Density-Functional Theory Study of Electronic and Structural Properties of Doped Polypyrroles

Renato Colle[†,‡] **and Alessandro Curioni***[‡,§]

Contribution from the Dipartimento di Chimica Applicata, Università di Bologna, Viale Risorgimento 2, I-40136 Bologna, Italy, Scuola Normale Superiore, I-56126 Pisa, Italy, and IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland

Received October 13, 1997

Abstract: Electronic and structural properties of polypyrroles oxidized by different concentrations of chlorine atoms or molecules are studied with the use of a density functional method implemented with plane waves and pseudo-potentials for the core electrons. The calculated properties are compared with those obtained for the neutral system that are in good agreement with the available experimental data. The role of the counterion in the oxidation process is studied extensively and shown to be crucial for the localization of charge and structural defects.

I. Introduction

For the past 20 years, organic, conducting polymers have constituted a major field of chemistry and physics research.[1−3] Interest in these materials is focused on their unique combination of the attractive mechanical properties of polymers and the electronic properties of metals or semiconductors.

Although the engineering of materials based on organic polymers has been developing on a large scale and many organic, conductive polymers have been synthesized,[1] our understanding of certain crucial chemical and physical properties of these systems is far from complete. In particular, it would be interesting, from both a theoretical and a practical point of view, to understand the electronic and structural modifications produced in these polymers by the inclusion of doping agents. This knowledge would allow, indeed, the optimization of the synthesis of new materials having specific conduction and mechanical properties by choosing the appropriate doping agent.

Theoretical studies have mainly been restricted to the use of semiempirical methods[4,5] and model Hamiltonians[6,7] that although sometimes capturing the essential physics of a specific problem, are inadequate in many cases and may lead to false conclusions.

This is especially true if these approaches are used in a context in which they have not been parametrized, such as for studying doped polymers and, in general, polymeric systems strongly perturbed by external agents. The complex nature of the chemical bonds that are involved in these problems and the fact that the inclusion of doping agents produces bond breakings and bond formations requires the use of ab initio procedures rather than semiempirical methods. It is generally much more difficult, however, to implement such procedures efficiently in large chemical systems, which is why very few and simplified calculations have been performed to date on doped polymers.[8]

In this paper we present the first ab initio calculations of several electronic and structural properties of doped polypyrroles, simulated as three-dimensional (3D) periodic arrangements of infinite chains with one chlorine atom or molecule added per unit cell. The polypyrrole was chosen because it is one of the prototypical organic polymers that become conducting when properly doped. The chlorine atom and molecule were used as doping agents because they are the simplest species that produce, after reduction, the chlorine anion, a typical counterion in both electrochemically and chemically p-doped polymers.

Our calculations allow us to compare the structural and electronic properties of doped polypyrroles with those of the corresponding neutral polymer and to study the dependence of these properties on the concentration of the doping agent, and thus to understand the role of the counterion. With regard to the first point, the use of periodic boundary conditions allows us to study different doping regimes simply by changing the size of the unit cell that includes the doping agent. With regard to the second point, we performed calculations on positively charged polypyrroles from which one electron has been removed every given number of pyrrole rings, but without the presence of counterions. A comparison between the properties of oxidized polypyrroles with and without doping agents yields useful information on the role of the counterion.

Our calculations were performed in the framework of the density-functional theory (DFT) with the Kohn−Sham (KS) formalism[9] implemented in a code[10] that uses plane waves

---

* To whom correspondence should be addressed: Alessandro Curioni, IBM Research Division, Zurich Research Laboratory, CH-8803 Rüschlikon, Switzerland.

[†] Universita di Bologna.

[‡] Scuola Normale Superiore.

[§] IBM Research Division, Zurich Research Laboratory.

(1) *Handbook of Conducting Polymers*; Skotheim, Terje A., Ed.; Marcel Dekker: New York, 1986, and references therein.

(2) Salaneck, W. R.; Clark, D. T.; Saumelsen, E. J. *Science and Application of Conducting Polymers*; Adam Hilger: Bristol, 1991.

(3) Salaneck, W. R.; Lundstron, I.; Ranby, B. *Conjugated Polymers and Related Materials: The Interconnection of Chemical and Electronic Structure;* Oxford University: London, 1993.

(4) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555, and references therein.

(5) Beljonne, D.; Bredas, J. L. *Phys. Rev. B* **1994**, *50*, 2841.

(6) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P. *Rev. Mod. Phys.* **1988**, *60*, 781.

(7) Brédas, J. L.; Elsenbaumer, R. L.; Chance, R. R.; Silbey, R. *J. Chem. Phys.* **1983**, *78*, 5656, and references therein.

(8) Otto, P.; Bakhshi, A. K.; Ladik J. *Theochem.* **1986**, *28*, 209.

(9) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(10) CPMD Version 2.5, Copyright 1994 IBM Corporation.

S0002-7863(97)03561-0 CCC: $15.00

(PWs) and atomic pseudo-potentials, together with the Car–Parrinello (CP) method[11] for the dynamical properties.

The polypyrrole is represented as a lattice of infinite regular chains of pyrrole rings, whose only degrees of freedom are internal to the chosen unit cell. It is well-known from the experimental data that the real polypyrroles are materials with a low degree of crystallinity, being a mixture of pyrrolic chains with large weight dispersion and a mass density usually of the order of 1 g/cm^3. Therefore, it is clear that the polypyrrole represented as a lattice of infinite chains of pyrrole rings is a simplified model that, however, retains the essential physics of the problem, constitutes the natural starting point for interpreting the experimental data, and allows one to perform sufficiently accurate ab initio calculations.

This paper is structured as follows. In section II, we describe the main technical features of the method used for our calculations. In section III, we present various electronic and structural properties calculated on neutral polypyrrole using a progressively larger unit cell to check the stability of the results. In section IV, we discuss the properties of chemical oxidized polypyrroles obtained by inserting one doping agent (chlorine atom or molecule) every given number of pyrrole rings. These results are compared with those obtained for positively charged polypyrroles with one electron removed every unit cell, but without explicitly including the counterion. Finally, in section V, we summarize the main conclusions that can be drawn from these calculations.

II. Computational Procedures

All the calculations presented in this paper were performed with a code that implements the KS equations[9] and the CP method[11] using a basis set of PWs together with a specific type of atomic pseudo-potentials. Such a code[10] has been successfully applied to the study of several chemical systems.[12−14]

Let us specify the type of calculations performed on these polymers.

We used the DFT in the framework of the local spin density (LSD) approximation with Becke (B) gradient correction[15] for the exchange energy and Perdew (P) gradient correction[16] for the correlation energy. It is well-known, in fact, that the resulting generalized gradient approximation predicts bond lengths, bond angles, frequencies, and other structural properties correctly. Regarding the choice of the exchange-correlation functional, we observe that the BP functional has been well tested in the context of PW expansions. On the other hand, our test calculations, performed on these systems using other functionals such as Becke-Lee-Yang-Parr (BLYP),[17] confirm the BP results.

We point out the importance of using the LSD approximation to study open-shell systems or processes that involve bond breaking and/or bond formation. In a wave function approach, indeed, the correct treatment of these problems requires a many-determinant description that can be, at least partially, reproduced only by using the LSD approximation.

Pseudo-potentials are essential if one uses a PW expansion of the KS orbitals. Having performed several tests on sample molecules with different bonding environments, such as ammonia, ethene, and pyrrole, we used the Vanderbilt ultrasoft pseudo-potentials (USPP)[18] to account for interactions between the valence electrons and the atomic cores for all the atoms of our systems. The USPP are fully nonlocal, separable potentials constructed without imposing norm conservation. They allow a relevant reduction of the energy cutoff in PW expansions, while still maintaining a reasonable degree of transferability, as shown by the satisfactory results obtained in calculations performed on different chemical systems.[19−20] An energy cutoff of 35 Ry was imposed in the PW expansion. Note that using these pseudo-potentials, we obtain the convergence of the energy values with a cutoff of only 25 Ry, but the correct description of the nuclear forces requires a cutoff of 35 Ry. Details of the construction of the USPP can be found in ref 18.

Finally, we observe that norm-conserving pseudo-potentials, such as those proposed by Troullier and Martins,[22] although usually more transferable and accurate, yield comparable results only when we use a cutoff higher than 55 Ry for the nitrogen atom.[13] Therefore, they are more expensive for calculations on polymeric systems.

III. Electronic and Structural Properties of Neutral Polypyrroles

The crystalline model chosen to represent neutral polypyrroles is characterized by a periodic array of infinite chains with a tetragonal unit cell containing an (α-α') *trans*-dipyrrole unit on the *x*,*y* plane, where *x* is the chain axis shown in Figure 1. The real-space basis vectors used in our calculations are

$$\vec{a} = a\hat{x}, \qquad a = 13.5664 \text{ au}$$

$$\vec{b} = b\hat{y}, \qquad b = 1.2a$$

$$\vec{c} = c\hat{z} \qquad c = \text{a}$$

where the value of the parameter *a* has been derived from preliminary calculations on the isolated dipyrrole and optimized on the crystalline structure.

The resulting volume of the unit cell is $V = 2996$ (au)^3, the mass density is ≈ 0.5 g/cm^3, and the mean interchain distance ≈ 7 Å. The latter is of the order of the charged carrier hopping distance in the real polypyrroles,[23] whereas the mass density has been chosen somewhat lower than in a typical pyrrole polymer in order to maintain the same interlayer distance also in the subsequent calculations when doping agents were included. On the other hand, one should remember that the local density in real polypyrroles can be very different from the average density.

We obtained the ground-state structure of the neutral polymer using, as variational parameters for the energy, the coordinates of the nuclei inside the given unit cell. As our CP code utilizes only the Γ point to sample the first Brillouin zone, we improved the structural optimization by repeating calculations with unit cells having one, two, and three primitive cells inside, i.e., two,

---

[11] Car, R.; Parrinello, M. *Phys. Rev. Lett.* **1985**, *55*, 2471.

[12] Curioni, A.; Andreoni, W.; Hutter, J.; Schiffer, H.; Parrinello, M. *J. Am. Chem. Soc.* **1994**, *116*, 11251. Curioni, A.; Sprik, M.; Andreoni, W.; Schiffer, H.; Hutter, J.; Parrinello, M. *J. Am. Chem. Soc.* **1997**, *119*, 7218.

[13] Andreoni, W.; Curioni, A.; Holczer, K.; Prassides, K.; Keshavarz, M.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1996**, 118, 11335.

[14] Marchi, M.; Hutter, J.; Parrinello, M. *J. Am. Chem. Soc.* **1996**, 118, 7847.

[15] Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

[16] Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

[17] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

[18] Vanderbilt, D. *Phys. Rev. B* **1993**, *47*, 10142.

[19] Meir, R. J.; van Doremaele, G. H. J.; Iarlori, S.; Buda, F. *J. Am. Chem. Soc.* **1994**, *116*, 7274.

[20] Curioni, A.; Andreoni, W.; Hutter, J.; Schiffer, H.; Parrinello, M. *J. Am. Chem. Soc.* **1994**, *116*, 11251.

[21] Tuckerman, M. E.; Laasonen, K.; Sprik, M.; Parrinello, M. *J. Phys. Chem.* **1995**, *99*, 5749; *J. Chem. Phys.* **1995**, *103*, 150.

[22] Troullier, N.; Martins, J. *Phys. Rev. B* **1991**, *43*, 1993.

[23] Maddison, D. S.; Unsworth, J.; Roberts, R. B. *Synth. Metals* **1988**, *26*, 99.

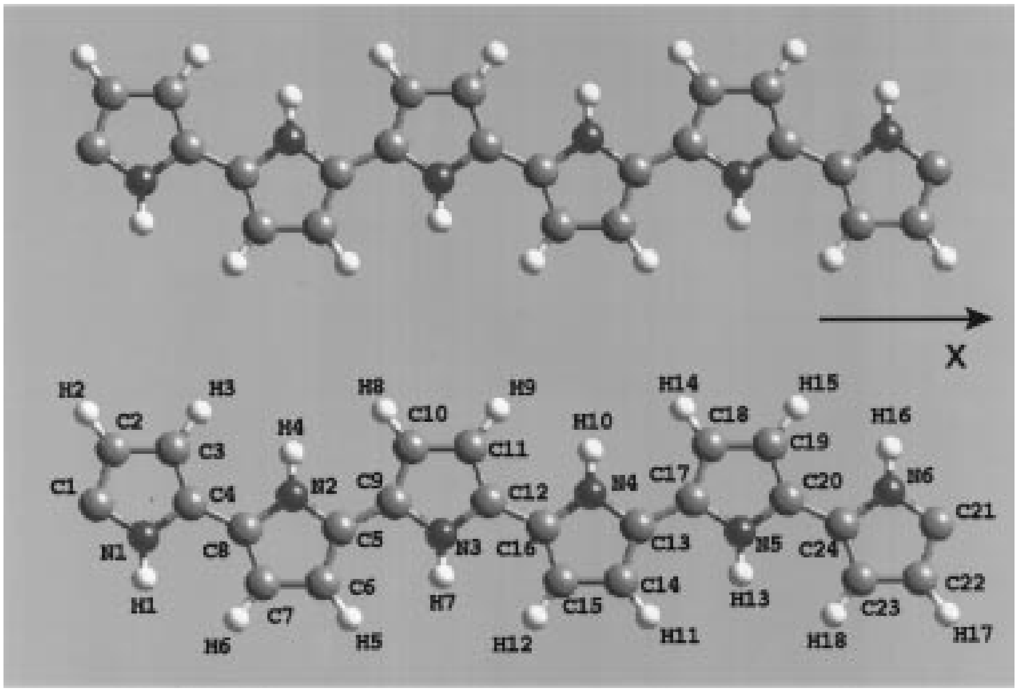

Figure 1. Structure of two neighboring pyrrole chains on the (*x*,*y*) plane with the labeling of the atoms of the pyrrole rings.

Table 1. Summary of Bond Distances (Å) and Bond Angles (deg) of the Neutral Polypyrrole[a]

	UC1	UC2	UC3	Brocks[25]	Andre[26]
N1−C1	1.386	1.390	1.390	1.406	1.384
C1−C2	1.382	1.395	1.396	1.405	1.373
C2−C3	1.446	1.423	1.419	1.433	1.418
C4−C8	1.463	1.437	1.433	1.462	1.448
N1−H1	1.026	1.024	1.023	1.035	0.990
C2−H2	1.090	1.091	1.090	1.095	1.080
C1−N1−C4	109.9	110.2	110.3	111.0	109.0
N1−C1−C2	107.7	107.2	106.8	106.2	107.5
C1−C2−C3	107.4	107.8	107.9	108.2	108.0
C3−C4−C8	132.8	132.3	132.0	125.9	131.0
H1−N1−C1	125.0	124.9	124.9	121.6	125.5
C3−C4−C8−C7	0.0	0.0	0.0	0.0	0.0

[a] UC1, 2, and 3 stand for supercells with 2, 4, and 6 rings.

four, and six pyrrole rings, respectively. Then, we studied the dispersion of the Hartree-Fock bands calculated with the CRYSTAL package[24] to rule out any critical dependence of the energy levels on the $\vec{k}$ vector (see below for a detailed analysis). Being interested in statical properties, we recall that the use of the only Γ point to sample the first Brillouin zone is justified if the unit cell is sufficiently large.

The geometrical parameters obtained from the structural optimizations of the pyrrolic chain are listed in Table 1, where they are compared with those calculated by Brocks et al.[25] by using the local density approximation (LDA), and with the data obtained by averaging the X-ray experimental data available for the crystalline dipyrrole and terpyrrole.[26] Note that the structural data obtained from polypyrrole samples are difficult to interpret, but suggest a structure of (α-α′) linked rings in the transplanar conformation, with an estimated inter-ring distance of approximately 1.43 ± 0.09 Å.[27]

It is clear from Table 1 that the structural parameters can be considered stabilized when a unit cell of four pyrrole rings (two primitive cells) is used. Note also that the major geometrical changes resulting from increasing the size of the unit cell, concern the carbon backbone of the ring. More specifically, one observes a clear reduction of the single/double bond alternation that indicates a larger delocalization of the π orbitals.

A quantitative analysis can be performed by defining the function $F(d_1,d_2) = d_1/ d_2$, where d_1 is the length of the $C_2{-}C_3$ bond (formally a single bond) and d_2 that of the $C_1{-}C_2$ bond (formally a double bond). This function yields a measure of the relative importance of the "aromatic" character with respect to the "quinoid" character of the conjugation, where quinoid means a structure in which $C_2{-}C_3$ and $C_4{-}C_8$ have a larger double-bond character than in the standard (aromatic) configuration of the dipyrrole. By enlarging the size of the unit cell, we obtain $F = 1.046$, 1.020, and 1.015, respectively, results that indicate a trend toward a larger quinoid character, i.e., toward a less pronounced alternation of single and double bonds in the carbon backbone.

Another interesting result is the almost perfect planarity of the optimized structure of the pyrrolic chains. We tested this result by changing the starting point of the optimization process and looking for the presence of an out-of-plane minimum. In all these calculations, however, the optimization process has converged to the planar structure reported in Table 1. A comparison of these parameters with those obtained by Brocks et al.[25] using LDA with norm-conserving pseudo-potentials and two k points to sample the first Brillouin zone shows that Brocks's structure is somewhat more expanded than ours, even if its F function has a similar value ($F = 1.020$).

Another experimental quantity that can be reproduced by our calculations is the profile of the density of states (DOS) obtained by convoluting the KS eigenvalues with a Gaussian function having a half-width of ~0.5 eV. Such a value yields a broadening comparable to that of a typical spectral line in the photoabsorption spectra recorded on these materials.

---

(24) Dovesi, R.; Saunders: V. R.; Roetti, C. CRYSTAL92 program, Theoretical Chemistry Group, University of Turin, Italy, and SERC Daresbury Laboratory, UK.

(25) Brocks, G.; Kelly, P. J.; Car, R. *Synth. Met.* **1993**, *57*, 4243.

(26) Andre, J. M.; Vercauteren, D. P.; Street, G. B.; Bredas, J. L. *J. Chem. Phys.* **1984**, *80*, 5643.

(27) Petrillo, C.; Borra, S.; Cagnolati, R.; Ruggeri, G. *J. Chem. Phys.* **1994**, *101*, 11004.

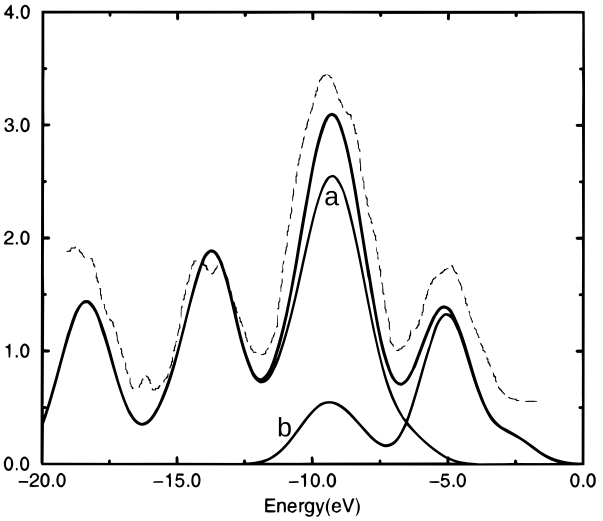

Figure 2. UPS spectrum (dashed line), recorded on neutral polypyrrole, compared with the calculated DOS (top, solid line). This quantity is decomposed into a contribution of σ electrons (a) and one of π electrons (b).

Figure 2 compares the calculated DOS with the experimental ultraviolet photoelectron spectroscopy (UPS) spectrum recorded on a polypyrrolic sample.[28,29] The analysis of these two spectra shows that the theoretical DOS, normalized to the number of states per ring, reproduces the experimental spectrum very well. Furthermore, by expanding the KS orbitals on a basis of localized functions, one can separate the contributions due to the σ and π electrons and analyze their characteristics. In particular, we see that the density of π states around −10 eV is due primarily to bonding interactions between the lone pair on the nitrogen and the π orbitals on the carbon atoms, whereas the density around −5 eV is due primarily to carbon−carbon bonding interactions. Finally, the density of σ states has its absolute maximum at approximately −10 eV, which indicates a significant, although indirect, coupling between the σ and π orbitals delocalized on the carbon backbone. This result suggests possible significant drawbacks of using π -only models to study nondegenerate ground states of conjugated polymers.

Finally, as our code does not yield the k dispersion of the bands, we analyzed the Hartree−Fock bands produced by the CRYSTAL package[24] using the unit cell UC2 of Table 1 with 1D periodicity. For these calculations we used a 6-21G basis set plus polarization functions, with 30 k points to sample the first Brillouin zone. Figure 3 shows the energy bands around the gap, which are 2-fold degenerate at the end of the Brillouin zone due to the existence of a 2-fold screw axis. We observe that these bands are characterized by a smooth dependence on the k parameter, which justifies the use of the only Γ point to sample the first Brillouin zone.

IV. Electronic and Structural Properties of Doped Polypyrroles

In this section we discuss the results of calculations of the electronic and structural properties of doped polypyrroles obtained by adding one chlorine atom or molecule every given number of pyrrole rings.

Note that a direct comparison of our results with experimental values is difficult because the available data are often strongly dependent on the experimental procedures used for preparing the polymeric sample and also on the type of measurement performed.

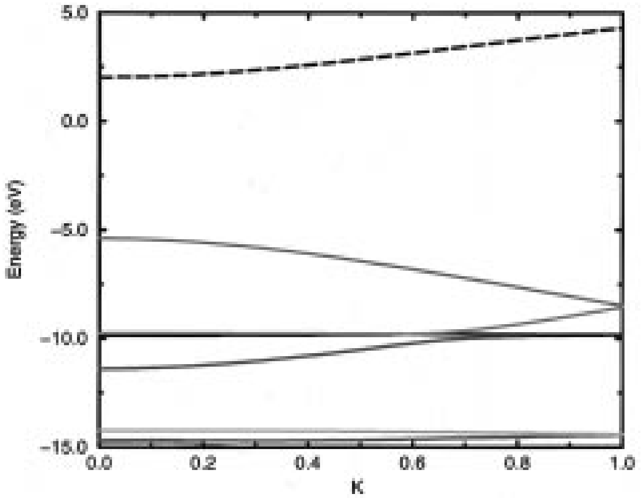

Figure 3. Hartree−Fock energy bands of the levels around the gap of the neutral polypyrrole. The dashed line corresponds to the lowest unoccupied molecular orbital (LUMO) level.

We started with a crystalline polypyrrole having the unit cell UC2 (Table 1) plus one Cl atom per unit cell located ~2.5 Å above the plane of the rings. Structural optimizations were performed using a “simulated annealing” procedure[30] to find the region where the absolute minimum of the energy is located and then a “quasi-Newton method”[31] to better refine the final values of the structural parameters. Different local minima on the energy surface are, in fact, quite frequent in such complicated systems, and the identification of the “experimental” configuration is a difficult task. Figure 4 shows the optimized structure together with the electronic charge density of the system; the characteristic parameters of this structure are reported in Table 2. From the analysis of these data we observe the following

(1) The doped polypyrrole loses its planarity and achieves an asymmetric structure with a conjugation of the π orbitals appreciably reduced.

(2) Each Cl atom is mainly coordinated to a single chain with a distance between Cl atom and nearest chain reduced to 2.13 Å. The atom is localized above one pyrrole ring close to the N−H bond.

(3) There is a quinoid-like deformation of the chain structure. This deformation is centered on the pyrrole ring nearest the Cl atom, and the defect is widespread over only two side rings, the last one maintaining its aromatic character. This fact is confirmed by the F function, the values of which are 0.993, 0.982 (ring closest to Cl), 0.994, and 1.014, respectively, and by the inter-ring bond lengths 1.427, 1.426, 1.433, and 1.432 Å.

(4) The Mulliken population analysis yields a value of −0.59 au for the net atomic charge of the chlorine atom and an alternation of positive and negative charges on the four pyrrole rings of the unit cell, which are 0.43, −0.17, 0.45, and −0.12 au, respectively. The small negative charge on the pyrrole ring closest to the Cl atom suggests a covalent-like interaction between Cl atom and nearest ring. This fact, which could in part be an artifact of the Mulliken population analysis, is confirmed by the charge density distribution shown in Figure 4

---

(28) Ford, W. K.; Duke, B.; Salaneck, W. R. *J. Chem. Phys.* **1982**, *57*, 5030.

(29) Mintmire, J. W.; White, c. t.; Elert, M. L. *Synth. Met.* **1988**, *25*, 109.

(30) Kirchpatrick, S.; Gelatt, C. D.; Vecchi, M. P. *Science* **1983**, *220*, 671.

(31) Press: W. H.; Flannery, B. P.; Teukolosky, S. A.; Vetterling, W. T. *Numerical Recipes*; Cambridge University: Cambridge, 1989.

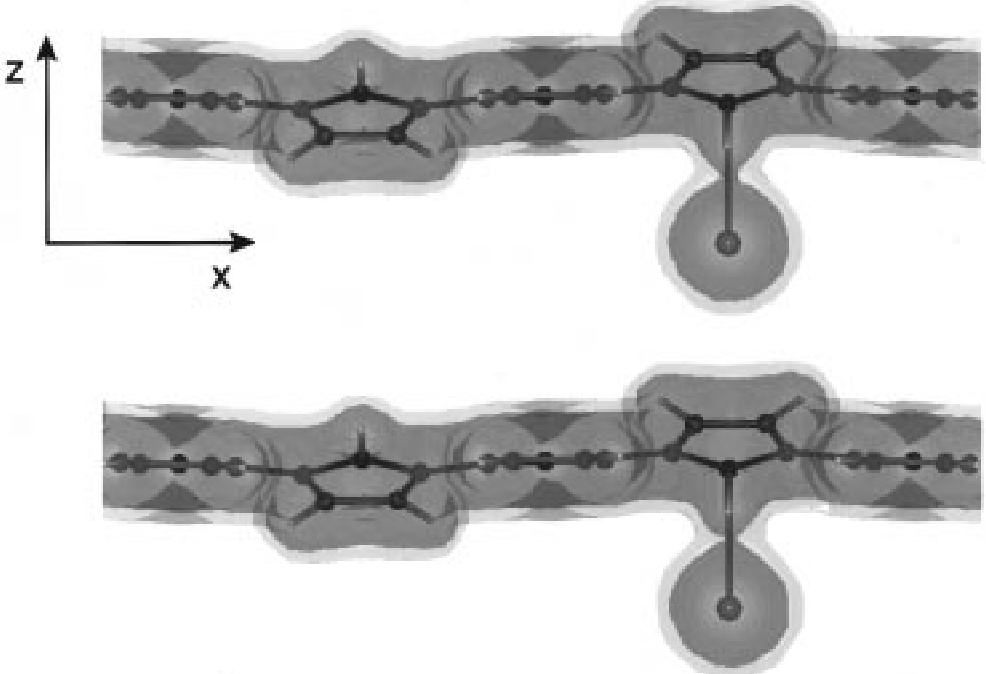

Figure 4. Isosurfaces [0.05 au (dark) and 0.02 au (light)] of the electronic charge density of two pyrrole chains doped by one chlorine atom every four pyrrole rings.

Table 2. Bond Distances (Å) and Dihedral Angles (deg) of Cl-Doped Polypyrrole (Doping Ratio 25%)[a]

N1−C1	1.396	N3−C9	1.391
N1−C4	1.392	N3−C1	1.394
C1−C2	1.410	C9−C10	1.409
C2−C3	1.400	C10−C11	1.402
C3−C4	1.411	C11−C12	1.410
C4−C8	1.427	N3−H7	1.026
N1−H1	1.026	C10−H8	1.090
C2−H2	1.089	C11−H9	1.088
C3−H3	1.088	C12−C16	1.433
N2−C5	1.384	N4−C13	1.389
N2−C8	1.384	N4−C16	1.398
C5−C6	1.419	C13−C14	1.405
C6−C7	1.397	C14−C15	1.411
C7−C8	1.421	C15−C16	1.405
C5−C9	1.426	C13−C17	1.432
N2−H4	1.102	N4−H10	1.026
C6−H5	1.090	C14−H11	1.090
C7−H6	1.090	C15−H12	1.090
Cl−H4	2.128	Cl−N1	5.213
Cl−N2	3.099	Cl−N3	5.177
Cl−N4	5.213	Cl′ −N2	4.682
C3−C4−C8−C7	30.4	C6−C5−C9−C10	28.9
C11−C12−C16−C15	27.1	C14−C13−C17−C18	27.1

[a] Cl′ indicates the nearest image of Cl.

Table 3. Bond Distances (Å), Bond and Dihedral Angles (deg), and Mayer Bond-Order Differences (ΔB), Calculated with Respect to the Neutral Polypyrrole, for Oxidized Polypyrrole (Oxidation Degree 25%)

		ΔB
Bond Length		
N1−C1	1.392	−0.01
C1−C2	1.412	−0.12
C2−C3	1.399	0.12
C4−C8	1.428	0.07
N1−H1	1.026	−0.05
C2−H2	1.089	−0.02
Bond Angles		
C1−N1−C4	110.3	
N1−C1−C2	106.7	
C1−C2−C3	108.2	
C3−C4−C8	130.3	
H1−N1−C1	124.5	
Dihedral Angles		
C3−C4−C8−C7	14.5	
C6−C5−C9−C10	14.5	
C11−C12−C16−C15	14.5	
C14−C13−C17−C18	14.5	

and suggests an “active” role of the counterion in a hypothetical conduction process.

(5) An analysis of the KS eigenvalues and eigenvectors indicates the presence of three levels corresponding to the *p* states of the chlorine atom at energies just below the highest occupied molecular orbital (HOMO) level. One of these states is clearly stabilized by the strong interaction of the chlorine atom with the hydrogen of the N−H group belonging to the nearest pyrrole ring. This analysis is confirmed by the structure of the excess spin density distribution reported in Figure 5, which has no component between the hydrogen and the chlorine atom, but is mainly delocalized along the pyrrolic chain. The presence of a small spin density on the chlorine atom confirms that the charge transfer from the three pyrrole rings toward the Cl atom is not complete.

Let us compare these results with those obtained for an oxidized polypyrrole with one hole every four rings, but without the presence of counterions. We observe, preliminarily, that removing one electron per unit cell produces a metallic state with a half-filled band that is unstable in a strictly one-dimensional (1D) system. Stabilization can be achieved either via structural deformations or by means of 3D interactions. In our computational scheme, the global electroneutrality of the system is achieved by introducing a background of uniformly spread negative charge.

The parameters of the optimized structure are listed in Table 3 together with the Mayer bond-order differences calculated with respect to the bond orders in neutral polypyrrole. The oxidized structure presents an out-of-plane deformation that is smaller

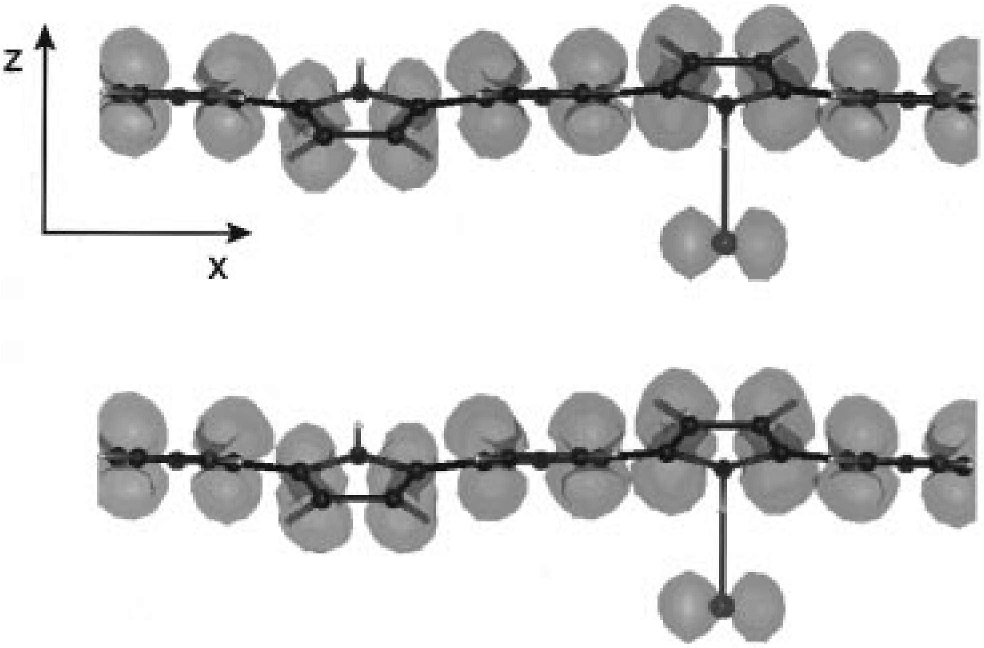

Figure 5. Isosurface (0.002 au) of the excess spin density of two pyrrole chains doped by one chlorine atom every four rings.

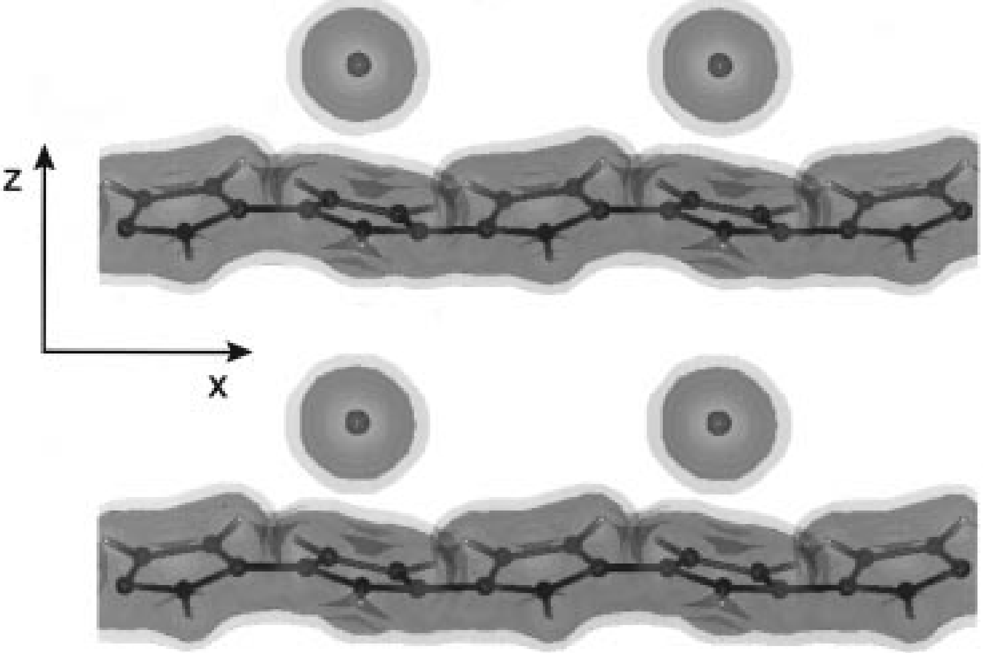

Figure 6. Isosurface (0.1 au) of the electronic charge density of two pyrrole chains doped by one chlorine atom every two pyrrole rings.

than in the chemically doped system and characterized by an overall and uniform quinoid-like deformation without localization of the defect. This analysis is also confirmed by the F function that has the same value ($F = 0.980$) on each ring and by the Mulliken population analysis, which yields the same net positive charge on each ring. The main structural changes pertain to the carbon backbone, with only minor modifications in the region of the nitrogen. This deformation constitutes a way to eliminate the intrinsic instability of the quasi-1D metal by means of 3D interactions.

A comparison with the system oxidized by adding one Cl atom every four pyrrole rings shows that the doping agent localizes both the positive charge and the structural modifications and thus produces larger and more asymmetric deformations. To study the effects of different concentrations of doping agent on the electronic and structural properties of these systems, we considered a polypyrrole doped by one Cl atom every two pyrrole rings (doping ratio 50%). The optimized structure of this polymer is shown in Figure 6 together with the electronic charge density of the system, whereas the characteristic parameters of the structure are listed in Table 4.

These calculations were performed using the unit cell UC1 of Table 1 with one Cl atom inside. Therefore, as shown by our preliminary calculations on the neutral chain, the resulting structure is not completely optimized with respect to the increase of the size of the unit cell. However, the effects due to the inclusion of the Cl atoms are much greater than those due to the incomplete structural optimization and can be summarized as follows:

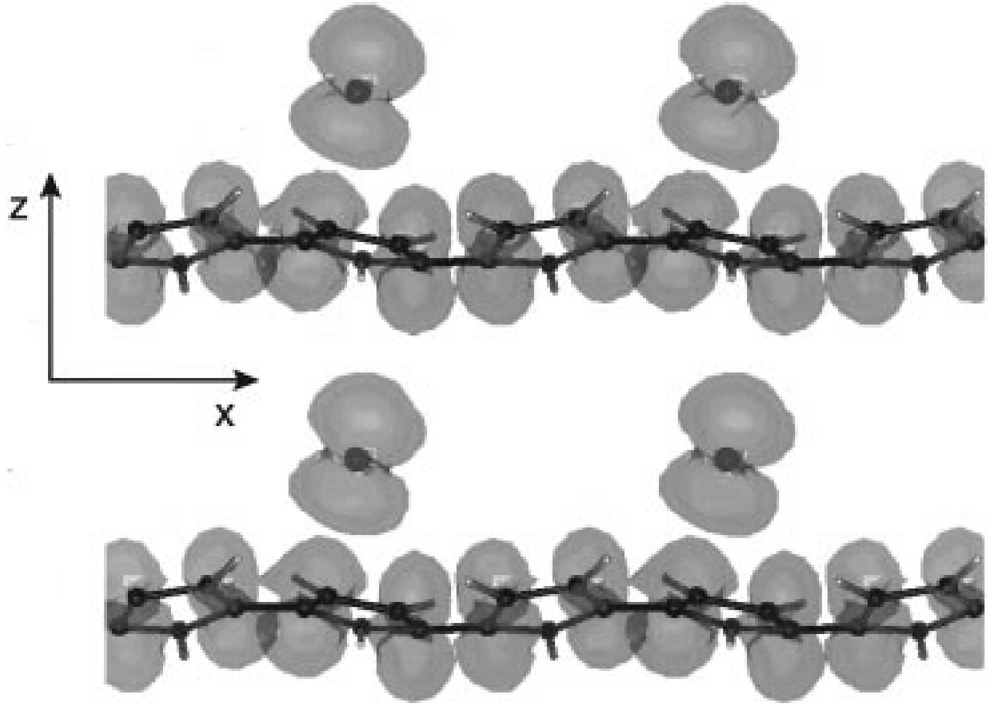

Figure 7. Isosurface (0.002 au) of the excess spin density of two pyrrole chains doped by one chlorine atom every two rings.

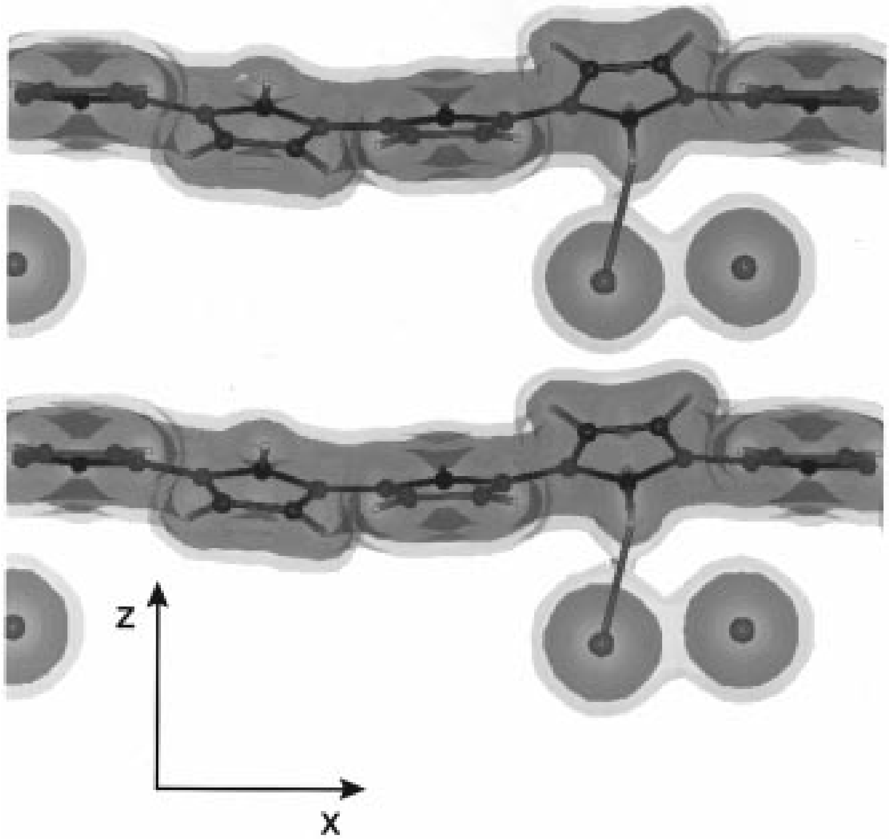

Figure 8. Isosurface (0.1 au) of the electronic charge density of two pyrrole chains doped by one chlorine molecule every four pyrrole rings.

(1) Each chlorine atom is not symmetrically located between the two pyrrole rings of a unit cell and interacts simultaneously with two chains on different layers (the minimum distances are 3.16 and 3.57 Å, respectively). Two neighboring chains are thus appreciably coupled by the doping agent, a fact that produces a real 3D structure.

(2) The presence of the Cl atom induces a quinoid-like deformation mainly on the closest ring (−0.627 au). This means that the interaction between Cl atom and pyrrolic chain has a greater ionic character than in the previous case where the doping ratio was 25%.

The analysis of the charge density distribution in Figure 6 and of the excess spin density in Figure 7 shows that the interaction between Cl atoms and pyrrolic chains does not present the covalent-like character of the previous case. Instead, these density distributions suggest a prevalent ionic interaction

Table 4. Bond Distances (Å) and Dihedral Angles (deg) of Cl-Doped Polypyrrole (Doping Ratio 50%)[a]

N1−C1	1.399	C5−C9	1.463
N1−C4	1.390	N2−C8	1.379
C1−C2	1.400	N2−C5	1.386
C2−C3	1.413	C5−C6	1.412
C3−C4	1.405	C6−C7	1.408
C4−C8	1.459	C7−C8	1.407
N1−H1	1.027	N2−H4	1.028
C2−H2	1.089	C6−H5	1.089
C3−H3	1.089	C7−H6	1.089
Cl−N1	5.115	Cl1−C6	3.450
Cl−N2	3.286	Cl1−C7	3.752
Cl−C5	3.160	Cl1−C8	3.637
Cl′−H4	3.570		
N1−C4−C8−C7	−25.9	C3−C4−C8−N2	−24.8
N2−C5−C9−C10	43.8	C6−C5−C9−N2	33.5

[a] Cl′ indicates the nearest image of Cl.

Table 5. Bond Distances (Å) and Dihedral Angles (deg) of Cl_2-Doped Polypyrrole (Doping Ratio 50%)[a]

N1−C1	1.395	N3−C9	1.387
N1−C4	1.395	N3−C1	1.394
C1−C2	1.408	C9−C10	1.412
C2−C3	1.405	C10−C11	1.396
C3−C4	1.410	C11−C12	1.411
C4−C8	1.432	N3−H7	1.025
N1−H1	1.025	C10−H8	1.088
C2−H2	1.090	C11−H9	1.090
C3−H3	1.089	C12−C16	1.437
N2−C5	1.391	N4−C13	1.397
N2−C8	1.391	N4−C16	1.397
C5−C6	1.411	C13−C14	1.406
C6−C7	1.402	C14−C15	1.410
C7−C8	1.412	C15−C16	1.407
C5−C9	1.431	C13−C17	1.437
N2−H4	1.047	N4−H10	1.026
C6−H5	1.090	C14−H11	1.090
C7−H6	1.091	C15−H12	1.090
Cl1−N2	4.19	Cl2−C10	3.79
Cl1−H4	3.79	Cl2−H8	3.80
Cl1′−N2	3.37	Cl2′−C9	3.400
Cl1′−H4	2.46	Cl2′−H4	3.04
Cl1−Cl2	2.81		
C3−C4−C8−C7	25.7	C6−C5−C9−C10	39.9
C11−C12−C16−C15	19.4	C14−C13−C17−C18	32.7

[a] Cl1′ indicates the nearest image of Cl1.

having a polarization of the chlorine charge perpendicular to the pyrrole chain (see Figure 7).

Let us, finally, consider the system doped by adding one chlorine molecule every four pyrrole rings. The optimized structure is shown in Figure 8 together with the electronic charge density of the system, whereas the values of the main structural parameters are listed in Table 5. From the analysis of these data we observe the following:

(1) The two Cl atoms are located asymmetrically in the unit cell: one is closer to a chain, and the other is almost equidistant from two neighboring chains. Therefore, the two positions are different from that of a Cl atom in the system doped by one Cl atom every two pyrrole rings.

(2) The distance between two chlorine atoms increases to 2.81 Å from the initial molecular value of 2 Å. This means that the Cl−Cl bond has been appreciably weakened, but not completely broken.

(3) The values of the F function on the four rings are quite similar (0.997, 0.993, 0.989, and 1.002) and indicate a slight preference for a quinoid-like structure. It is also evident that one Cl atom interacts mainly with the second and third rings of the unit cell, where the structural deformations are larger.

(4) The Mulliken population analysis yields net atomic charges on the two chlorine atoms of −0.390 and −0.42 au, and a global net charge on each pyrrole ring of 0.37, −0.04, 0.53, and −0.05 au. Such an alternating charge distribution is very similar to that observed in the polypyrrole doped by one Cl atom every four rings. On the other hand, the oxidation efficiency of one Cl_2 molecule is appreciably smaller than that of two Cl atoms, and the charge density distribution shown in Figure 8 indicates that the interaction between a chlorine molecule and pyrrole chain is not completely ionic.

A possible scenario suggested by these results is the formation of a partial charge-transfer complex of the type $[Py_4^{+\delta}{-}Cl_2^{-\delta}]$. Weak complexes of this type have been proposed for adducts resulting from the interaction of one chlorine molecule with a system having delocalized π electrons[32] and have been recently observed for the interaction of molecular oxygen with poly(3-alkylthiophenes).[33]

V. Conclusions

The main conclusions that can be drawn from these calculations are the following:

(1) A gradient-corrected DFT calculation predicts a planar structure of the pyrrolic chains in the neutral polymer and allows one to reproduce very satisfactorily the experimental UPS spectra recorded on these systems.

(2) The inclusion of a doping agent, with a concentration of ∼25%, causes out-of-plane distortions of the pyrrolic chains and produces a localized defect with an excess of positive charge. Calculations performed on these systems without the explicit presence of the counterion do not yield the same local distortions.

(3) The charge transfer from a pyrrolic chain to a chlorine atom is, in general, not complete and the resulting interaction still presents a covalent character that involves interactions with the σ skeleton of the pyrrolic chain.

(4) Localization effects decrease with increasing concentration of the doping agent. The Cl atoms tend to couple neighboring chains, and their interaction with the pyrrole chains becomes more ionic.

(5) The oxidation efficiency of the Cl_2 molecule is generally lower than that of separate Cl atoms at the same concentration. The stable species resulting from the inclusion of one Cl_2 molecule every four pyrrole rings can be viewed as a charge-transfer complex of the type $[Py_4^{+\delta}{-}Cl_2^{-\delta}]$.

Acknowledgment. One of us (A.C.) wants to acknowledge Wanda Andreoni for many useful discussions.

JA9735618

---

[32] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 549−551.

[33] Abdou, M. S. A.; Orfino F. P.; Son, Y.; Holdcroft S. *J. Am. Chem. Soc.* **1997**, *119*, 4518.