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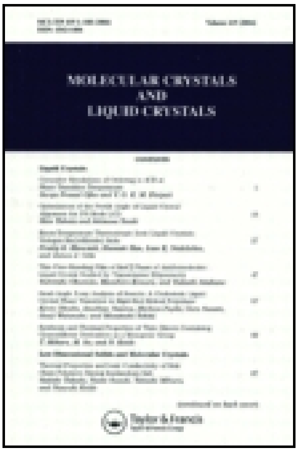

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Novel Conducting Polymers from Dihydrobenzodipyrroles

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NOVEL CONDUCTING POLYMERS FROM DIHYDROBENZODIPYRROLES

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Abstract Anodic coupling of the three isomeric dihydrobenzodipyrroles (1)-(3) produces polymeric films the conductivities of which (0.2-5 S cm^{-1}) are higher than those presented by chemically prepared samples (10^{-4}-10^{-1} S cm^{-1}). Results are reported also for the three dimethyl homologues (4)-(6). Comparison of conductivity data and behaviour of the methyl substituted (4)-(6), allow us to conclude that the sites involved in the polymerization of (1) are the α pyrrolic positions.

INTRODUCTION

In order to devise new structures capable of undergoing oxidative polymerization to electroconductive materials we have followed the basic idea of interposing in between two electron-rich heteroaromatics a conjugated spacer.[1-4] In this line we report on the electropolymerization of the three dihydrobenzodipyrroles (1)-(3) and on the three dimethyl derivatives (4)-(6). Compound (1) is interesting because it can be looked at either as an α,α'-dipyrrole bridged at positions 3,3' with a -CH=CH- group or, alternatively, as an indole derivative fused to a pyrrole ring. The methyl derivatives (4)-(6) have been synthetized to elucidate the regiochemistry of the polymerization of the parent (1), on the assumption that positions occupied by a methyl group would not undergo coupling.

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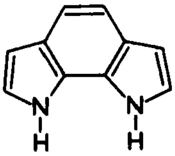

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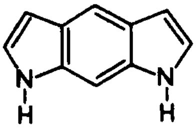

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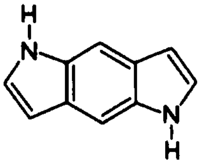

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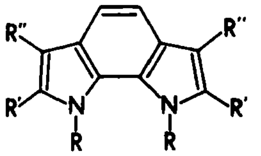

4: R = Me ; R' = R'' = H
5: R' = Me ; R = R'' = H
6: R'' = Me ; R = R' = H

RESULTS AND DISCUSSION

We have previously reported on a simple expeditious preparation of the benzodipyrroles (1)-(3).[5] The synthesis consists of two steps: double condensation of *N,N*'-dimethylformamide diethyl acetal with the suitable dinitroxylene leads to the isolation of a bis-enamine, the catalytic (H_2/Pd-C) reduction of which converts the nitro groups into amino functionalities that, *in situ*, immediately cyclize to the desired pyrrole derivative without the isolation of any intermediate.

The *N,N*'-dimethyl homologue (4) was prepared by methylation of (1) with MeI under phase transfer catalysis conditions.[6]

For the preparation of the 2,7-dimethyl homologue (5) we followed a synthetic route[6] consisting of : a) protection of nitrogen atoms with 2-(trimethylsilyl)ethoxymethyl chloride (SEM-Cl), b) lithiation and subsequent methylation of the α pyrrolic positions, c) removal of the protecting groups.

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The 3,6-dimethyl homologue (6) was prepared by $NaBH_4$ reduction of the bis-methiodide of the Mannich bis-base, in turn obtained from (1);[6] this electrophilic substitution is regioselective at positions 3 and 6.

Electrochemical experiments were performed at room temperature in nitrogen degassed CH_3CN solutions, $1\text{-}5\times10^{-3}$ M in substrate and 0.1 M in tetraethylammonium perchlorate (TEAP). The reference electrode was $Ag/AgClO_4$ (0.1 M in CH_3CN) (ca. 0.3 V vs. SCE).

The cyclic voltammograms of the substrates (1)-(3), as previously reported,[7] show an irreversible oxidation peak followed by a fast chemical process. Peak potentials are reported in Table I. Repetitive cycling with a starting potential of -0.6 V and a switching potential, typically 0.1 V beyond the peak, produces immediately and progressively the build up of a reversible process.

The cyclic voltammogram of a film coated electrode, transferred to blank acetonitrile solution, shows the reversible redox cycle observed in the film forming solution (Figure 1): polymer redox potentials are reported in Table I.

TABLE I Oxidation peak potentials E_{pa}, polymer redox potentials E° and conductivity data for compounds (1)-(3)

Monomer	E_{pa}/V^a	$E°/V^a$	$\sigma/S\ cm^{-1}$
(1)	0.40	0.15	5 (0.11)[b]
(2)	0.30	0.00	3 (0.5×10^{-2})[b]
(3)	0.27	-0.15	0.2 (0.2×10^{-3})[b]

[a] At 0.1 V s^{-1}.

[b] Conductivities of chemicals samples ($FeCl_3$) in round brackets.[8]

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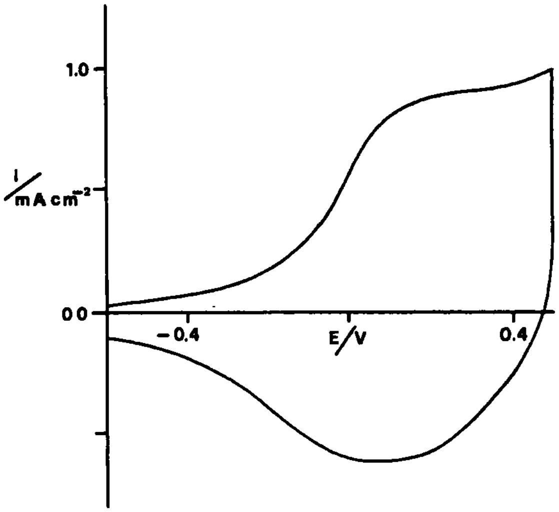

FIGURE 1 Cyclic voltammogram of poly-(1)-coated electrode. Scan rate: 0.1 V s^{-1}.

The conductivities (Table I) follow the trend observed for samples prepared chemically by FeCl$_3$,[8] but at a much higher level, comparable with that for polypyrrole. It can be noted that in both cases the polymer obtained from (1) is the most conducting in the series.

Surprisingly all the three dimethyl derivatives (4)-(6) gave rise to polymerization with a behaviour similar to that of the unsubstituted monomer (1). Peak potentials are in the order (4)>(6)>(5) (Table II) and are all lower than that of the unsubstituted monomer due to the presence of the electron donor methyl group.[6] Conductivities are given in Table II. The lowest one is observed for the polymer of (5), while the conductivity of the polymer of (4) is similar to that observed for poly-(*N*-methylpyrrole). The highest conductivity is displayed by the polymer of (6), only a little lower than that of the unsubstituted monomer.

For all the compounds (1)-(6) it results that ca. 0.5 electrons are reversibly exchanged per monomeric unit and these data are in

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accord with microanalytical data.

TABLE II Oxidation peak potentials E_{pa}, polymer redox potentials $E°$ and conductivity data for compounds (4)-(6).

Monomer	E_{pa}/V^a	$E°/V^a$	$\sigma/S\ cm^{-1}$
(4)	0.37	0.25	$1x10^{-2}$
(5)	0.12	0.03	$5x10^{-6}$
(6)	0.22	-0.07	1

[a] At 0.1 V s^{-1}.

Initially we expected that methyl substitution at the positions in which the parent compound (1), undergoes the oxidative coupling would inhibit the polymerization but, surprisingly, both (5) and (6) undergo oxidative polymerization: this means that the competition between positions α and ß to the nitrogen atoms or coupling is rather strong and blocking in (1), the preferred position of coupling by methyl substitution,does not inhibit the coupling at the other site.

Since the polymer obtained from the ß,ß'-dimethyl derivative (6), necessarily linked through the α positions, exhibits a conductivity similar to that of the parent (1), it must be concluded that coupling in (1) occurs at the α,α'-positions.

The small decrease in conductiviy of (6) with respect to (1) is analogous to the decrease presented by the poly-(3,4-dimethylpyrrole) with respect to polypyrrole.[9] The effect of methyl substitution at the nitrogen atoms in (4) induces in the corresponding polymer, in comparison with the polymer of the unsubstituted parent (1) a considerable decrease (fall off a factor of 10^{-2}) in conductivity: the same qualitative but not quantitative trend is found for poly-(*N*-methylpyrrole) relative to polypyrrole where the ratio of conductivities is reported to be of the order of 10^{-5}[10].

From this work it can be concluded that the "spacer " approach we have followed is fruitful: heterocycles with terminal polymerogenicity can generate conductive materials. The way is now open to functionalization at the spacer. Furthermore the regiochemistry of polymerization has been elucidated through specific methyl substitution of the monomer.

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