in eV. <sup>b</sup> The dihedral angle  $\theta_i$  refers to the inter-ring dihedral angle formed by repeating units  $i$  and  $i+1$ . The dihedral angle  $\chi_i$  refers to the substituent of the repeating unit  $i$ .

relative energy interval of 1.3 kcal/mol and adopt an *anti-gauche* conformation. Interestingly, the side groups of the two conformations of lower energy (I-2 and II-2), which are practically isoenergetic, are almost perpendicular to the Py rings (i.e.,  $\chi \approx -90^\circ$ ). These features are illustrated in Figure 3a, which depicts the lowest energy conformation. Inspections of the IP and  $\varepsilon_g$  values listed in Table 1 reveal relative variations lower than 0.2 and 0.4 eV, respectively, which should be essentially attributed to the differences in  $\theta$ .

In order to obtain more information about the stability of the *anti-gauche* conformation predicted for 2-NCMPy, the potential energy curve associated with the rotation of the inter-ring dihedral angle  $\theta$  was calculated using a flexible rotor approximation (i.e., molecular geometry optimizations were performed at the B3LYP/6-31G(d) level considering fixed values of  $\theta$ ). In addition, the transition states at  $\theta = 0^\circ$  (*syn*) and  $180^\circ$  (*anti*) were obtained using the synchronous transit-guided quasi-Newton (STQN) algorithm.<sup>53</sup> The N-substituents were arranged perpendicularly to the Py rings, as is displayed in Figure 3a. The resulting energy profile, which was obtained by scanning  $\theta$  in steps of  $20^\circ$ , is displayed in Figure 4. As it can be seen, the *syn-gauche* conformation is not an energy minimum, which must be attributed to the steric interactions between the hydrogen atoms of the adjacent substituents. These repulsive interactions are maximum in the planar *syn* conformation ( $\theta = 0^\circ$ ), which is destabilized by 11.5 kcal/mol with respect to the lowest energy minimum. The steric interactions induced by the substituents are less repulsive in the *anti* conformation, which is unfavored by 7.1 kcal/mol.



**Figure 3.** Selected energy minima calculated for 2-NCMPy and 3-NCMPy at the B3LYP/6-31G(d) level: (a) I-2, (b) I-3, and (c) II-3.



**Figure 4.** Potential energy curve for the internal rotation of 2-NCMPy as a function of the inter-ring dihedral angle  $\theta$  using B3LYP/6-31G(d) geometry optimizations. Energies are relative to the global minimum.

The results obtained for 3-NCMPy are included in Table 1. As it can be seen, the values of  $\theta_1$  (i.e., the inter-ring dihedral angle formed by the first two repeating units) for I-3 and II-3 (Figures 3b and 3c, respectively), which are isoenergetic, are very similar to those obtained for I-2 and II-2, respectively. Moreover, the dispositions of the substituents for the first two repeating units of the trimer were also similar to those of the dimer. Thus, the two minima of lowest energy obtained for 3-NCMPy differ from those of 2-NCMPy in the third repeating

**Table 2.** Electronic Properties ( $\epsilon_g$ ,  $IP^{KT}$ ,  $IP^{ASCF}$  and EA; all in eV) Predicted by Different Theoretical Methods for an Infinite Chain of PNCMPy Arranged in *anti* and *anti-gauche*<sup>a</sup>

	<i>anti-gauche</i>				<i>anti</i>			
	$\epsilon_g$	$IP^{KT}$	$IP^{ASCF}$	EA	$\epsilon_g$	$IP^{KT}$	$IP^{ASCF}$	EA
B3LYP/6-31G(d)	4.5 (0.92)	5.8 (0.28)	6.1 (0.96)	1.3 (0.84)	2.2 (1.00)	4.7 (0.97)	5.1 (0.99)	2.5 (1.00)
B3PW91/6-31+G(d,p)	4.4 (0.90)	6.1 (0.49)	6.5 (0.97)	1.6 (0.76)	2.2 (1.00)	5.0 (0.97)	5.6 (0.99)	2.8 (0.99)
TD-DFT-B3P86/6-31G(d)	4.3 (0.73)				1.8 (1.00)			
	$\epsilon_g$				IP			
Electrochemical measures	2.4				5.3			
Optical measures	2.5							
					EA			
					2.9			

<sup>a</sup> The coefficients  $R^2$  derived from the linear regression analyses used to extrapolate the properties obtained for *n*-NCMPy oligomers towards an infinite polymer chain (i.e., calculated property against  $1/n$ ) are displayed in parentheses. Experimental values measured for PNCEPy are included for comparison.

unit, which adopts a *gauche-gauche* conformation. Comparison between **III-3** and **III-2** reveals the same features. These results evidence that, in order to reduce the repulsive steric interactions induced by the third repeating unit of the trimer, the inter-ring dihedral angle defined by the second and third units ( $\theta_2$ ) evolves from the *anti-gauche* to the *gauche-gauche*. However, the torsional profile displayed in Figure 4 shows that the *gauche-gauche* arrangement is within the low-energy region.

**Calculation of the Electronic Properties.** *n*-NCMPy oligomers with  $n = 3, 6, 9, 12$ , and  $15$ , were constructed using the most stable conformation of 2-NCMPy (i.e., **I-2** in Table 1). These structures were optimized at the B3LYP/6-31G(d) level considering two different situations: (i) optimizations were performed without any restriction, and (ii) optimizations were performed fixing all the inter-ring dihedral angles at  $180^\circ$  (i.e., the *anti-gauche* found in **II-2** was changed to *anti*, even though the arrangement of the N-substituent was preserved). Previous studies on different polythiophene derivatives and PPy indicated that the all-*anti* planar conformation allows obtain good estimations of the electronic properties for infinite polymer chains.<sup>54–56</sup> Although the *anti* conformation has been identified as a maximum of energy in the torsional profile of 2-NCMPy (Figure 4), the comparison between the idealized all-*anti* and the *anti-gauche* is expected to explain the influence of the geometrical distortions induced by the N-substituents on the electronic properties of poly[*N*-(2-cyanoalkyl)pyrrole]s.

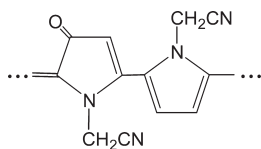
Table 2 compares the experimental values of  $\epsilon_g$ , IP, and EA with those predicted at the B3LYP/6-31G(d), B3PW91/6-31+G(d,p) and TD-DFT-B3P86/6-31G(d) levels for an infinite chain of PNCMPy, which were estimated by extrapolating the linear variation of such electronic properties against  $1/n$ .<sup>54–56</sup> Inspection of the regression coefficients ( $R^2$  in Table 2) indicates that the behavior followed by the properties calculated for the *anti-gauche* is not linear in some cases. Specifically, the  $R^2$  calculated for the  $IP^{KT}$  and EA ranges from 0.28 to 0.84 depending on the method and on the property. Furthermore, the  $\epsilon_g$  derived from TD-DFT calculations also shows a low  $R^2$  (0.73). On the other hand, although the  $\epsilon_g$  and  $IP^{ASCF}$  calculated at the B3LYP/6-31G(d) and B3PW91/6-31+G(d,p) levels follows a linear behavior, the values extrapolated for an infinite polymer chain are considerably overestimated with respect to the experimental ones (i.e.,  $\sim 2$  and  $\sim 1$  eV, respectively). These features should be attributed to the steric interactions produced by the *N*-cyanomethyl groups, which induced significant

conformational distortions during the geometry optimization process (i.e., the initial *anti-gauche* arrangement evolved toward the *gauche-gauche* one in some cases). These structural changes not only disturbed the expected linear behavior but also reduced the  $\pi-\pi$  conjugation effects. Similar findings were reported in a previous study devoted to examine the electronic properties of poly(*N*-hydroxymethylpyrrole).<sup>54</sup> Calculations on *N*-hydroxymethylpyrrole-containing oligomers (*n*-MeOHPy) showed that some dihedral angles changed from the initial *anti-gauche* conformation toward a *gauche-gauche* one, producing both the loss of the linear behavior and the overestimation of the  $\epsilon_g$ . In order to overcome such limitations, the *n*-MeOHPy oligomers were reoptimized considering all the inter-ring dihedral angles fixed at  $180^\circ$ .<sup>54</sup>

The electronic properties predicted for the all-*anti* conformation of PNCMPy are included in Table 2. Inspection of the  $R^2$  values reveals a perfect linear behavior in all cases. Moreover, the calculated values are in excellent agreement with the experimental values determined in this work. Specifically, the  $\epsilon_g$ ,  $IP^{KT}$ ,  $IP^{ASCF}$ , and EA values predicted at the B3PW91/6-31+G(d,p) level differ from electrochemical measures by less than 0.3 eV only. On the other hand, the  $\epsilon_g$  calculated at the TD-DFT level for an idealized planar chain is 0.7 eV lower than the experimental value, which represents a reduction of 2.5 eV with respect to the value predicted with the same methodology for the *anti-gauche* conformation. The TD-DFT methodology typically provides an accurate description of the experimental  $\epsilon_g$  values (results displayed in Table 2), suggesting that the calculated oligomers do not satisfactorily represent the chemical and/or conformational characteristics of PNCEPy.

As can be seen in the torsional profile displayed in Figure 4, there is a maximum of energy at  $\theta = 180^\circ$ , which makes the *anti* conformation  $\sim 7$  kcal/mol less stable than the *anti-gauche* one. Moreover, an early crystallographic study on *N,N*-dimethyl-2,2'-bypyrrole (i.e., the dimer formed by two repeating units of *N*-methylpyrrole) evidenced that this dimer adopts a *gauche-gauche* conformation also in the solid state.<sup>57</sup> The loss of planarity produced by the *N*-methyl substitution allowed to explain the higher oxidation peak potential measured for the dimer of *N*-methylpyrrole as compared to the dimer of pyrrole and the smaller conductivity of PNMPy as compared to PPy.<sup>57,58</sup> Obviously, these findings are against the assumption that PNCMPy chains adopt a planar *anti* conformation, as seemingly suggested by the very good agreement between experimental and calculated

Scheme 3



electronic properties. On the contrary, recent studies on PNCEPy, PNMPy, and PPy have evidenced that polymer chains made of N-substituted repeating units grow following a multidirectional mechanism, which should be attributed to their tendency to form chemical cross-links.<sup>29,59</sup> Specifically, PPy was found to form linear chains with some irregularities,<sup>59</sup> while branched molecules with many irregularities are the most stable for PNMPy<sup>59</sup> and PNCEPy<sup>29</sup> because of the steric repulsions induced by the N-substituents. The formation of  $\alpha$ - $\beta$  and/or  $\beta$ - $\beta$  linkages should favor the planarity in small tracts of PNCMPy. In addition to these observations, there is a chemical oxidative process, which was found to be characteristic of poly-[N-(2-cyanoalkyl)pyrrole]s,<sup>29</sup> that is, expected to affect the electronic properties of PNCEPy. Therefore, explicit analysis of this specific process is presented in the next subsection.

**Effects of the Oxidative Process on the Electronic Properties.** Our previous experimental study evidenced the presence of a strong and sharp band at  $1740\text{ cm}^{-1}$  in the FTIR spectrum of PNCEPy, which was assigned to the stretching vibration of carbonyl groups.<sup>29</sup> The origin of these C=O groups corresponds to the oxidative process undergone by some five-membered rings, as is illustrated in Scheme 3. Thus, although the carbonyl group typically absorbs at  $1700\text{ cm}^{-1}$ , the conjugation with the unsaturated groups of the polymer backbone produced a shift toward a higher wavenumber. Obviously, the presence of carbonyl groups interacting with the  $\pi$ -conjugated system is expected to induce significant changes in both the structural and optical properties of PNCEPy. In order to provide a careful study of these changes, calculations have been performed on oligomers containing  $n$  repeating units of NCMPy and  $x$  carbonyl groups, hereafter denoted  $n\text{-NCMPy}(\text{CO})_x$ . The carbonyl groups were located at the  $\beta$ -position of selected pyrrole rings, as is displayed in Scheme 3. The molecular geometries of all the generated oligomers, which were initially arranged considering an *anti-gauche* conformation, were reoptimized at the Hartree–Fock (HF) level using the 6-31G(d) basis set. The resulting geometries were used for single-point calculations at both the B3LYP/6-31G(d) and TD-DFT-B3P86/6-31G(d) levels. The carbonyl groups were distributed on the oligomers with  $n$  ranging from 3 to 12 considering two different situations: (i) each oligomer contains a single carbonyl group, which is located in the first repeating unit, i.e.,  $n\text{-NCMPy}(\text{CO})_x$  with  $x = 1$ ; and (ii) one of every three repeating units, starting from the first one, contains a carbonyl group, i.e.,  $n\text{-NCMPy}(\text{CO})_x$  with  $x \approx n/3$ . Calculations on  $n\text{-NCMPy}(\text{CO})_1$  were performed considering two different electronic states: (i) charge = 0 and spin multiplicity = 2, i.e., (0, 2); and (ii) charge = +1 and spin multiplicity = 3, i.e., (+1, 3). The (0, 2) state was significantly more stable than the (+1, 3) one, independently of the size of the oligomer and, therefore, only the results obtained for the former case are displayed in this work. Calculations on  $n\text{-NCMPy}(\text{CO})_x$  with  $x \approx n/3$  were performed considering only the (0, 1) electronic state, i.e., charge = 0 and spin multiplicity = 1. It is worth noting that  $n\text{-NCMPy}(\text{CO})_1$  oligomers allow one to examine the extension of the influence of

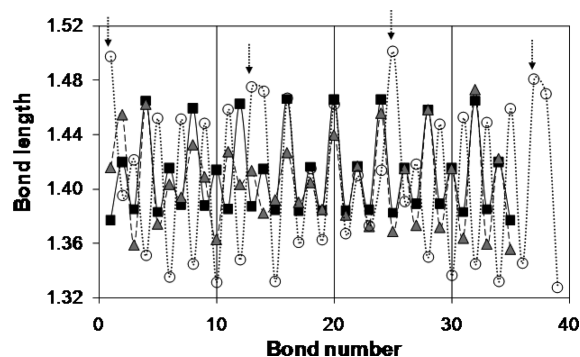


Figure 5. Bond length alternation pattern along the conjugated  $\pi$ -system of 9-NCMPy (■; solid line), 9-NCMPy(CO)<sub>1</sub> (▲; dashed line), and 10-NCMPy(CO)<sub>4</sub> (○; dotted line). The position of carbonyl groups is marked with arrows. Bond lengths are in angstroms.

the carbonyl group, while  $n\text{-NCMPy}(\text{CO})_{\sim n/3}$  oligomers show the effect of the concentration of carbonyl groups.

The bond length alternation pattern calculated for the conjugated  $\pi$ -system of 9-NCMPy, 9-NCMPy(CO)<sub>1</sub>, and 10-NCMPy(CO)<sub>4</sub> are represented in Figure 5. As it can be seen, the C–C bond lengths found for  $n\text{-NCMPy}$  corresponds to a typical benzenoid structure, in which the inter-ring bond lengths are larger than the intraring ones. This regular pattern is altered for the two oligomers containing carbonyl groups. Specifically, the presence of a single carbonyl group located at the first unit produces a relatively homogeneous distribution of intraring C–C lengths and a shortening of the inter-ring bond length with respect to 9-NCMPy. These effects decrease progressively and are completely erased after the fifth repeating unit, which shows the benzenoid pattern found for 9-NCMPy. On the other hand, 10-NCMPy(CO)<sub>4</sub> presents a quinoid-like structure, in which the inter-ring bond length corresponds to that of a double bond. Moreover, this structure is reinforced at every unit with a carbonyl group (indicated by arrows in Figure 5).

Table 3 lists the electronic properties extrapolated for infinite chains using the results calculated for  $n\text{-NCMPy}(\text{CO})_x$  oligomers with  $x = 1$  and  $x \approx n/3$ . It is worth noting that in all cases a good linear behavior ( $R^2 \geq 0.84$ ) was obtained for the variation of the computed electronic properties with the inverse of the chain length ( $1/n$ ). Interestingly, the  $\epsilon_g$  value derived from single point calculations at the TD-DFT-B3P86/6-31G(d) level on  $n\text{-NCMPy}(\text{CO})_1$  oligomers is in excellent agreement with the experimental measure. In contrast, the  $\epsilon_g$  estimated using B3LYP/6-31G(d) calculations is significantly overestimated, which should be attributed to a drastic underestimation of the EA. On the other hand, the  $\epsilon_g$  values obtained at both the TD-DFT and DFT levels for a  $n\text{-NCMPy}(\text{CO})_{\sim n/3}$  chain with  $n \rightarrow \infty$  are underestimated with respect to the experimental ones. Indeed, DFT calculations evidence a significant overestimation of the EA when the number of units that has undergone the oxidative process is one of every three.

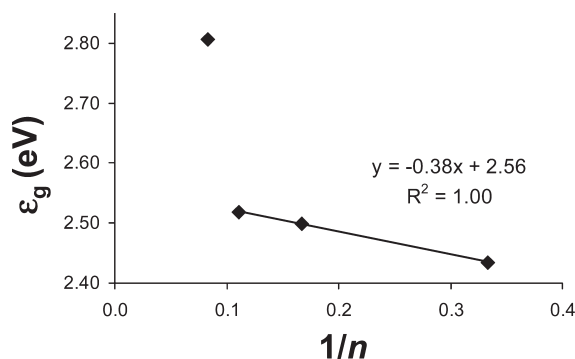
Figure 6 shows the evolution of the  $\epsilon_g$  calculated at the TD-DFT-B3P86/6-31G(d) level against  $1/n$  for  $n\text{-NCMPy}(\text{CO})_1$ . As it can be seen,  $\epsilon_g$  behaves linearly for  $n = 3, 6$ , and  $9$  up with values pretty close to the experimental measures. In opposition to what it is usually observed, the band gap grows with  $n$  showing a negative slope. Furthermore, 12-NCMPy(CO)<sub>1</sub> shows a drastic increment of  $\epsilon_g$  indicating that the properties of this oligomer are not dominated by the carbonyl group. Thus, the carbonyl group



**Table 3.** Electronic Properties ( $\epsilon_g$ ,  $IP^{KT}$  and EA; all in eV) Predicted by Different Theoretical Methods for an Infinite Chain of PNCMPy Considering Oxidative Processes on Selected Repeating Units<sup>a</sup>

	$n\text{-NCMPy}(\text{CO})_1$			$n\text{-NCMPy}(\text{CO})_{\sim n/3}$		
	$\epsilon_g$	$IP^{KT}$	EA	$\epsilon_g$	$IP^{KT}$	EA
B3LYP/6-31G(d)	5.0 (0.94)	6.0 (0.88)	1.0 (0.84)	1.3 (0.97)	4.9 (0.88)	3.7 (0.96)
TD-DFT-B3P86/6-31G(d)	2.6 (1.0)			1.0 (0.84)		

<sup>a</sup> Specifically, calculations have been performed considering  $n\text{-NCMPy}(\text{CO})_1$  and  $n\text{-NCMPy}(\text{CO})_{\sim n/3}$  oligomers with  $n$  ranging from 3 to 12 (see text). The coefficients  $R^2$  derived from the linear regression analyses used to extrapolate the properties obtained for oligomers towards an infinite polymer chain (i.e., calculated property against  $1/n$ ) are displayed in parentheses.

**Figure 6.** Evolution of the  $\epsilon_g$  calculated at the TD-DFT-B3P86/6-31G(d) level for  $n\text{-NCMPy}(\text{CO})_1$  against  $1/n$ .

plays a crucial role in oligomers made up to nine repeating units but its influence vanishes for larger molecules. The overall of these results suggest that the ratio between the number of N-substituted pyrrole units with and without carbonyl groups, which seems to be comprised between 1:11 and 1:2, appears to be closer to the former than to the latter value (i.e.,  $\sim 1:8$ ). This feature combined with the experimental evidence of the multi-directional growing of PNCEPy<sup>29</sup> and the hypotheses that oxidative processes in pyrrole electropolymerization correspond to termination steps,<sup>60,61</sup> allow one to propose an idealized model for poly[N-(2-cyanoalkyl)pyrrole]s bearing short alkyl groups. This consists of a highly cross-linked structure made of very small branches (i.e., tracts of nine or even less repeating units) with a carbonyl group in the last repeating unit of each one.

## CONCLUSIONS

The electronic properties of PNCEPy have been determined experimentally and compared with those predicted theoretically for PNCMPy. Films of PNCEPy were prepared by anodic polymerization using a constant potential of 1.40 V. Cyclic voltammograms were recorded to estimate the IP (5.3 eV), EA (2.9 eV) and  $\epsilon_g$  (2.4 eV). The  $\epsilon_g$  value was also measured using the UV-vis absorption spectrum, which showed the  $\pi\text{--}\pi^*$  transition peak at 372 nm (i.e., 2.5 eV), in excellent agreement with the electrochemical estimation.

A systematic conformational analysis considering all the possible arrangements of 2-NCMPy and 3-NCMPy as starting points for geometry optimizations allow us to propose a model, which presents minimum repulsive interactions between consecutive repeating units, for idealized chains of poly[N-(2-cyanoalkyl)pyrrole]s bearing short alkyl groups. This is defined by the inter-ring dihedral angles, which adopt alternatively the

*anti-gauche* and *gauche-gauche* conformations, and the side groups arranged perpendicularly to the Py rings.

DFT and TD-DFT calculations indicated that the electronic properties of poly[N-(2-cyanoalkyl)pyrrole]s bearing short alkyl groups are not only influenced by the effect of the conformation on the conjugation of the  $\pi$ -system but also by the existence of carbonyl groups attached to the pyrrole ring of selected repeating units. Thus, previously detected secondary oxidative processes produce significant changes, which extend up to around nine repeating units, in both the optical and geometrical molecular properties. A systematic study on  $n\text{-NCMPy}(\text{CO})_x$  oligomers with  $x = 1$  and  $x \approx n/3$  allow us to conclude that poly[N-(2-cyanoalkyl)pyrrole]s present a cross-linked structure formed by small branches, the last repeating unit of each one bearing a carbonyl group.

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