Substituent Effects on the Electrochemical Properties of Pyrroles and Small Oligopyrroles

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The electrochemical oxidation of several oligopyrroles, either unprotected, partially blocked, or totally blocked on their α-terminal positions or N-substituted, has been investigated in acetonitrile by cyclic voltammetry. For all the studied oligopyrroles, reversible voltammograms have been obtained at moderate to high scan rates, whereas chemical evolutions of the cation radicals have been observed at lower scan rates. The one-electron redox potentials, *E*°, of the oligopyrrole/oligopyrrole cation-radical couples have been measured and the lifetimes of the cation radicals have been estimated. The stabilities of the cation radicals have been examined as a function of the chain length and the nature of the substituent.

Introduction

Polypyrroles have been widely studied materials for a number of years, due to their special redox and conductive properties (the literature on polyheterocycles is very abundant; for reviews see ref 1). In this field, short oligomers (from 2 to several units of monomer) are very attractive molecules both for fundamental studies and as materials precursors. A better understanding of the properties of the polymer itself and of the electropolymerization processes can be expected from the study of the properties of these compounds. Also, they are interesting molecules to obtain new type of materials due to the regular structure of the oligomer. For these different reasons, the oxidation of oligothiophenes has been extensively studied (for a review see for example[2]). Less has been done in pyrrole series, but recently, the syntheses of several unprotected oligopyrroles have been described.[3−5] The electrochemical oxidation of small oligopyrroles (bipyrrole (*n* = 2), terpyrrole (*n* = 3), and quinquepyrrole (*n* = 5)) has been investigated by cyclic voltammetry and the standard potentials *E*° have been determined at low scan rates or at low temperatures.[6] Some UV−visible spectra have also been reported for the most stable of the cation radical (quinquepyrrole).[6]

Concerning the substitution effects on the electrochemical properties of heterocycles, a lot of investigations have been devoted to the oxidation of oligothiophenes with α-blocking groups different from hydrogen. These studies mainly concerned the oxidation of oligothiophenes where a large variety of substituent was examined (see, for example, refs 7−14 and references therein), or the oxidation of pyrrole−thiophene mixed oligomers (see refs 15−17). In these investigations, blocking groups have been shown to stabilize the electrogenerated cation radicals, by blocking the α-reactive position on which the polymerization is known to take place. In some cases, long lifetime thiophenic cation radicals have been obtained and characterized (see, for example, refs 7−16). More recently, the oxida-

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tion of several α-diphenyloligopyrroles was investigated and it was found that the chemical stability of the monocation radicals and dications was significantly increased by phenyl substitution.[17,18]

The active research on substituted thiophene oligomers made it interesting to investigate the behavior of purely pyrrole oligomers toward substitution and chain-length effects. As the aromaticity energy is higher for thiophenes (29 kcal/mol) than for pyrroles (23 kcal/mol), the behavior of pyrrole oligomers is not expected to be entirely symmetric with respect to the thiophene case.[19] For example, in recent investigations concerning the electrochemical oxidation of substituted pyrroles and thiophenes bearing one or two *tert*-butyl groups on the α-positions, it has been found that the cation radicals from the *tert*-butylated compounds were more stable in the thiophene series than in the pyrrole series.[22] More generally, the pyrrolic cation radicals probably have a lower tendency to rearomatize and therefore may give way to a wider range of mechanisms. Also, it has been previously demonstrated that the first step of the oxidative polymerization of pyrrole involves the coupling between two cation radicals of pyrrole and not the reaction of the cation-radical with another neutral molecule of pyrrole.[20,21] However, it is questionable that the same type of reactivity remains valid with longer oligomers which are formed upon polymerization.

In the present paper, we report on the electrochemical properties of several oligopyrroles, ranging from one- to four-ring compounds, either unblocked, or blocked on the α-positions by one or two groups. For all studied oligopyrroles, the redox potentials, $E°$, for the first oxidation have been measured from the reversible oxidation voltammograms using millimetric electrodes or ultramicroelectrodes when high scan rates were required. Some indications regarding the reactivity of the studied oligopyrrole cation radicals were also deduced from the cyclic voltammetry data. The effects of N-substitution or α-susbtitution on these properties were investigated.

Experimental Section

Monomer Synthesis. The synthesis of the 2,5-di-*tert*-butylpyrrole (**13**) was performed according to previous reports starting from pinacolone and bromopinacolone.[23–25] 2-*tert*-Butylpyrrole (**12**) was prepared according to previously published procedure,[26] with a slight modification of the purification process: after distillation of a mixture of 3-*tert*-butylpyrrole and 2-*tert*-butylpyrrole (**12**) (85 °C under 10 mmHg), 2-*tert*-butylpyrrole was separated by selective crystallization at −18 °C from the pure mixture. Structure was confirmed by NMR ¹H data and elemental analysis. NMR ¹H (ppm): 6.70 (m, 1

H, α-pyrrolic H); 6.00 and 6.15 (m, 2 H, β-pyrrolic H); 1.30 (s, 9 H, C(CH₃)₃). Anal (%): Calculated for $C_8H_{13}N$: C, 77.99; H, 10.64; N, 11.37. Found: C, 77.91; H, 10.63; N, 11.23. Mp < 50 °C.

Oligopyrrole Synthesis. The unblocked oligopyrroles **1**−**6** were prepared according to previously published procedures and have already been described.[4] The terpyrrole and the quaterpyrrole were kept in the N-protected form. Just before making the solution, the N-protected terpyrrole **5** was heated with 3 equiv of sodium hydroxide in dry methanol under argon for 2 h; then, the unreacted hydroxide was neutralized with a saturated solution of ammonium chloride, and the resulting solution was extracted with dichloromethane and purified by chromatography (dichloromethane with 1% ethanol). For the quaterpyrrole **3**, which is air-sensitive, the N-protected oligo-quaterpyrrole **6** was simply heated for 10 min in high vacuum at 180 °C. Then, the sealed glass tube was transferred into a glovebox and opened in it to make the solution with deoxygenated acetonitrile. This methodology has been adapted to the methylbipyrrole and *tert*-butylbipyrrole preparations according to the above-described procedures to improve the existing methods [27–31] for the synthesis of the *tert*-butylbipyrroles which were unknown. In these syntheses, the first step is the preparation of a 2-(azacyclopent-1-enyl)pyrrole followed by a rearomatization.

2-[(5-Methyl)-azacyclopent-1-enyl]pyrrole. 20.8 mL (0.3 mol) of pyrrole is placed into a cooled (0 °C) Erlenmeyer flask fitted with a condenser. 5.6 mL (0.06 mol) of phosphorus oxychloride was slowly added under nitrogen with magnetic stirring. After this addition, a solution of 7 g (0.07 mol) of 5-methyl-2-pyrrolidinone in dichloromethane was slowly added, and the mixture was stirred for 1 h at room temperature before being poured into an iced 3 M sodium acetate solution (150 mL). At 0 °C, the aqueous phase pH was adjusted to 10 with aqueous soda and then was extracted two times with 50 mL of dichloromethane. The organic phase was dried and evaporated. After recrystallization in methanol, a white solid was obtained with a 41% yield. IR (cm⁻¹): 3125 (ν(NH)), 3100−3000 (ν(Csp²-H)), 2950 (ν(Csp³-H)). NMR ¹H (ppm): 6.90 (m, 1 H, α-pyrrolic H); 6.55 (m, 1 H, β-pyrrolic H); 6.25 (m, 1 H, β-pyrrolic H); 4.15 (q, 1 H, N−CH−Me); 2.90 (2 H) 2.15 (1 H) 1.50 (1 H), alicyclic H; 1.30 (d, 3 H, CH₃). Mp = 110 °C (lit: 109−110 °C)[27]

5-Methyl-2,2′-bipyrrole (7). In a flask fitted with a condenser and a magnetic stirrer was added 0.5 g (3.37 mmol) of 2-[(5-methyl)-azacyclopent-1-enyl]pyrrole, 0.36 g (3.37 mmol) of palladium on carbon (Pd/C 10%) and 35 mL of triglyme. The mixture was heated 45 min at 200 °C under nitrogen and filtered, and the solvent was evaporated. The product was purified on a silica gel column, using dichloromethane as eluant. A gray solid was obtained, which was identified as the 5-methyl-2,2′-bipyrrole. NMR ¹H (ppm): 6.75 (m, 1 H, α-pyrrolic H); 6.25−5.90 (m, 4 H, β-pyrrolic H); 2.30 (s, 3 H, CH₃). Anal (%): Calculated for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.17. Found: C, 73.87; H, 6.90; N, 19.23. Mp = 135 °C (lit: 134−135 °C).[27]

2-[(5-Methyl)-azacyclopent-1-enyl]-5-methylpyrrole. The same procedure than for 2-[(5-methyl)-azacyclopent-1-enyl]pyrrole was applied using 2-methylpyrrole (prepared by a standard LiAlH₄ reduction procedure of 2-formylpyrrole (Aldrich) in THF), instead of pyrrole. Yield 90% of non recrystallized product. NMR ¹H (ppm): 6.40 (m, 1 H, β-pyrrolic H); 5.90 (m, 1 H, β-pyrrolic H); 4.20 (q, 1 H, N−CH−Me); 2.80 (2H) 2.20 (1H) 1.50 (1H), alicyclic H; 2.30 (s, 3 H, pyrrole-CH₃); 1.30 (d, 3 H, CH₃).

5,5′-Dimethyl-2,2′-bipyrrole (8). Rearomatization of 2-[(5-methyl)-azacyclopent-1-enyl]-5-methylpyrrole was performed in a similar way as for 5-methyl-2,2′-bipyrrole (**7**); the product was precipitated from dichloromethane with addition of hex-

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ane, after a first chromatography. Yield 13%. NMR ^{1}H (ppm): 7.90 (large s, 2 H, NH); 6.00 and 5.85 (m, 4 H, β-pyrrolic H); 2.30 (s, 6 H, CH₃). Mp = 189 °C (lit.: 190–191 °C).[27]

2-[Azacyclopent-1-enyl]-5-*tert*-butylpyrrole. The same procedure as for 2-[(5-methyl)-azacyclopent-1-enyl]pyrrole was applied using 2-*tert*-butylpyrrole (**12**) instead of pyrrole. Yield 51% of nonrecrystallized product. NMR ^{1}H (ppm): 8.00 (large s, 1 H, NH); 6.40 (d, 1 H, β-pyrrolic H); 6.00 (d, 1 H, β-pyrrolic H); 3.90 (m, 2 H, N−CH₂); 2.90 (2 H) 2.00 (2 H), alicyclic H; 1.30 (s, 9 H, C(CH₃)₃).

5-*tert*-Butyl-2,2′-bipyrrole (11) and 5,5′-Di-*tert*-butylpyr-role-2,2′-bipyrrole (10). Rearomatization of 2-[azacyclopent-1-enyl]-5-*tert*-butylpyrrole was performed in a similar way as for 5-methyl-2,2′-bipyrrole (**7**); however, TLC allowed us to detect the formation of a side product besides the expected 5-*tert*-butyl-2,2′-bipyrrole (**11**) (and also tars). Filtration over a short silica gel column allowed us to isolate the mixture of two products. A chromatography (dichloromethane 50%/pentane 50%) allowed the separation of the 5-*tert*-butyl-2,2′-bipyrrole (**11**) (yield = 24%), and of 5,5′-di-*tert*-butyl-2,2′-bipyrrole (**10**) (yield = 10.5%) which was purified by another chromatographic separation (dichloromethane 50%/pentane 50%). NMR ^{1}H data for **10** (ppm): 7.90 (large s, 2 H, NH); 6.05 and 5.90 (m, 4 H, β-pyrrolic H); 1.30 (s, 18 H, C(CH₃)₃). NMR ^{1}H data for **11** (ppm): 7.90 and 8.20 (large s, 2 H, NH); 6.75 (m, 1 H, α-pyrrolic H); 6.20–5.90 (m, 4 H, β-pyrrolic H); 1.30 (s, 9 H, C(CH₃)₃).

5-Methyl-5′-(*tert*-butyl)-2,2′-bipyrrole (9). The same general two-step procedure used in all our bipyrrole syntheses was followed. The first step was the condensation of 2-*tert*-butylpyrrole (**12**) with 5-methyl-2-pyrrolidinone, which gave 2-[(5-methyl)-azacyclopent-1-enyl]-5-*tert*-butylpyrrole, whose NMR ^{1}H spectra were practically identical with that of 2-[azacyclopent-1-enyl]-5-*tert*-butylpyrrole, except that the proton signal α to the nitrogen was modified (m, 1.50 ppm) in accordance with the introduction of the methyl group. The second step was the rearomatization of 2-[(5-methyl)-azacyclopent-1-enyl]-5-*tert*-butylpyrrole in 5-methyl-5′-*tert*-butyl-2,2′-bipyrrole (**9**). NMR ^{1}H data for **9** (ppm): 7.90 (large s, 2 H, NH); 6.05 and 5.90 (m, 4 H, β-pyrrolic H); 2.30 (s, 3 H, CH₃); 1.30 (s, 9 H, C(CH₃)₃).

Electrochemical Apparatus and Procedure. Electrochemistry experiments were performed with a three-electrode setup using a platinum counter electrode and a calomel reference electrode. Acetonitrile (Merck, Uvasol, less than 0.01% of water) was used with tetraethylammonium tetrafluoroborate electrolyte (Fluka, *puriss.*, used as received). Oligopyrroles were purified by chromatography just before the electrochemical experiments. Solutions were kept under argon to avoid degradation of the oligopyrrole by air. Electrochemical instrumentation consisted of a PAR Model 175 universal programmer and of home-built potentiostat equipped with a positive feedback compensation device.[32] The data were acquired with 310 Nicolet oscilloscope, and the potential values reported are averaged out of several reproducible experiments; all potentials were internally calibrated against the ferrocene/ferricinium couple ($E = 0.405$ V vs SCE) for each experiment. Fast electrochemical experiments were performed using 10 μm diameter disk gold or platinum ultramicroelectrodes. Equipment and procedures were the same than previously published procedures.[33]

Results and Discussion

Oxidation of Unsubstituted Oligopyrroles. The electrochemical oxidation of the bipyrrole **1** has previously been investigated by classical voltammetry on millimetric electrodes at low or moderate scan rates.[6] At low scan rates (0.1 V·s^{-1}) and for an initial concentration in the millimolar range, the bipyrrole **1** exhibits

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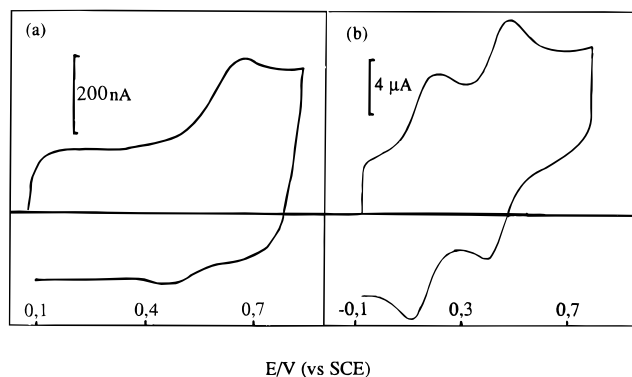(33) Andrieux, C. P.; Hapiot, P.; Savéant, J.-M. *Chem. Rev. (Washington, D.C.)* **1990**, *90*, 723.

Figure 1. Cyclic voltammetry of oligopyrroles (a) **1** and (b) **3** ($C^\circ = 2 \times 10^{-3}$ mol·L^{-1}) in acetonitrile (+0.2 mol·L^{-1} NEt₄BF₄); (a) on a 10 μm diameter platinum ultramicroelectrode; (b) on a 1 mm glassy gold electrode. Scan rates = (a) 10 000 V·s^{-1}, (b) 0.1 V·s^{-1}.

a chemically irreversible oxidative wave and upon repetitive scanning of the oxidation wave the formation of polypyrrole was clearly observed.[6] A partial reversibility of the wave was observed at low temperature (−30 °C) for scan rates higher than 500 V·s^{-1}.[6] To compare with the other substituted oligopyrroles and to get information on the reactivity at room temperature, we have investigated the oxidation of the bipyrrole **1** by fast cyclic voltammetry on ultramicroelectrode in acetonitrile containing 0.2 mol·L^{-1} NEt₄BF₄ as supporting electrolyte. When increasing the scan rate above 10 000 V·s^{-1}, a small wave during the reverse scan can be observed indicative of a partial reversibility for the oxidation of **1** (see Figure 1a). This shows that the lifetime of the cation radical at 20 °C was in the range of the experimental time and thus allows its estimation in the microseconds range and the determination of the E°. The E° (0.60 V/SCE) measured at 20 °C for the oxidation of bipyrrole to its cation radical was very close to the previously reported value (0.57 V/SCE) measured at low temperature and at a scan rate around 1000 V·s^{-1}.[6]

Cyclic voltammetry of the oxidation of the quaterpyrrole **3** displays two reversible waves for all studied scan rates (0.05–200 V·s^{-1}). Simultaneously, no modification of the voltammetric behavior was observed upon repetitive cycling which shows that the cation radical of the quaterpyrrole was completely unreactive under these conditions.

The oxidation wave of the terpyrrole **2** has been reported to be reversible at 1 V·s^{-1}.[6] A detailed investigation of the electrochemical process as a function of the scan rate and with fast cyclic voltammetry shows that this process is more complicated (see Figure 2). By examining the voltammograms at a concentration of 10^{-3} mol·L^{-1}, the following changes can be observed as the scan rate was increased: at 0.1 V·s^{-1}, the voltammogram was almost completely irreversible and a cathodic peak IIIc was visible at a much lower potential (0.1 V/SCE) after the peak Ia has been scanned beforehand, at 1 V·s^{-1} the voltammogram appeared as reversible [34] (peak IIc), at higher scan rates the reversibility decreased, and at 50 V·s^{-1} the voltammogram was

(34) A difference was found between our E° (0.28 V/SCE) measured at 5000 V·s^{-1} and the published value (0.22 V/SCE) obtained at low scan rate 1 V·s^{-1},[6] because the authors have considered the apparent reversibility observed at low scan rates.
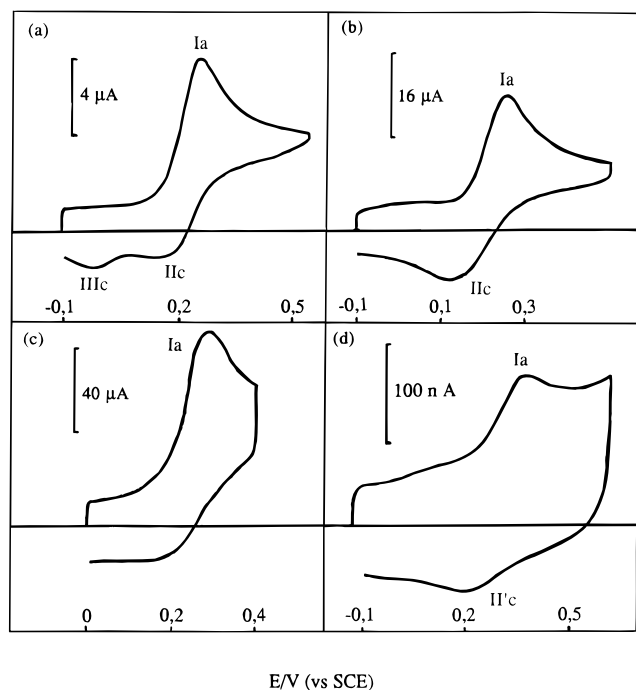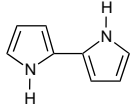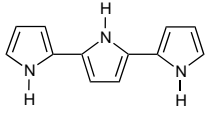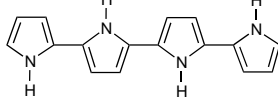
Figure 2. Cyclic voltammetry of terpyrrole **2** ($C° = 2 \times 10^{-3}$ mol·L^{-1}) in acetonitrile (+0.2 mol·L^{-1} NEt$_4$BF$_4$) at different scan rates. Scan rates = (a) 0.1 V·s^{-1}; (b) 1 V·s^{-1}; (c) 50 V·s^{-1}; (d) 13 000 V·s^{-1}; (a, b, c) on a 1 mm diameter gold electrode, (d) on a 10 μm diameter platinum ultramicroelectrode.

completely irreversible. At still higher scan rates ($v > 2000$ V·s^{-1}), the reversibility reappeared (peak II′c) and then increased again. From these experiments, it is clear that the reversibility which was previously observed at low scan rate (1 V·s^{-1})[6] did not correspond to the direct reduction of the cation radical which was only visible at a much higher scan rate (2000 V·s^{-1}). Moreover, it has been found that the electrolysis of the terpyrrole **3** led as a final product to the dimeric cation radical (sexipyrrole).[6] The peak IIIc visible at 0.1 V·s^{-1} (Figure 2a) can be ascribed to the reduction of the sexipyrrole cation radical in agreement with its redox potential (see below). Thus, the apparent reversibility (peak IIc) observed between 0.5 and 20 V·s^{-1} corresponds to the reduction of an electrogenerated species, which is different from the cation radical and also from the final sexipyrrole cation radical. One possible explanation for this behavior may be found in the reversible formation of another intermediate, certainly a coupling product. Reversible dimerizations are common in organic electrochemistry and for example, similar situations were observed in several instances: for example see the reduction of aromatic molecules[35] or the oxidation of hindered phenols in basic media ([36,37] and references therein). (A detailed analysis of this process will be the subject of future investigations.) Thus, to determine the lifetime of the terpyrrole cation radical (or the $E°$ of the couple terpyrrole/terpyrrole cation-radical), the curves recorded at high scan rate must be considered. Taking into account these considerations, we measured the redox potential $E°$ for the oligopyrrole/oligopyrrole cation radical couples as the

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Table 1. Electrochemical Characteristics of Unsubstituted Oligopyrroles

compound	compound no.	$E°$/V(SCE)[a]	scan rate/ (V·s^{-1})[b]
	1	0.60$_0$	5000−10000
	2	0.28$_0$	2000−4000
	3	0.16$_0$[c] 0.43$_5$[c]	rev[d]

[a] Reference SCE electrode was calibrated against the ferrocene/ferrocenium couple 0.405 V (vs SCE). Error ±0.01 V. [b] Lowest scan rate for the observation of a partial reversibility for a 10^{-3} mol·L^{-1} concentration. [c] First and second oxidation waves. [d] Reversible at all scan rates (0.05 V·s^{-1}).
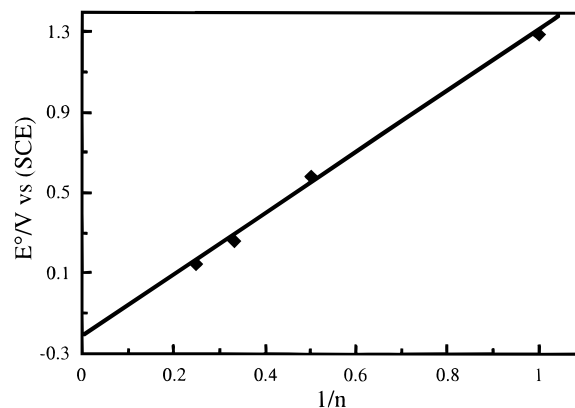

Figure 3. Variation of $E°$ for the first one-electron oxidation of unprotected oligopyrrole vs $1/n$ when n is the number of pyrrole units in the oligomer.

midpoint between the forward and the reverse scans from the reversible voltammograms. The $E°$ values are listed in Table 1, as well as the lowest scan rate needed to observe a partial reversibility of the first oxidation wave (around 10−20% of a full reversible wave) corresponding to the reversible formation of the cation radical.

From Figure 3, the oxidation potentials decrease when the length of the oligomer increases as we can expect from similar variations in thiophene series.[9,12,14] The $E°$ values vary linearly with the inverse of the number of pyrrole $1/n$ ($r = 0.996$) and the extrapolated $E°$ for an infinite oligomer gives a value of −0.21 V/SCE, which is in the range of the apparent oxidation potential of polypyrrole. Similar correlations have previously been observed.[6,17]

The scan rate for which the voltammograms become reversible gives a direct estimation of the lifetime of the produced cation radicals. In an earlier report, it was found that the partial reversibility of the oxidation wave of the monomeric pyrrole was reached at around 30 000 V·s^{-1}.[20] In the case of the unsubstituted bipyrrole **1**, a partial reversibility was observed at around 10 000 V·s^{-1}, indicating a small increase of the stability of the cation radical of the bipyrrole in comparison with the one from the pyrrole monomer. More surprisingly,

passing from bipyrrole **1** to terpyrrole **2** does not bring appreciable further stabilization (only a factor of 2−3). On the contrary, a large change for the stability of the cation radical takes place when we consider the oxidation of the quaterpyrrole **3**. In this case, not only the first oxidation wave was found to be reversible at slow scan rate (0.1 V·s^{-1}) but also the second wave which corresponds to the formation of the dication. This behavior shows a large stabilization of the cation radical of the quaterpyrrole **3**. Its lifetime increases by at least 4 orders of magnitude in comparison with the data obtained for the terpyrrole **2**. It is clear that the weak difference between the $E°$ values of the terpyrrole **2** and of the quaterpyrrole **3** does not account for the large reactivity difference observed between the two corresponding cation radicals. These results show that there is only a slight reactivity difference between the cation radical and the dication in large oligopyrroles such as quaterpyrrole **3**, as has also been found for longer oligopyrroles ($n = 5$ and $n = 7$).[6,17,18] The same results indicate that oligopyrrole cation radicals require at least four rings to be stabilized, in agreement with the doping level values usually observed in polypyrroles.[38] From the analogy with the conclusions obtained for the oxidation of several pyrrole monomers,[20,21] it is likely that the cation radical of bipyrrole decays by reaction with another cation radical to form higher oligomers or polypyrrole.

$$BP \rightarrow BP^{\bullet+} + e^-$$

$$BP^{\bullet+} + BP^{\bullet+} \xrightarrow{k_{\text{dim}}} \text{dimer}$$
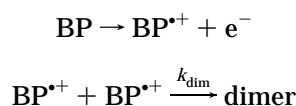
If we assume that the decay of the cation radicals is mainly due to the reaction with another cation radical, we can derive an estimation of the dimerization rate constants from the comparison between the experimental voltammograms and simulated curves.[33,35] We estimate $k_{\text{dim}} = 1.2 \times 10^9$ and 5×10^8 L·mol^{-1}·s^{-1} for the cation-radical from the bipyrrole and the terpyrrole, respectively. For the quaterpyrrole, the reversibility observed at low scan rate indicates that k_{dim} is lower than 10^4 L·mol^{-1}·s^{-1}.

Oxidation of N-Substituted Oligopyrroles. Substitution on the N-position of the pyrrole by strong withdrawing groups is frequently used to stabilize the monomers or the oligopyrroles. We have examined the electrochemical oxidation of such oligopyrroles (compounds **4**, **5**, and **6**), in acetonitrile. Cyclic voltammetry experiments (see Figure 4) were performed and the standard oxidation potentials, $E°$, and scan rates (to observe the reversibility of the oxidation wave) were measured (see Table 2).

The introduction of a butoxycarbonyl (BOC) substituent or of a −SO$_2$Ph substituent shifts the first oxidation potential to a more positive value (640 mV between bipyrroles **1** and **4**, 540 mV between terpyrroles **2** and **5**, and 900 mV between quaterpyrroles **3** and **6**). However, the effects of the N-substitution on the reactivity of the corresponding cation radicals are more difficult to predict. It is noticeable that a large increase of the oxidation potential does not result in an increase of the reactivity of the cation radical. While the lifetime
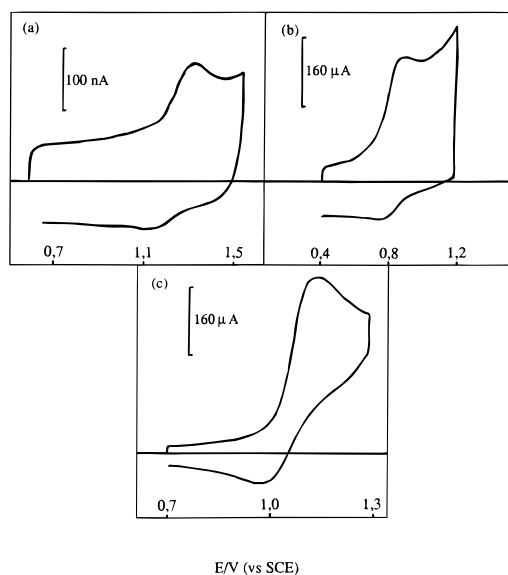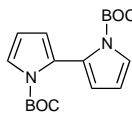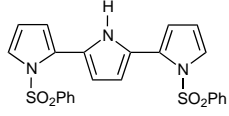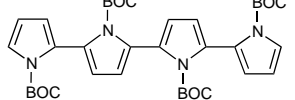
(38) Pernaut, J.-M.; Geniès, E. M. *Synth. Met.* **1985**, *10*, 117.

Figure 4. Cyclic voltammetry of oligopyrroles (a) **4**, (b) **5**, and (c) **6** in acetonitrile (+0.2 mol·L^{-1} NEt$_4$BF$_4$): (a) on a 10 μm diameter platinum ultramicroelectrode; (b), (c) on a 1 mm gold electrode. Scan rates = (a) 5000 V·s^{-1}, (b) 500 V·s^{-1}, (c) 200 V·s^{-1}. (a, c), ($C° = 2 \times 10^{-3}$ mol·L^{-1}) and (b) ($C° = 10^{-3}$ mol·L^{-1}).
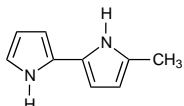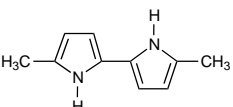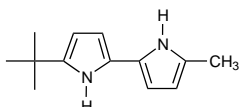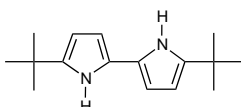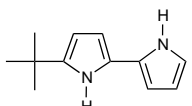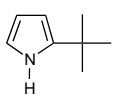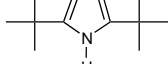
Table 2. Electrochemical Characteristics of N-Substituted Oligopyrroles

compound	compound no.	$E°$/V(SCE)^a	scan rate/ (V·s^{-1})^b
BOC-bipyrrole structure	**4**	1.24$_0$	2000−4000
SO$_2$Ph-terpyrrole structure	**5**	0.81$_5$	200−400
BOC-quaterpyrrole structure	**6**	1.06$_5$	100−200

^{a} Reference SCE electrode was calibrated against the ferrocene/ferrocenium couple 0.405 V (vs SCE). Error ±0.01 V. ^{b} Lowest scan rate for the observation of a partial reversibility for an initial 10^{-3} mol·L^{-1} concentration.

of the cation radical of the protected quaterpyrrole **6** cation radical was shorter than in the case of the unprotected compound, the contrary was observed with the cation radicals of the bis-sulfonated terpyrrole **5** or the bipyrrole **4** which were slightly more stable than the one of unprotected oligopyrroles. The substitution by a withdrawing group has two opposite effects. On the one hand, if we admit that the carbon−carbon bond formation involves the reaction between two cation radicals, the N-substitution will reduce the reactivity of the cation radical against the dimerization by decreasing the spin density on the α-terminal positions. On the other hand, it will increase the redox potential and thus makes the cation radical more sensitive to nucleophilic attack by the solvent or impurities.[14] An indication confirming this hypothesis can be found in our experiments where we did not observe the deposition of a coupling product or of a polymer on the electrode with the N-substituted compounds (no modi-

Table 3. Electrochemical Characteristics of α-Substituted Pyrroles and Bipyrroles

compound	compound no.	$E°/V(SCE)^a$	scan rate/ $(V·s^{-1})^b$
[structure]	7	0.46_0	5000−10000
[structure]	8	0.30_0	5000−10000
[structure]	9	0.31_5	totally reversible at 10000 V·s^{-1} ^{c}
[structure]	10	0.33_0	1−2
[structure]	11		irreversible at 1000 V·s^{-1}
[structure]	12	1.12_5	10000−20000
[structure]	13	0.94_5	0.05−0.1

^{a} Reference SCE electrode was calibrated against the ferrocene/ferrocenium couple 0.405 V (vs SCE). Error ±0.01 V. ^{b} Lowest scan rate for the observation of a partial reversibility for an initial 10^{-3} mol·L^{-1} concentration. ^{c} $E°$ measured at 4000−10 000 V·s^{-1}, it was not possible to estimate the lowest scan rate to observed the chemical stability of the cation radical, see text.

fication of the electrode response upon cyclic scanning). It shows clearly that there is a change in the nature of decay between the cation radicals from the N-substituted and the nonsubstituted oligomers. This effect explains the role of a BOC or a −SO$_2$Ph substituent to protect the oligopyrroles from air degradation which occurs by oxidation. This protection comes from an increase of the oxidation potential and not by a stabilization of the cation radical.

Oxidation of the α,α′-Substituted Pyrroles and Bipyrroles. In the case of oligothiophenes, it is well-known that the properties of oligomers (redox potential, stability of the cation radical) can be changed to a large extent by substituting the α-terminal positions of the thiophene backbone. As we mentioned in the Introduction, by substituting these positions by donor or withdrawing groups, it has been possible to prepare oligothiophenes for which the cation radical was stable.[7−16] In some cases, both the anion radical and cation radical of the oligothiophene were very stable.[14] Thus, it is interesting to compare the effect of similar modifications performed on oligopyrroles and to characterize the redox properties of the new compounds. We have investigated the effect of substitution by methyl and *tert*-butyl groups on α-terminal positions of pyrrole and bipyrrole on the oxidation potential and of the stability of the corresponding cation radicals. The results are summarized in Table 3 and typical voltammograms of the oxidation of α-substituted pyrroles are displayed in Figure 5. It
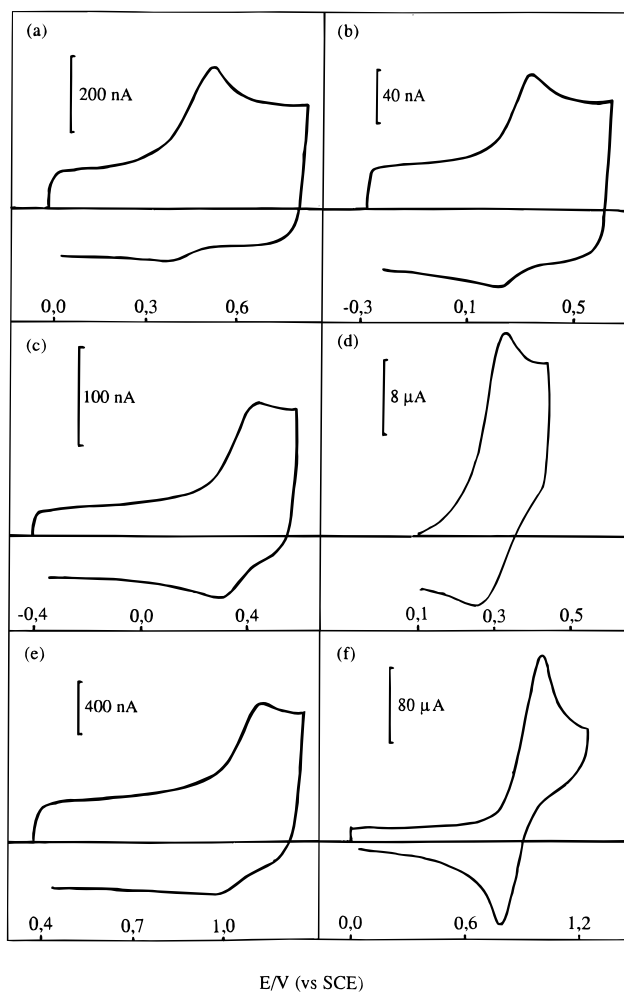

Figure 5. Cyclic voltammetry of oligopyrrole (a) **7**, (b) **8**, (c) **9**, (d) **10**, (e) **12**, (f) **13** ($C° = 2 × 10^{-3}$ mol·L^{-1}) in acetonitrile (+0.2 mol·L^{-1} NEt$_4$BF$_4$); (a, b, c, e) on a 10 μm diameter platinum ultramicroelectrode; (d, f) on a 1 mm gold electrode. Scan rates = (a) 10 000 V·s^{-1}, (b) 6000 V·s^{-1}, (c) 4000 V·s^{-1}, (d) 5 V·s^{-1}, (e) 20 000 V·s^{-1}, (f) 5 V·s^{-1}.

is noticeable that for the oxidation of the 5,5′-dimethyl-2,2′-bipyrrole (**8**), the cyclic voltammograms recorded at different scan rates indicate some complications in the oxidation mechanism as we found previously for the oxidation of the terpyrrole **2**. For the oxidation of **9**, the partial reversibility observed at low scan rate increased only for a very large variation of the scan rate (a variation too large for a simple electron transfer followed by a coupling of two cation radicals), suggested also some complications in the interpretations of the curves. For this reason, the scan rate for which the reversibility due to the cation radical appeared is not reported in Table 3. For these compounds, the values reported in the table were measured at high scan rates (4000 V·s^{-1}).

From the comparison of the unsubstituted bipyrrole **1** with the mono- and the dimethylbipyrrole **7** and **8**, one can see that the substitution of one or two methyl groups on the α-position decreases the oxidation potential as expected for a donor substituent. However, the cation radicals of the mono- or of the dimethylated bipyrroles are not stabilized by the substitution since the reversibility of the voltammetric curves is reached with **7** and **8** at the same scan rates as in the case of unprotected bipyrrole **1**. Unfortunately, we did not find

any measurements concerning the lifetime of the cation radical from the 5,5′-dimethylbithiophene to make a direct comparison between thiophene and pyrrole series. On the other hand, small substituents like the α-methoxy or α-bromo substituent groups have been found to bring substantial stabilizations to the cation radical of bithiophene,[12] which is not the case with bipyrrole.

Substitution by a *tert*-butyl group also lowers significantly the oxidation potential. The decrease is slightly smaller with a *tert*-butyl group than with a methyl group in agreement with the donor effect of each substituent.[39] However, a large stabilization of the cation radicals was observed with the bi-*tert*-butylated compounds. This is clearly visible with the 5,5′-di-*tert*-butyl-2,2′-bipyrrole (**10**) cation radical which was quite stable (reversible wave for 2 V·s⁻¹) and with 2,5-di-*tert*-butylpyrrole (**13**) (reversible for 0.1 V·s⁻¹). The cation radical of the mixed 5-methyl-5′-*tert*-butyl-2,2′-bipyrrole (**9**) was also more stable than the one from the dimethyl compound, indicating that the stabilization effect is certainly not only due to steric effect but also to electronic effects, because only one position was really protected. We were not able to study at high scan rates the oxidation of 5-*tert*-butyl-2,2′-bipyrrole (**11**) for which we wanted to check this point. We only obtained a broad oxidation wave which was certainly due to the presence of impurities and to the difficulties of purification of this oligomer. However, no reversibility was observed in this case at a rate in the order of 500 V·s⁻¹ as we also observed for the oxidation of 2-*tert*-butylpyrrole (**12**).

In addition, as previously observed in the thiophene series,[22] it is clear that the stability of the cation radical decreases from the blocked pyrrole monomer **13** (2,5-di-*tert*-butylpyrrole) to the dimer **10** (5,5′-di-*tert*-butyl-2,2′-bipyrrole), since the cation-radical formation of the monomer **13** was reversible at 0.05 V/s against 10 V/s for the dimer **10**. It is probable that this unexpected reactivity order is linked to the spin density on the β positions of the cation radical, which has been shown

to increase with the rings number in pyrrolic series.[40]

If we compare 5,5′-di-*tert*-butyl-2,2′-bipyrrole (**10**) and 2,5-di-*tert*-buytlpyrrole (**13**) (blocked on the two α-terminal positions by *tert*-butyl groups) with 5-*tert*-butyl-2,2′-bipyrrole (**11**) and 2-*tert*-buytlpyrrole (**12**) (blocked on only one α-terminal positions by the *tert*-butyl group), one can observe the great difference of reactivity of their cation radicals. For the pyrrole **10** and bipyrrole **13**, the lifetimes of the cation radical were very long (one to several seconds) whereas for pyrrole **11** and bipyrrole **12** it was necessary to use fast voltammetry on ultra-microelectrode to reach reversibility of the wave. A possible argument is that the α-α′ positions (where the polymerization takes place) are too hindered to allow the cation radical to react with an another molecule (or cation radical). On the contrary, for **11** and **12**, the cation radical can react very rapidly by its still-free position.

Conclusion

Pyrrole oligomers are easier to oxidize than the corresponding pyrrole monomers. The standard potential, $E°$, for the oligopyrrole/oligopyrrole cation-radical couples varies linearly with the inverse of the chain length, the longest oligomer being the easiest to oxidize. Surprisingly, and contrary to the results found in thiophene series, the lifetimes of the unsubstituted oligopyrrole cation radicals do not change much with the chain length between the monopyrrole ($n = 1$) and the terpyrrole ($n = 3$) (less than a factor of 10). On the contrary, a large stabilization of the cation radical was found when passing from the terpyrrole ($n = 3$) to the quaterpyrrole ($n = 4$).

Substitution on the α-terminal positions or the nitrogen modifies the standard potentials in agreement with the donor or withdrawing effects of the substituents. Somewhat surprisingly, α-terminal methyl groups were not found to stabilize considerably the cation-radical of oligopyrroles. Significant stabilization of the cation radical was only observed with *tert*-butyl substituents.

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(40) Waltman, R. J.; Bargon, J. *Tetrahedron* **1984**, *40*, 3963.