4058 *J. Org. Chem.* **2001,** *66,* 4058−4061

Diradical Dications of *m*- and *p*-Phenylenebis[2,5-di(2-thienyl)-1-pyrrole]: Weakly Coupled Diradicals

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Received November 27, 2000 (Revised Manuscript Received March 23, 2001)

Introduction

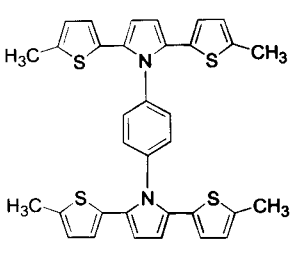
One main objective in the field of organic magnetic materials is the preparation of high-spin molecular compounds as key building blocks for ferromagnets.[1] The two well-known strategies to prepare these systems are the topological criterium[2−4] and the orthogonal alignment of spin carriers.[3c,5]

Our attention in the heterocyclic π-systems comes from the results obtained with molecular π-structures that accommodate both built-in radicals of high stability, derived from tris(2,4,6-trichlorophenyl)methyl radical, and easily doped blocks, made up by mixed pyrrol/thiophene trimers. In this context, molecular species with stable states of high multiplicity in a para arrangement π-system have been observed.[6]

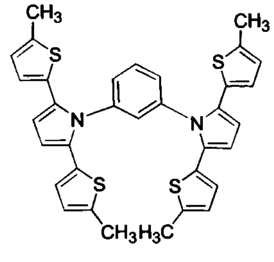
Now, we report our results on isomeric species of different topology, **1** and **2**, constituted by two mixed thiophene/pyrrol trimers linked by a phenylene unit, with the aim to ascertain the ground states of their diradical dication species, and to go further into the influence of the heteroatoms in the easily doped blocks.

Results and Discussion

Isomers **1** and **2** were prepared by the Paal−Knorr condensation[7] between 1,4-bis(5-methyl-2-thienyl)-1,4-butanedione (**6**)[8] and the corresponding 1,4- and 1,3-phenylendiamine. In both cases, the monocondensate intermediates **3** and **4**, respectively, were also obtained.



(1)



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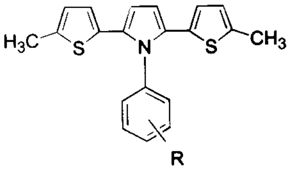
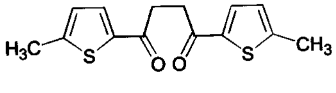


(3): R = *p*NH$_2$
(4): R = *m*NH$_2$
(5): R = H



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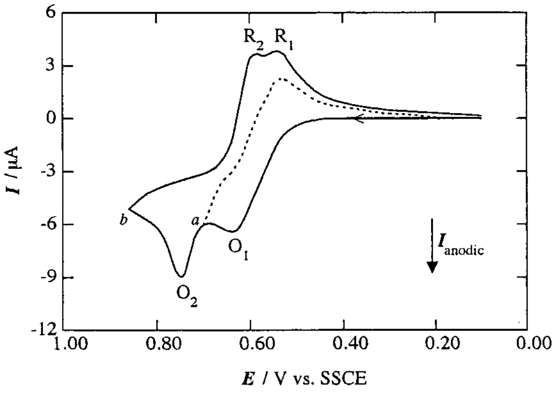

Figure 1. Cyclic voltammograms for the oxidation of **2** (1 mM) in CH_2Cl_2 containing TBAP (0.1 M) on Pt at 213 K. Initial and final potentials 0.100 V. Reversal potential: (a) 0.700, (b) 0.860 V. Scan rate 20 mV s^{-1}.

Cyclic voltammograms (CV) for the oxidation of **1** and **2** in CH_2Cl_2 solution containing *n*-tetrabutylammonium perchlorate (TBAP) (0.1 M) at room temperature show one reversible peak, $E°$ at 0.65 and 0.66 V vs SSCE (sodium chloride saturated calomel electrode), respectively, corresponding to a monoelectronic oxidation process, and a second irreversible also monoelectronic process with anodic peak potential E^a_p at 0.90 and 0.97 V, respectively. When lowering the temperature at 213 K, all processes are shifted at lower potentials, both anodic processes being quasi-reversibles for **2** under very anhydrous conditions,[9] at $E° = 0.59$ and 0.67 V, at scan rates (ν) ≤ 50 mV s^{-1} (Figure 1). Despite the similitude of the first redox pairs for **1** and **2** and the close resemblance of them to that of monomer 5[10] ($E° = 0.62$ V), the small splitting of the anodic processes of both trimeric moieties of the molecule in **1** and **2**[11] indicates a weak electronic influence between them. Therefore, oxidation takes place in one of the moieties to give the radical cation. This localized monocharged species is further oxidized in the other moiety in a second process to give the diradical dication.

With the aim of improving our knowledge on the geometry of the low-lying conformations of **1** and **2** and their doped species, we have studied the molecular structure of the simplest model 2,5-dimethyl-1-phenylpyrrole using ab initio quantum mechanical methods[12] (Figure 2). The minimum energy conformation of neutral and charged species corresponds to a torsional angle of 90.0° between the pyrrolyl and phenyl rings, and the inter-ring distance, C(Ph)−N = 1.423 Å for the neutral compound, elongates by 0.022 Å in the radical cation indicating a reduction in the bond strength.[13] In both cases, the inter-ring distance is consistent with a single-bond character.

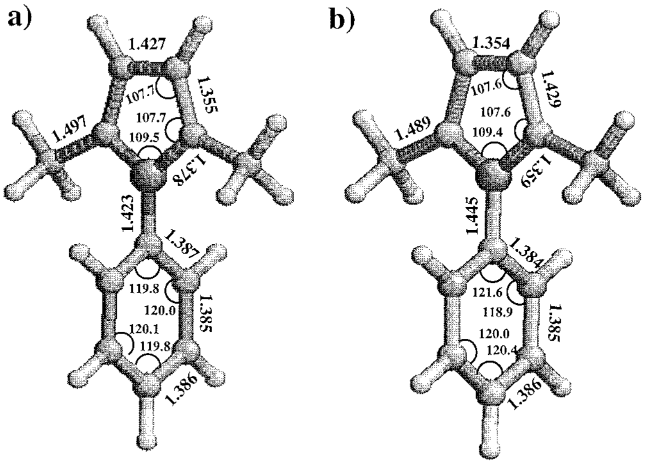

Figure 2. Lowest energy conformations of (a) neutral and (b) radical cation of 2,5-dimethyl-1-phenylpyrrole.

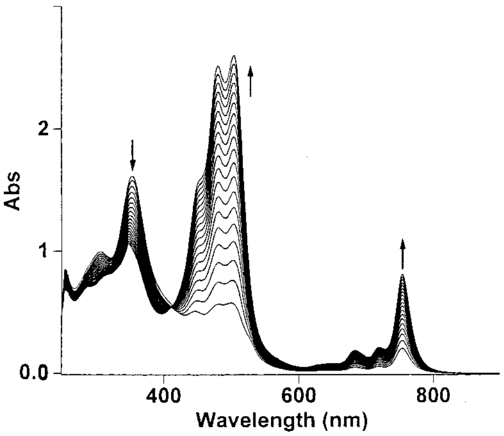

Figure 3. Evolution of the UV−vis spectra of a ~10^{-4} M solution of **5** in trifluoroacetic acid at 293 K during the conversion of **5** to $\mathbf{5}^{\bullet +}$.

The conformational aspects of **1** and **2** and the weak interaction between the two pyrrolyl chromophores through the phenylene ring are also confirmed by UV−vis spectra. Thus, the lowest $\pi-\pi^*$ maxima in the absorption spectra of both isomers ($\lambda_{max} = 331$ and 326 nm for **1** and **2**, respectively) in $CHCl_3$ solution display a slightly hypsochromic shift relative to that of **5** ($\lambda_{max} = 344$ nm). In trifluoroacetic (TFA) acid, the evolution of the spectrum of **5** is shown in Figure 3. Figure 3 represents the oxidation of neutral **5** ($\lambda_{max} = 307$ and 354 nm) to the corresponding $\mathbf{5}^{\bullet +}$ radical cation which exhibits one strong absorption band at $\lambda_{max} = 485$ and 505 nm and a weak band at $\lambda_{max} = 753$ nm. The isosbestic point ($\lambda_{max} = 411$ nm) indicates the interconversion of only two species, $\mathbf{5} \rightarrow \mathbf{5}^{\bullet +}$. Remarkably, the spectra of dimers **1** and **2** in TFA acid show practically isoenergetic bands for the corresponding radical cations (480, 509, and 758 nm for $\mathbf{1}^{\bullet +}$ and 483, 511, and 760 nm for $\mathbf{2}^{\bullet +}$).

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(11) CV for the oxidation of **3** and **4** in the same conditions at room temperature, gave reversible peaks at $E° = 0.49$ V, for both isomers. This lower value is attributed to the electron-releasing effect of the amino group.

(12) The neutral system was investigated at the ab initio RHF level of theory and the radical cation at the UHF level. The standard 6-31G(d) basis set was used in both RHF and UHF calculations: Hariharam, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 203.

(13) Support for the values of the dihedral angles between phenyl and pyrrolyl planes in the neutral compounds **1** and **2** is given by the experimental value of 90° found in the structure of 1,4-bis(2,5-dimethylpyrrol-1-yl)benzene: Avila, D. V.; Davies, A. G.; Tocher, D. A.; Truter, M. R. *Acta Crystallogr., Sect. C* **1991**, *47*, 1662−1665.

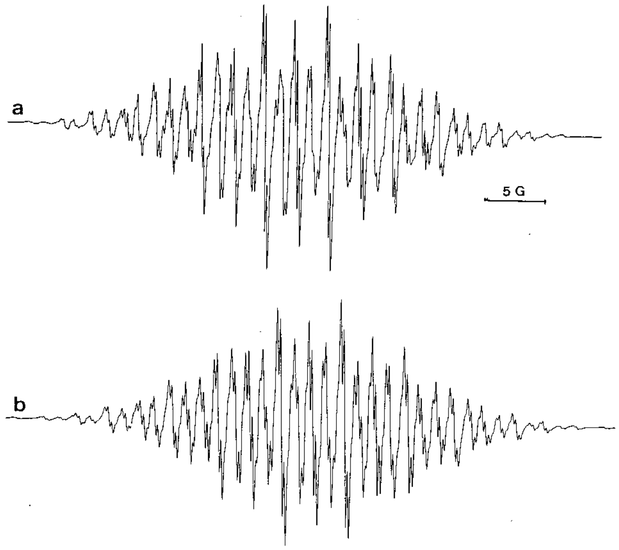

Figure 4. (a) EPR spectrum of $\mathbf{2}^{2\bullet+}$ in trifluoroacetic acid at rt, using a modulation amplitude, MA = 0.1. (b) Computer simulation using the values given in the text.

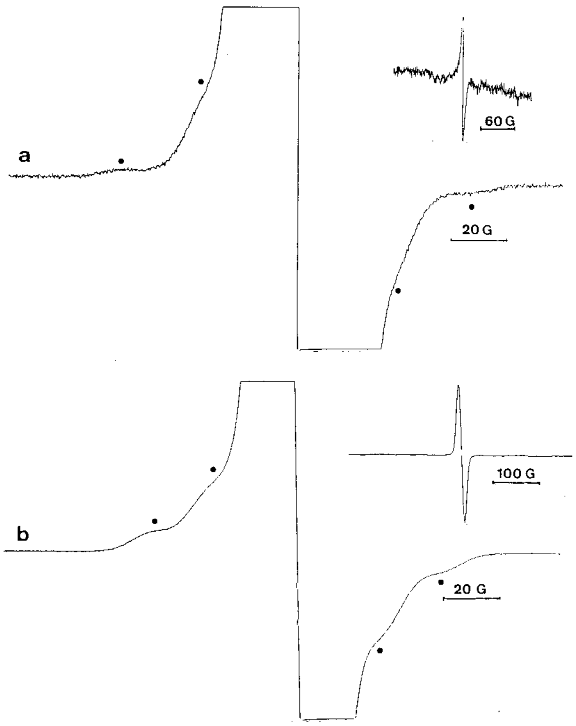

Figure 5. EPR spectrum of (a) $\mathbf{1}^{2\bullet+}$ and (b) $\mathbf{2}^{2\bullet+}$ in 1,1,1,3,3,3-hexafluoro-2-propanol and TFA acid (4:1) at 120 and 130 K, respectively, with peaks showing the $\Delta m_S = \pm 1$ transition. Insets show the signal corresponding to $\Delta m_S = \pm 2$ forbidden transitions at 4 K.

Degassed solutions of **1** and **2** in TFA acid examined by electron paramagnetic resonance (EPR) spectroscopy exhibited EPR spectra of the monooxidized species (radical cations) ($g = 2.0022$) (Figure 4) in close resemblance with those of the radical cations of the monomeric species **3** and **4**.[14] The simulation[15] was performed by using the following *hfs* values, which denote that the radical cation is mainly confined to one trimer unit of the molecule: a(6H) = 5.19 G; a(2H) = 3.75 G; a(2H) = 2.31 G; a(1N) = 2.58 G; a(2H) = 0.26 G. This phenomenum was reported by Davies et al. in 1,4-bis(2,5-dimethylpyrrol-1-yl)benzene.[16]

Diradical dications $\mathbf{1}^{2\bullet+}$ and $\mathbf{2}^{2\bullet+}$ were generated from the neutral compounds with thallium(III) trifluoroacetate as oxidant in a mixture (4:1) of 1,1,1,3,3,3-hexafluoro-2-propanol[17] and TFA acid. The EPR spectra in frozen solution at temperatures as high as 200 K clearly show a four-peak pattern in the $\Delta m_S = \pm 1$ region, characteristic of axial-symmetric triplet states, superimposed with an intense central line corresponding to $S = {}^1/_2$ species. Figure 5 displays both spectra at 120 K for $\mathbf{1}^{2\bullet+}$ and at 130 K for $\mathbf{2}^{2\bullet+}$. The presence of triplet states is confirmed by a weak transition in the $\Delta m_S = \pm 2$ region. The zero-field splitting $|D/hc|$ parameters for $\mathbf{1}^{2\bullet+}$ and $\mathbf{2}^{2\bullet+}$ are 0.0057 and 0.0047 cm^{-1}, respectively. From these parameters, the average distance between the radical centers[18] was estimated to be 7.7 and 8.2 Å, respectively, which suggests a delocalization of each unpaired electron into the thienyl rings. A Curie plot of the $\Delta m_S = \pm 2$ signal intensity versus $1/T$ (Figure 6) gives straight lines in both species in the range 4−90 K for $\mathbf{1}^{2\bullet+}$ and 4−50 K for $\mathbf{2}^{2\bullet+}$, indicating in both isomers a triplet ground state or nearly degenerate with a singlet state. The fact that ab initio MO calculations suggest perpendicular conformations for the chromophores either in meta or in para topology decreases drastically the energy gap between the triplet and singlet states due to dynamic spin polarization through the π-system. On the other hand, the small spin density at N (a(1N) = 2.58 G in the radical cations **3** and **4**), which is diffused into the thienyl rings, makes also very weak the interactions of the SOMOs with the σ and σ^* orbitals of the benzene ring in the twisted geometries. These interactions are responsible for the lifting of the degeneracy of the SOMOs in twisted structures.[19] Therefore, the noninfluence of the topology in the multiplicity of the ground states suggests most probably that the singlet and triplet are degenerated in both species $\mathbf{1}^{2\bullet+}$ and $\mathbf{2}^{2\bullet+}$.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were obtained in CDCl$_3$ solutions on a Varian Gemini XL200 spectrometer operating at 200 MHz for ^{1}H and 50 MHz for ^{13}C, respectively. Exact masses were obtained with a VG Autospec-Q (geometry EBEqQ) mass spectrometer with an acceleration voltage of 8.000 V and a resolving power of 10.000. EPR spectra of solutions of **1**−**4** in TFA acid were degassed by passing a stream of dry argon through the solution and recorded with a Varian E-109 spectrometer working in the X band (microwave power 0.5 mW) at room temperature. Solutions of **1** and **2** in 1,1,1,3,3,3-hexafluoro-2-propanol−TFA acid (4:1) with thallium(III) trifluoroacetate were degassed by three freeze−pump−

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[14] EPR spectra of $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ in similar conditions gave the same intense multiplet and also similar to that of $\mathbf{5}^{\bullet+}$, which denotes the negligible influence of the aromatic amino group in either the para or meta position

[15] Computer simulations were carried out by the public WINSIM program provided by Dulog, D.; Public EPR Software Tools, National Institute of Environmental Health Sciences, Bethesda, MD 1996.

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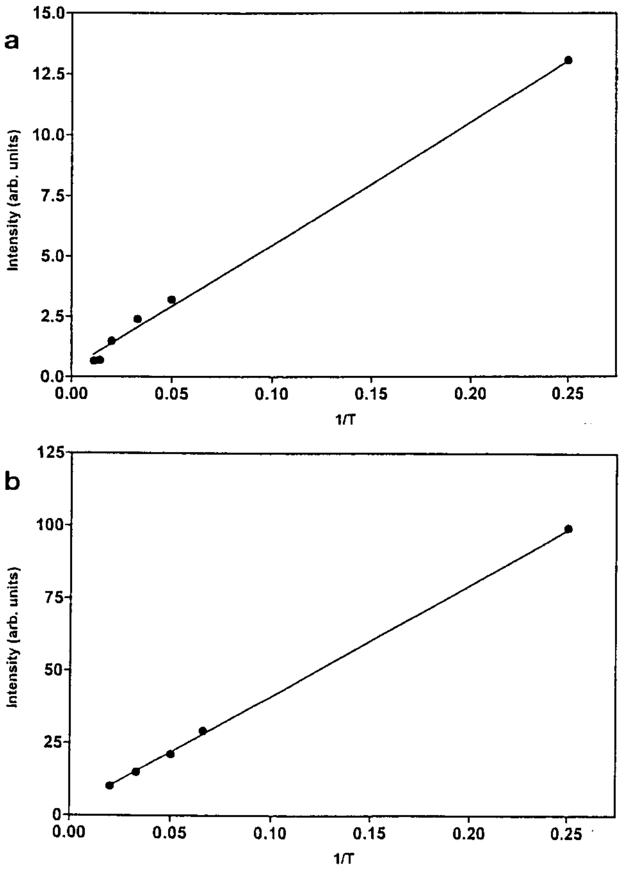

Figure 6. Temperature dependences of the $\Delta m_S = \pm 2$ EPR signal intensities for (a) $\mathbf{1}^{2\bullet+}$ (r^2 =0.996) and (b) $\mathbf{2}^{2\bullet+}$ (r^2 = 0.999).

thaw cycles before being inserted into the cavity of a Bruker ESP 300 spectrometer with a Bruker ER 4112 HV continuous-flow liquid helium cryostat and an Oxford Instruments temperature-controller system to obtain spectra at low temperatures (4 K). The cyclic-voltammetric measurements were carried out in a jacketed three-electrode cell under an argon atmosphere. The working electrode was a platinum sphere with an area of 0.093 cm^2 and the counter-electrode was a Pt wire. The reference electrode was an SSCE (sodium chloride saturated calomel electrode) connected to the cell through a salt bridge containing a 0.1 M TBAP$-$CH$_2$Cl$_2$ solution. Cyclic voltammograms were performed with standard equipment consisting of a PAR 175 universal programmer and an Amel 551 potentiostat connected to a Philips 8043 X-Y recorder. Scan rates ranging between 20 and 200 mV s^{-1} were studied. The volume of all test solutions was 25 mL. The temperature was kept at 25 °C.

Condensations of 1,4-Bis(5-methyl)-2-thienyl-1,4-butanedione (6) with Anilines. General Procedure. A solution of **6**, the appropriate aniline, and propionic acid in dry benzene was refluxed under argon in a flask equipped with a Dean$-$Stark trap with stirring in the dark. The resulting solution was cooled to room temperature, and a solid crystallized. (a) The solid was separated by filtration and recrystallized in benzene. The resulting crystals were identified as recovered **6** by TLC and ^{1}H NMR. (b) The benzene solution was poured into a saturated aqueous solution of NaHCO$_3$, and the mixture was extracted with chloroform. The organic solution, washed with water, dried over anhydrous Na$_2$SO$_4$, and evaporated at reduced pressure, yielded a residue that was flash chromatographed (silica gel), eluting first with CCl$_4$ and then with CHCl$_3$ to give the corresponding pyrrole and/or bispyrrole.

a. With 1,4-Phenylenediamine. Starting materials: 1,4-phenylenediamine (0.300 g, 2.77 mmol), **6** (1.7 g, 6.1 mmol), propionic acid (4 mL), benzene (90 mL). Reaction time: 4 days. Recovered **6**, 1 g (59%).The purification by flash chromatography, after elution with CHCl$_3$, gave the following: (a) **1**, 0.019 g (1%). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.31 (4H, s), 6.48 (4H, dq, J = 1, 3.6 Hz), 6.43 (4H, s), 6.27 (4H, d, J = 3.6 Hz), 2.41 (12H, s). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 138.80, 138.62, 132.37, 130.36, 129.88, 125.15, 124.67, 109.94, 15.19. Exact mass: calcd for C$_{34}$H$_{28}$N$_2$S$_4$ 592.1135, found 592.1126. (b) **3**, 0.474 g (49%). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.07 (2H, m), 6.70 (2H, m), 6.45 (2H, dq, J = 1, 3.6 Hz), 6.42 (2H, s), 6.34 (2H, d, J = 3.6 Hz), 3.85 (2H, s broad), 2.35 (6H, d, J = 1 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 147.00, 138.04, 133.05, 130.72, 130.41, 129.21, 125.07, 123.55, 115.27, 108.53, 15.09. Exact mass: calcd for C$_{20}$H$_{18}$N$_2$S$_2$ 350.0911, found 350.0907.

b. With 1-(4-Aminophenyl)-2,5-bis(5-methyl-2-thienyl)-pyrrole (3). Starting materials: **3** (0.200 g, 0.57 mmol), **6** (1 g, 3.59 mmol), propionic acid (7 mL), and benzene (50 mL). Reaction time: 9 days. Recovered **6**, 0.4 g (40%). The purification by flash chromatography, after eluting with CHCl$_3$, gave **1**, 0.150 g (44%).

c. With 1,3-Phenylenediamine. Starting materials: 1,3-phenylenediamine (0.300 g, 2.77 mmol), **6** (1.695 g, 6.1 mmol), propionic acid (6 mL), benzene (90 mL). Reaction time: 11 days. Recovered **6**, 0.431 g (25%).The purification by flash chromatography after eluting with CHCl$_3$ gave the following: (a) **2**, 0.075 g, (4.5%). ^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.42$-$7.12 (4H, m), 6.40 (4H, dq, J = 1, 3.6 Hz), 6.36 (4H, s), 6.15 (4H, d, J = 3.6 Hz), 2.37 (12 H, d, J = 1 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 139.14, 138.68, 131.99, 130.19, 129.78, 129.75, 129.02, 125.42, 125.26, 110.17, 15.15. Exact mass: calcd for C$_{34}$H$_{28}$N$_2$S$_4$ 592.1135, found 592.1133. (b) **4**, 0.265 g (27.3%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.19 (1H, t, J = 7.8 Hz), 6.76 (1H, ddd, J = 0.88, 2.1, 7.8 Hz), 6.72 (1H, ddd, J = 0.88. 2.1, 7.8 Hz), 6.61 (1H, t, J = 2.1 Hz), 6.45 (2H, dq, J = 1, 3.6 Hz), 6.41 (2H, s), 6.32 (2H, d, J = 3.6 Hz), 3.73 (2H, s broad), 2.36 (6H, d, J = 1 Hz). ^{13}C NMR (75 MHz, CDCl$_3$): δ = 147.09, 139.51, 138.07, 132.78, 129.96, 129.75, 125.14, 123.63, 120.00, 116.35, 115.55, 108.83, 15.07. Exact mass: calcd for C$_{20}$H$_{18}$N$_2$S$_2$ 350.0911, found 350.0911.

d. With 1-(3-Aminophenyl)-2,5-bis(5-methyl-2-thienyl)-pyrrole (4). Starting materials: **4** (0.206 g, 0.59 mmol), **6** (0.500 g, 1.80 mmol), propionic acid (3 mL), and benzene (50 mL). Reaction time: 3 days. Recovered **6**, 0.264 g (52%). The purification by flash chromatography, after eluting with CHCl$_3$, gave the following products: (a) **2**, 0.115 g (33%); (b) recovered **4**, 0.011 g (5%).

Acknowledgment. Financial support for this research from the MEC (Spain) through project PB96-0836 is gratefully acknowledged. V.M.D. thanks the MEC for a postdoctoral contract. We also thank the EPR service of the Centre d'Investigació i Desenvolupament (CSIC) and of the University of Barcelona for recording the spectra.

JO001656D