

# Theoretical Study of Chloropyrroles as Monomers for New Conductive Polymers

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Received: April 8, 2005; In Final Form: August 4, 2005

Electronic, structural, electrochemical, and spectroscopic properties of all ground-state neutral and singly ionized chlorine-substituted pyrroles and hexa(3-chloropyrrole) oligomer are studied using the density functional theory B3LYP method with the 6-31G(d,p) basis set. The effects of the number and position of the substituents on the electrochemical properties of the pyrrole ring have been studied and analyzed both quantitatively and qualitatively. By using the optimized structures obtained for these molecules and their cations, IR and NMR spectra have been predicted. The results of this study, including spin and charge distributions, show that, among all of these compounds, 3-chloropyrrole has the most suitable conditions for electropolymerization.

## 1. Introduction

Conducting polymers, such as polypyrrole (PPY) and polythiophene, synthesized via electropolymerization procedures, have received much attention since 1979 when Diaz et al. synthesized PPY on the surface of an electrode.<sup>1</sup> These polymers have been used as modifiers for the construction of chemically modified electrodes, which have found applications in many fields such as biosensors,<sup>2</sup> electrocatalysis,<sup>3</sup> and ion-selective electrodes.<sup>4</sup> PPY has received the most attention owing to its convenient preparation, good stability, and appropriate range of applications. PPY can be easily prepared by oxidative, either chemically or electrochemically, polymerization of pyrrole. However, synthetic conductive PPY is insoluble and infusible, which restricts its processing and applications in other fields. This problem has been extensively investigated, and new applications have also been explored in the past several years. For example, PPY-based polymers can be used to load and release drugs and biomolecules.<sup>5</sup> Because of strong adhesion to iron or steel pretreated with nitric acid, PPY polymers can be used as good adhesives in the related applications.<sup>6</sup> In a recent report,<sup>7</sup> PPY-modified tips for functional group recognition are applied in scanning tunneling microscopy, which has found numerous applications, especially in nanotechnology and nanoscience. Theoretical studies on the structure of polymers have contributed a lot to rationalizing the properties of known polymers<sup>8–15</sup> and to predicting those of yet unknown ones.<sup>16</sup> Further, structural studies on PPYs via *ab initio* evaluation of binding<sup>17</sup> and the Monte Carlo growth approach to the branch formation have so far been reported.<sup>18</sup>

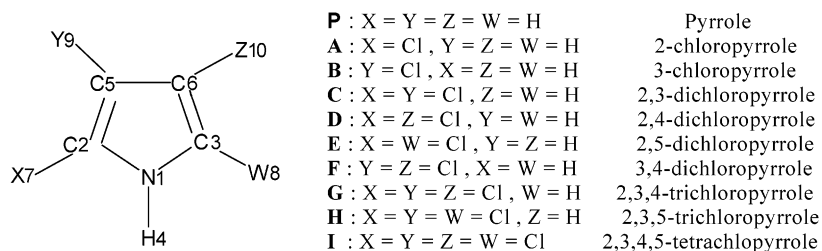
Poor processibility of PPY due to its insolubility and infusibility has retarded further investigation on the structure and the structure-related physical properties. To improve the processibility, many researchers have been engaged in the development of soluble or swollen PPY. At the same time, the electric properties and/or stability of chemically prepared PPY have also been investigated in many laboratories because of the importance of the stability of conducting polymers, which seems to be the main limiting factor in their practical applica-

tions. A review article has been published on the lengthy and fruitful history of the processibility of conducting polymers<sup>19</sup> in which several methods for PPY synthesis have been introduced. For example, several kinds of soluble PPY have been synthesized, such as poly(3-alkylpyrrole) with an alkyl group equal to or greater than a butyl group,<sup>20</sup> which has been found to be easily soluble in common solvents. However, the main problem is the complicated synthesis of 3-substituted pyrrole monomers. On the other hand, poly(*N*-substituted pyrrole)'s have much lower conductivity because of greatly suppressed conjugation along the polymer chain axis caused by the substituents on nitrogen.<sup>21,22</sup> At the same time, they are only partly soluble in some organic solvents even with long alkyl groups substituted on the nitrogen of pyrrole ring. Therefore, substitution of the pyrrole with functional groups may result in new possibilities for the modification of the properties of PPY. Although the engineering of materials based on organic conducting polymers has been developing on a large scale and many organic conductive polymers have been synthesized,<sup>23</sup> our understanding of certain crucial chemical and physical properties of these systems is far from being complete. In particular, it would be interesting, from both theoretical and practical points of view, to understand the electronic and structural modifications produced in these polymers by the inclusion of new functional groups. This knowledge would allow, indeed, the optimization of the synthesis of new materials having the desired electric conduction and mechanical properties by choosing the appropriate functional groups. In the previous papers of this series of studies,<sup>24,25</sup> we have reported *ab initio* and density functional theory (DFT) study on all fluoro- and halomethylpyrroles and their cations and anions. The main goal of this series of studies has been to find a suitable monomer for the preparation of corresponding conducting polymers with improved electrical and mechanical properties.<sup>24,25</sup> The DFT method<sup>26,27</sup> is a good quantum mechanical tool for the study of ground-state neutral and charged species, which is valid for the lowest state of each electronic symmetry.<sup>28</sup> In this paper, we report the results of our study on electronic and structural properties of different chloropyrrole monomers, Figure 1, as well as those of the hexa(3-chloropyrrole) oligomer, Figure 2, and their singly ionized cations.

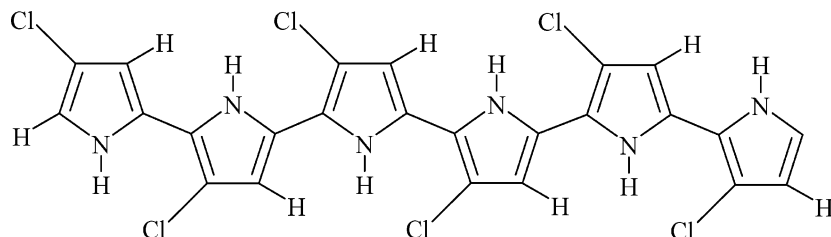
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**Figure 1.** All chlorine-substituted pyrrole isomers studied in this research.



**Figure 2.** Molecular structure of hexa(3-chloropyrrole), **B**-hexamer, studied in this work.

## 2. Computational Procedures

As in complex systems, the identification of the minimum-energy conformations is quite difficult because of the presence of several local minima on the energy surface. As shown in our previous works,<sup>24,25</sup> DFT has been a better method, in comparison with MP2 and HF methods, for the study of fluoro- and halomethylpyrrole series of compounds. To obtain accurate results, we have selected Becke–Lee–Parr hybrid density functional (B3LYP) level of theory with a large basis set 6-31G(d,p) to optimize structures of neutral chloropyrroles and hexa(3-chloropyrrole) oligomer and their cations. The fundamental vibrational frequencies for all chloropyrroles were calculated using optimized structures thus obtained.

In addition, <sup>1</sup>H and <sup>13</sup>C shielding constants have been calculated for the DFT–B3LYP/6-31G(d,p) optimized geometries. The harmonic vibrational frequencies obtained with B3LYP/6-31G(d,p) calculations have been used to characterize the stationary points as local minima and to obtain zero-point vibrational energy (ZPE). All of the ab initio calculations described herein have been carried out by employing the *Gaussian 94W* program package.<sup>29</sup>

## 3. Results and Discussion

**3.1. Structural Analysis.** Table 1 compares the structural parameters obtained at the B3LYP/6-31G(d,p) level of theory for the studied chloropyrroles. The optimized values of dihedral angles for all species studied in this research show that all of the molecules and their cation radicals follow the same structural pattern and both series of species are planar (dihedral angles are either 0° or 180°).

Structures of hexa(3-chloropyrrole), **B**-hexamer, (shown in Figure 2) and its cation have also been optimized, and their ground-state electronic and structural properties have been calculated and studied. We have selected this oligomer because its structure is large enough to exhibit a conformational behavior resembling that of a typical polypyrrole chain, and the electronic properties are sufficiently similar to those of the polymer.<sup>30</sup> The results of the calculations reported in previous works show that an infinite neutral chain of the pyrrole ring in a 3-D periodic arrangement is planar.<sup>18,25</sup> Geometry optimization of **B**-hexamer was carried out with a number of different initial points (with different conformations) without any geometry constraints or any symmetry restrictions. Optimization of all the different initial

conformations resulted in a single coplanar conformation for all rings. Geometry optimization of both the neutral and singly ionized **B**-hexamer species resulted in a planar and (α–α′)-trans conformation for all consecutive pairs of monomers.

To characterize the relative importance of the *aromatic* character with respect to the *quinoid* character of each monomer, we have calculated and used the *quinoid* coefficient  $F_n$ <sup>24–25,30</sup> as

$$F_n = 2R_{56}/(R_{25} + R_{36}) \quad (1)$$

where  $R_{56}$  is the length of the C5–C6 bond (formally a single bond) and  $[(R_{25} + R_{36})/2]$  is the average length of the C2–C5 and C3–C6 bonds (formally double bonds) in the same pyrrole ring (subscript  $n$  stands for the sequence number of the pyrrole rings in the case of the **B**-hexamer). The *quinoid* term refers to a structure in which the C5–C6 and inter-ring bonds have a greater double-bond character compared to the standard *aromatic* configuration.<sup>24</sup> The calculated values of the  $F_n$  coefficient for all chloropyrroles and their cations are listed in Table 2. As shown in this table, 3-chloropyrrole **B** has the smallest value of the  $F_n$  coefficient. Therefore, the *quinoid* character of monomer **B** is greater than that of other chloropyrroles. It can be concluded that, for the cation polymer structure of this monomer, the *quinoid* structure is more favorable. This shows that double bonds in this molecule are more delocalized. Consequently, formation of the *quinoid* structures, involved in the polymer chain growth, is more probable for this monomer. This implies that, compared with other chloropyrroles, this monomer has higher capability for electropolymerization as well as higher electric conductance. Furthermore, a smaller *quinoid* coefficient obtained for 3-chloropyrrole suggests that its polymer may have the least structural changes when subjected to an external electric field inducing electric current.

Analysis of the values of the  $F_n$  coefficient and other characteristics for **B**-hexamer and its cation reported in Table 2 shows that, for both the neutral **B**-hexamer and its cation, central rings of the chain have greater *quinoid* character than the terminal rings have. The radical cation of the **B**-hexamer shows a *quinoid* structure localized in the central part of the chain, whereas its *aromatic* conjugation is concentrated on the terminal rings. Thus, the only possible rotations are those around the terminal inter-ring C–C bonds, which are more likely to maintain their single-bond character. This result is confirmed

**TABLE 1: B3LYP/6-31G(d,p) Optimized Bond Lengths (in Å) and Angles (in deg) and  $F_n$  Coefficients Obtained for Chloropyrroles<sup>a</sup>**

molecule	N1–C2	N1–C3	C2–C5	C3–C6	C5–C6	$F_n$
pyrrole	1.375	1.375	1.378	1.378	1.425	1.034
	<i>1.363</i>	<i>1.363</i>	<i>1.433</i>	<i>1.433</i>	<i>1.374</i>	<i>0.962</i>
A	1.371	1.378	1.375	1.377	1.426	1.036
	<i>1.374</i>	<i>1.359</i>	<i>1.432</i>	<i>1.428</i>	<i>1.376</i>	<i>0.962</i>
B	1.374	1.373	1.377	1.378	1.421	1.031
	<i>1.334</i>	<i>1.397</i>	<i>1.455</i>	<i>1.396</i>	<i>1.396</i>	<i>0.982</i>
C	1.372	1.376	1.379	1.376	1.423	1.033
	<i>1.354</i>	<i>1.380</i>	<i>1.457</i>	<i>1.399</i>	<i>1.390</i>	<i>0.973</i>
D	1.369	1.378	1.376	1.376	1.423	1.034
	<i>1.392</i>	<i>1.342</i>	<i>1.404</i>	<i>1.444</i>	<i>1.388</i>	<i>0.975</i>
E	1.374	1.374	1.374	1.374	1.428	1.039
	<i>1.369</i>	<i>1.369</i>	<i>1.427</i>	<i>1.427</i>	<i>1.377</i>	<i>0.965</i>
F	1.372	1.372	1.378	1.378	1.425	1.034
	<i>1.363</i>	<i>1.364</i>	<i>1.428</i>	<i>1.428</i>	<i>1.391</i>	<i>0.974</i>
G	1.370	1.376	1.380	1.376	1.427	1.036
	<i>1.374</i>	<i>1.360</i>	<i>1.433</i>	<i>1.423</i>	<i>1.392</i>	<i>0.974</i>
H	1.376	1.373	1.377	1.374	1.426	1.036
	<i>1.358</i>	<i>1.382</i>	<i>1.448</i>	<i>1.407</i>	<i>1.387</i>	<i>0.971</i>
I	1.374	1.374	1.378	1.378	1.430	1.038
	<i>1.370</i>	<i>1.370</i>	<i>1.430</i>	<i>1.430</i>	<i>1.392</i>	<i>0.974</i>

molecule	C2N1C3	C2N1H4	C3N1H4	N1C2C5	N1C2X	N1C3W
pyrrole	109.7	125.1	125.1	107.6	121.1	121.1
	<i>109.0</i>	<i>125.4</i>	<i>125.4</i>	<i>108.3</i>	<i>121.7</i>	<i>121.7</i>
A	108.9	124.7	126.4	109.0	120.4	120.9
	<i>108.5</i>	<i>125.2</i>	<i>126.3</i>	<i>108.6</i>	<i>122.5</i>	<i>121.5</i>
B	110.2	124.7	125.1	106.5	122.5	121.3
	<i>109.8</i>	<i>125.3</i>	<i>124.9</i>	<i>106.9</i>	<i>124.0</i>	<i>120.7</i>
C	108.4	124.2	126.4	107.8	121.4	121.0
	<i>109.0</i>	<i>125.0</i>	<i>125.9</i>	<i>107.3</i>	<i>124.0</i>	<i>120.7</i>
D	109.3	124.7	125.9	109.3	120.5	122.1
	<i>109.0</i>	<i>124.8</i>	<i>126.2</i>	<i>109.3</i>	<i>121.1</i>	<i>123.2</i>
E	108.2	125.9	125.9	109.0	120.3	120.3
	<i>108.1</i>	<i>125.9</i>	<i>125.9</i>	<i>108.8</i>	<i>122.2</i>	<i>122.2</i>
F	110.5	124.8	124.8	107.2	122.5	122.5
	<i>109.2</i>	<i>125.4</i>	<i>125.4</i>	<i>108.4</i>	<i>122.7</i>	<i>122.7</i>
G	109.8	124.3	125.9	108.3	121.4	122.2
	<i>108.9</i>	<i>125.0</i>	<i>126.1</i>	<i>108.5</i>	<i>122.8</i>	<i>122.4</i>
H	108.7	125.4	125.9	107.8	121.2	120.4
	<i>108.6</i>	<i>125.8</i>	<i>125.6</i>	<i>107.7</i>	<i>123.5</i>	<i>121.3</i>
I	109.2	125.4	125.4	108.3	121.2	121.2
	<i>108.7</i>	<i>125.6</i>	<i>125.6</i>	<i>108.7</i>	<i>122.6</i>	<i>122.6</i>

<sup>a</sup> Corresponding values for cations are given in the lower row with italic fonts. See Figure 1 for the definition of bond lengths.

by the inspection of the  $F_n$  coefficient values and the inter-ring bond lengths reported in Table 4.

**3.2. Electric Charge Distribution, Dipole Moment, and Polarizability.** Atomic electric charges calculated for chloropyrroles and their cations using Mulliken population analysis have been reported in Table 2. In addition, the spin density distribution over the ring atoms of the cation radicals have been calculated and presented in Table 3. From the analysis of the data reported in these two tables, one can consider that, for all chloropyrroles and their cations, the positive charge is distributed mainly on the  $\alpha$ -carbon atom (C2 in Figure 1), whereas spin density is distributed primarily on  $\beta$ -carbon atom (C3 in Figure 1). On the basis of the results obtained in this study, one can conclude that, among all of these chloropyrroles, monomers **B** and **F** can be electropolymerized under suitable conditions. The higher positive charge on C3 for monomer **F** shows that, possibly, the electropolymerization rate for monomer **F** is greater than that for monomer **B** (opposite to what has been obtained for fluoropyrroles<sup>24</sup>). Furthermore, the higher negative charge on C6 carbon ( $\beta'$  position in Figure 1) suggests that cationic polymerization of monomers **B** and **F** from position C6 is not possible. In other words, propagation of the polymer chain

through C3 carbon for **B** and **F** monomers is the only favored path of polymerization. Therefore, it can be predicted that **B** and **F** polymers will have the least (or ideally no) twisted junctions.

The calculated net electric charges and spin densities over all of the six rings of the **B**-hexamer cation radical have been listed in Table 4. For singly ionized **B**-hexamer, the positive charge is localized mainly on the two end rings, whereas the spin density is distributed primarily on the central rings of the chain. This clearly suggests that the tendency of the propagating cation radical chain (formed in the electropolymerization addition of the **B** monomer) is not reduced by the increase in the number of its monomers (its size). Furthermore, branching from the middle rings of the polymer (could be formed otherwise by the positive charge resonance over the central rings of the propagating cation polymer) is not thermodynamically favored. This, in turn, results in more straight-chain polymers with higher conductivity and density.

It has been discussed previously that one of the most important parameters affecting the bulk conductivity of a polymer is the order (orientations) of the polymer chains in the condensed phase, so that the conductivity of a single polymer chain is altered when symmetry and nonisotropic interactions are changed. Alignment of the dipole moments of monomers in solution with respect to the orientation of the polymer chain determines the electrochemical properties of the polymer formed on the electrode surface. In addition, the orientation of the monomer in the double layer of the solution in the electropolymerization cell depends on both the size and the direction of the dipole moment vectors of both monomers and the polymer chain.<sup>24,25</sup> It is, therefore, necessary to study the dipole moments of these chloropyrroles to be able to predict their electropolymerization behavior. The total dipole moment and its components calculated in this study for all chloropyrroles are presented in Table 5. Obviously, the size and the direction of the dipole moment depends mainly on the positions (symmetry) of substituents rather than on the number of substituents. The analysis carried out on the calculated dipole moments shows that, for all chloropyrroles, orientation of the dipole moment vector is toward the nitrogen atom.

It can be seen from Table 5 that the size of the total dipole moment vector for monomer **F** is greater than that for other chloropyrroles studied in this research. Also, monomer **B** has a slightly greater dipole moment and, therefore, has a higher solubility in polar solvents as compared to pyrrole.

Values of the polarizability tensor elements calculated and reported in Table 5 for all chloropyrroles can be used in the prediction and the interpretation of the light scattering and intensities of the vibrational Raman spectra of these compounds. Higher polarizability is an index of the reactivity of the compound and its environmental instability. Table 5 shows that monomers **A** and **B** have the least polarizabilities after pyrrole. This suggests that polymers of these two monomers may have the highest resistance to chemical and electrical degradation when applied as electric circuit wires or devices. The zero or negligibly small values of the out-of-plane off-diagonal  $\alpha_{xz}$  and  $\alpha_{yz}$  polarizabilities (not reported here for brevity) show that all of these compounds are planar. The residual in-plane off-diagonal  $\alpha_{xz}$  polarizabilities can be attributed to the breakdown of molecular symmetry by the chlorine substitutions.

**3.3 Ionization Potential.** Results of the present computations have been used to calculate ionization energies for chloropyrroles (ionization energy of a molecule is the energy difference between the cationic and neutral forms of that molecule). This

**TABLE 2: Charge Distribution on the Nitrogen and Carbon Atoms in the B3LYP/6-31G(d,p) Optimized Structures of Pyrrole and Chloropyrroles (and Their Cations)**

molecule	$\delta_N$	$\delta_{C2}$	$\delta_{C3}$	$\delta_{C5}$	$\delta_{C6}$
pyrrole	-0.048 (-0.456)	0.070 (0.198)	0.070 (0.198)	-0.128 (-0.075)	-0.128 (-0.075)
A	-0.489 (-0.462)	0.087 (0.140)	0.076 (0.191)	-0.115 (-0.051)	-0.128 (-0.082)
B	-0.492 (-0.461)	0.087 (0.229)	0.083 (0.167)	-0.131 (-0.124)	-0.116 (-0.068)
C	-0.493 (-0.470)	0.094 (0.168)	0.087 (0.175)	-0.123 (-0.100)	-0.114 (-0.073)
D	-0.496 (-0.466)	0.098 (0.130)	0.094 (0.222)	-0.100 (-0.047)	-0.133 (-0.126)
E	-0.491 (-0.469)	0.090 (0.141)	0.090 (0.141)	-0.115 (-0.057)	-0.115 (-0.057)
F	-0.496 (-0.472)	0.097 (0.220)	0.098 (0.220)	-0.123 (-0.114)	-0.123 (-0.114)
G	-0.50 (-0.475)	0.103 (0.158)	0.101 (0.214)	-0.113 (-0.090)	-0.123 (-0.115)
H	-0.496 (-0.126)	0.098 (0.164)	0.099 (0.135)	-0.125 (-0.102)	-0.098 (0.159)
I	-0.50 (-0.130)	0.104 (0.158)	0.104 (0.158)	-0.113 (-0.092)	-0.113 (-0.093)

**TABLE 3: Distribution of Spin Density over Nitrogen and Carbon Atoms in the B3LYP/6-31G(d,p) Optimized Structures of Pyrrole and Chloropyrrole Cations**

molecule	N	C2	C3	C5	C6
pyrrole	-0.118	0.537	0.577	0.046	0.046
A	-0.096	0.393	0.486	0.074	0.036
B	-0.054	0.459	0.404	0.230	-0.138
C	-0.085	0.386	0.418	0.187	-0.102
D	-0.055	0.331	0.474	-0.069	0.135
E	-0.087	0.370	0.370	0.064	0.064
F	-0.106	0.521	0.521	-0.004	-0.005
G	-0.088	0.390	0.484	0.026	-0.006
H	-0.072	0.382	0.330	0.130	-0.044
I	-0.081	0.373	0.373	0.023	0.023

**TABLE 4: B3LYP/6-31G(d,p) Optimized Values of the Inter-Ring Bond Length,  $R_{n,n+1}$  (in Å), and Calculated Values of  $F_n$  Coefficient in Hexa(3-chloropyrrole) or B-Hexamer and Its Cation, Both with Planar Conformations<sup>a</sup>**

ring no. $n$	neutral B-hexamer		B-hexamer cation			
	$F_n$	$R_{n,n+1}$	$F_n$	$R_{n,n+1}$	charge	spin
1	1.021	1.445	1.006	1.428	0.173	0.142
2	1.013	1.442	0.986	1.419	0.184	0.215
3	1.012	1.442	0.983	1.419	0.176	0.226
4	1.012	1.442	0.985	1.423	0.165	0.199
5	1.012	1.444	0.993	1.434	0.150	0.145
6	1.023		1.013		0.152	0.073

<sup>a</sup> In the last two columns, overall electric charge and spin density of each ring of the B-hexamer cation have been listed, respectively. The subscript  $n$  denotes the progressive number of the ring in the chain.

**TABLE 5: Calculated Electric Dipole Moments ( $\mu$ ), Polarizability Tensor Elements ( $\alpha$ ), and Ionization Potentials (IP) for the B3LYP/6-31G(d,p) Optimized Structures of Pyrrole and Chloropyrroles**

molecule	$\mu$ (Debye)			$\alpha$ (bohr) <sup>3</sup>				IP (eV)
	$\mu_x$	$\mu_y$	$\mu_{tot}$	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{xy}$	
pyrrole	0.00	1.90	1.90	53.10	52.30	18.24	0.00	7.81
A	-1.21	-1.48	1.91	58.78	73.66	22.94	-0.82	7.78
B	-0.96	-3.45	3.59	56.40	74.71	22.95	-0.74	7.92
C	2.57	2.36	3.48	81.67	61.59	27.52	0.23	7.86
D	-1.31	-2.30	2.65	98.09	62.68	27.61	0.10	7.90
E	0.00	0.54	0.54	96.31	65.60	27.60	0.00	7.75
F	4.41	0.94	4.50	81.90	74.98	27.53	1.54	8.13
G	-1.24	-3.66	3.86	102.41	83.92	32.06	1.45	8.03
H	-2.10	0.09	2.10	95.77	94.26	32.14	14.03	7.85
I	2.34	-1.79	2.95	106.68	110.92	36.55	7.76	7.95

aspect of our study has been presented in the last column of Table 5. Since the ionization energies are directly proportional to the electrochemical oxidation potentials of the compounds, it can be said that the electrochemical stability of monomer **B** is slightly higher than that of monomer **A** and pyrrole itself.

**3.4. Spectroscopic Properties. A. Vibrational Spectra.** The fundamental harmonic vibrational frequencies for all chloro-

pyrroles were calculated using optimized structures at the B3LYP/6-31G(d,p) level of theory. No imaginary frequency was obtained in these calculations. This confirms that all optimized geometries correspond to the local minima on the potential energy surfaces. In Table 6, IR frequencies and intensities calculated for chloropyrroles are presented. The whole set of vibrational frequencies is divided into a low-frequency group (below 1000 cm<sup>-1</sup>) and a high-frequency group (above 1000 cm<sup>-1</sup>). Table 6 shows that values of the low frequencies for all of the chloropyrroles are smaller than those for pyrrole. Of the two monochloro derivatives, compound **B** has higher low frequencies. Also, of the two dichloro derivatives, compound **F** has almost the highest low frequencies. This feature can be regarded as a higher protection from thermal (environmental) disintegration for **B** and **F** compounds compared to other chloropyrroles. This also indicates that the relative stabilities of these two molecules are higher than those of their corresponding isomers. The thermally/optically activated chemical reactions of chloropyrroles can occur via their high-frequency modes also, but at higher temperatures.

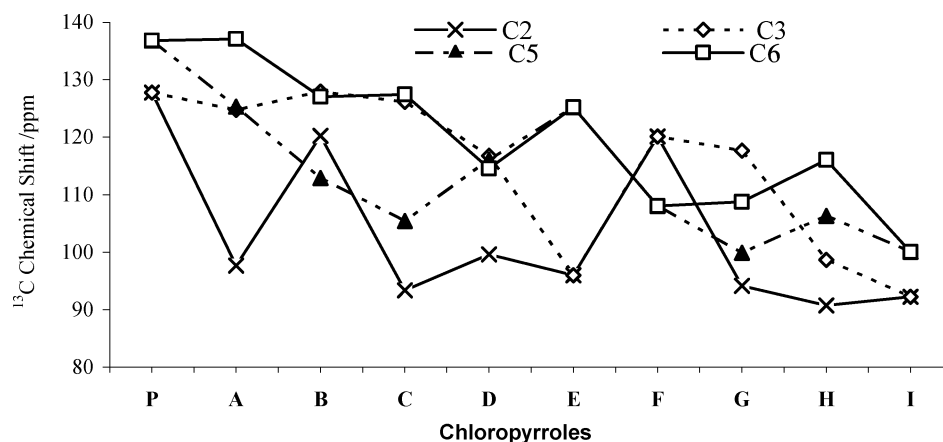
Thermal activation of the low-frequency modes, which are mainly related to the bending modes of vibration, has a significant effect on the electrical conductivity characteristics of the corresponding polymers. This means that the electrical conductivity of the corresponding polymers of the monomers with the bending modes of vibration with lower frequencies decrease more rapidly with increasing temperature. Such a behavior reduces the applicability of these polymers in the electronic circuits working at variable or high temperatures. From the vibrational frequency data reported in Table 6, it can be concluded that temperature has the least effect on the electrical conductivity of the corresponding polymers of monochloropyrrole **B** and dichloropyrrole **F** compared to other chloropyrroles.

**B. NMR Chemical Shifts.** The NMR chemical shifts can be used to predict ring currents and estimate the aromaticity in this series of chloropyrroles. Aromaticity can be defined as the ability of a compound to sustain an induced ring current; such compounds are thus called diatropic. Antiaromatic compounds are called paratropic. Several methods can be used to determine how long a compound can sustain an induced ring current. The most important ones are based on NMR chemical shifts and diamagnetic susceptibilities. In this study, the isotropic and anisotropic magnetic shieldings for the <sup>1</sup>H and <sup>13</sup>C nuclei have been calculated for the B3LYP/6-31G(d,p) optimized geometries of all chloropyrroles using individual gauges for atoms in molecules (IGAIM) method. The isotropic and anisotropic chemical shielding constants are defined as  $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$  and  $\Delta\sigma = [\sigma_{zz} - (\sigma_{xx} + \sigma_{yy})]/2$ , respectively. The <sup>1</sup>H and <sup>13</sup>C shieldings for tetramethylsilane (TMS) have also been calculated as references. On a comparative basis, relative

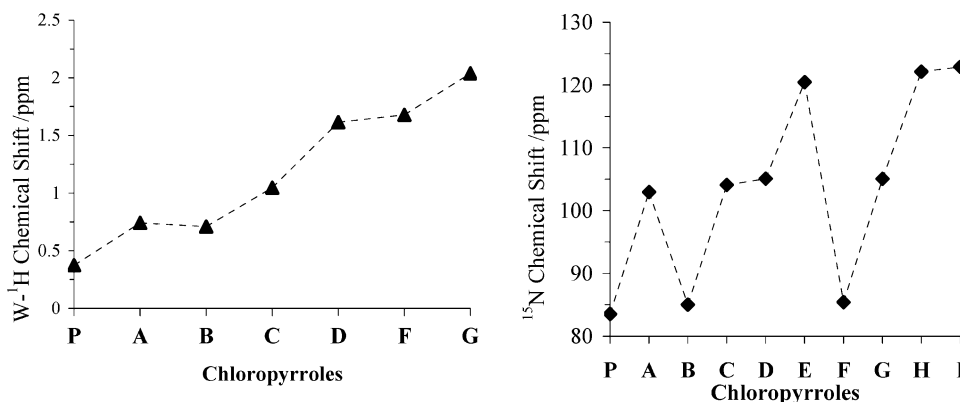
**TABLE 6: Calculated IR Frequencies in  $\text{cm}^{-1}$  (Intensities in  $\text{km/mol}$ ) for the B3LYP/6-31G(d,p) Optimized Structures of Pyrrole and Chloropyrroles<sup>a</sup>**

molecule	low-frequency range	high-frequency range
pyrrole	461(77), 641(0.98), 734(111), 825(3.5), 875(1.3)	1052(11.9), 1075(2.3), 1101(8), 1165(2.3), 1180(2.7), 1318(1.9), 1436(4.5), 1470(7), 1517(9), 1594(4), 3247(3.2), 3258(5.7), 3275(7), 3688(55)
a	217(0.5), 302(0.66), 439(69.4), 83(7.6), 703(60.7), 789 (39.8), 888(2.8), 944(25.6),	1052(11.9), 1098(8.7), 1138(11.9), 1222(7.9), 1282(1.5), 1436(13.2), 1468(33.7), 1490(26.1), 1598(29.8), 3258(3.4), 3278(1.13), 3286(0.7), 3684(77.8)
b	239(1.3), 452(90.9), 475(5.3), 620(2.1), 639(5.2), 677(13.2), 761(57.5), 841(6.5), 898(3.9), 933(38.8)	1064(7.9), 1093(16.2), 1166(3.3), 1236(44), 1271(6.9), 1420(7.8), 1522(2), 1592(25.2), 3287(1.2), 3688(73.6)
c	242(1.1), 364(1.9), 430(85.5), 490(1.3), 530(9.6), 614(0.75), 639(9.46), 702(43.1), 840(8.1), 905(14.3), 994(56.7)	1092(9.4), 1145(4), 1229(7.7), 1262(31), 1423(12.2), 1472(22.8), 1502(8.9), 1598(43), 3684(96.7)
d	279(0.6), 372(1.2), 398(0.8), 429(79.3), 561(21.2), 631(17.1), 714(8.8), 798(48), 944(12.6), 960(38.2)	1089(9.5), 1130(20.3), 1237(1.8), 1266(23), 1410(30.2), 1471(24.5), 1495(16), 1595(76), 3295(1.5), 3298(1.2), 3681(98)
e	194(0.6), 409(62.1), 419(1.9), 545(20.5), 631(8.8), 772(79), 940(35.8), 972(3)	1060(16.2), 1123(3.7), 1249(1.7), 1258(1.1), 1461(55.4), 1472(56.1), 1599(74.4), 3274(0.9), 3681(98)
f	263(1.2), 370(1.8), 452(111), 530(9.2), 628(4), 768(38), 900(9.7), 996(74)	1084(15.8), 1237(2.7), 1286(59.3), 1386(8), 1481(0.8), 1535(1.4), 1587(27), 3295(1), 3686(94.5)
g	238(0.7), 273(0.9), 378(0.5), 423(103.5), 450(4.4), 532(5.7), 609(1.6), 611(12.4), 644(1.9), 720(17.5), 955(53.7)	1021(38.1), 1142(2.4), 1217(2.8), 1292(52), 1387(28.6), 1475(11.6), 1515(3.7), 1591(64.7), 3299(2.17), 3680(118.2)
h	273(0.96), 401(72.3), 430(2.7), 506(1), 619(1.5), 620(37.8), 625(14.3), 792(37.8), 970(10.6)	1028(52.4), 1109(4.1), 1275(23.7), 1405(11.3), 1464(45.8), 1485(25.1), 1598(108.3), 3295(2.2), 3679(117.3)
i	254(4.8), 373(0.8), 399(89.7), 537(5.1), 577(9.2), 613(4), 693(41)	1016(55.3), 1055(1.5), 1201(1.9), 1290(47.1), 1383(30.9), 1466(30.6), 1504(3.4), 1593(113.9), 3675(137.8)

<sup>a</sup> Some IR transitions of certain modes of vibration may not be active for certain compounds because of the symmetry-related rules. For brevity, vibrational frequencies with negligible IR intensities are not listed.



**Figure 3.** The IGAIM calculated values of  $^{13}\text{C}$  chemical shifts (in ppm) referenced to TMS,  $\Delta\sigma_r$ , for carbon atoms in the B3LYP/6-31G(d,p) optimized structures of pyrrole and chloropyrroles.



**Figure 4.** The IGAIM calculated values of chemical shifts (in ppm) of  $^1\text{H}$  at W position (see Figure 1) referenced to TMS (left) and of  $^{15}\text{N}$  referenced to nitromethane (right) for pyrrole and chloropyrroles based on the B3LYP/6-31G(d,p) optimized structures.

shielding constant  $\Delta\sigma_X(\text{relative})$  is defined as

$$\Delta\sigma_X(\text{relative}) = \sigma_X(\text{reference}) - \sigma_X(\text{compound}) \quad (2)$$

where  $\sigma_X(\text{compound})$  and  $\sigma_X(\text{reference})$  are isotropic chemical shieldings of the nucleus X in the compound and in the reference molecules, respectively. The calculated values of the relative

shielding constants for different carbon nuclei in pyrrole, **P**, and chloropyrroles **A–I** are presented pictorially in Figure 3. It can be seen from this figure that the C3 nucleus has the highest magnetic shielding in compound **B** (which has a higher capability of electropolymerization; see section 3). The C3 carbon is the same carbon atom that has the lowest positive charge in comparison with all other carbon atoms in all chloropyrroles, except **A** and pyrrole (see Table 2). Also, the shielding constants for the C2 nucleus of compounds **B** and **F** are larger than those for the C2 nucleus of other chloropyrroles.

Figure 4 shows changes in the values of isotropic shielding constants for  $^1\text{H}$  (hydrogen nucleus) on the *W* position (see Figure 1) of the chloropyrroles. As this figure clearly shows, the highest value of the magnetic shielding belongs to the  $W-^1\text{H}$  of compound **B**. In addition, with the increase in the number of substituted chlorine atoms on the pyrrole ring, the magnetic shieldings of all nuclei decrease. The dashed lines in Figure 4 show the trend with increasing number of substituted chlorine atoms. These NMR data can be used to follow the electropolymerization or chemical polymerization processes based on the NMR signal of one, two, or more characteristic nuclei. No regularity could be derived from the  $^{15}\text{N}$  NMR chemical shifts presented in Figure 4. An electron nuclear double resonance (ENDOR) study would be much more appropriate in the study of the electric charge–nuclear spin interaction. However, such a study is beyond the scope of the present work.

#### 4. Conclusion

Density functional theory B3LYP/6-31G(d,p) computations have been carried out to study structural, electronic, electrochemical, and spectroscopic properties of all chloropyrroles successfully. On the basis of the optimized structural parameters (including *quinoid* character), charge distribution, size, and direction of electric dipole moment vector, and vibrational frequencies, it was shown that compounds **B** and **F** are possible candidates to replace pyrrole in the synthesis of corresponding conducting polymers with modified characteristics. Generally, halogen-substituted organic compounds have higher ignition (or combustion) temperatures and have less reactivity with atmospheric oxygen, and thus have higher resistance to fire. Therefore, use of polychloropyrroles instead of polypyrrole may increase the safety factor of the future electronic and electric devices based on the synthetic metals. Also, the results of this research show that as potential candidates in the preparation of corresponding conducting polymers, chloropyrroles are inferior to fluoropyrroles.<sup>24</sup> Other aspects of the properties of these compounds, especially the thermodynamic and electrical characteristics, obtained from this computational study, will be presented in an independent paper.

**Acknowledgment.** We would like to thank the University of Isfahan for financial support as research grants and the University of Mazandaran for computer and research facilities.

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