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N-Substituted 2,5-Di(2-thienyl)pyrroles. Synthesis and Electrochemical Properties

T. S. El'shina[a], E. A. Sosnin[b], E. V. Shklyaeva[c], and G. G. Abashev[b,c]

[a] *Perm State National Research University, ul. Bukireva 15, Perm, Russia*
[b] *Institute of Technical Chemistry, Ural Branch, Russian Academy of Sciences, Perm, Russia*
e-mail: gabashev@psu.ru
[c] *Institute of Natural Sciences, Perm, Russia*

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Abstract—2,5-Dithienylpyrroles containing *p*-substituted benzene ring at the nitrogen atom were synthesized. The formylation and subsequent crotonic condensation of *N*-(4-nitrophenyl)-2,5-di (2-thienyl)pyrrole was performed. Electrochemical behavior of the compounds and electrochromic properties of 2,5-di(2-thienyl)-pyrrole containing *p*-semidine fragment at its nitrogen atom were studied.

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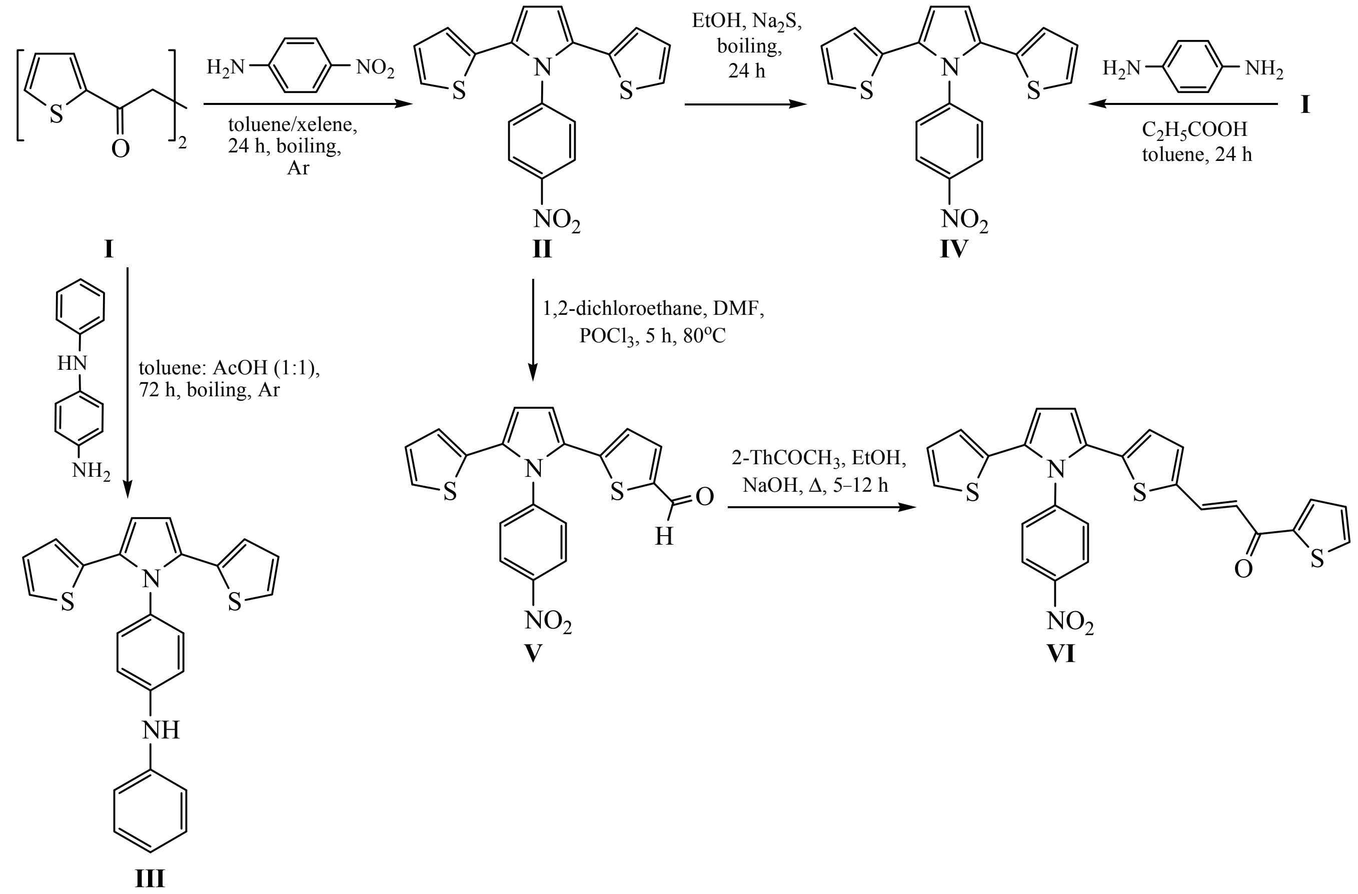
Among the conducting polymers polypyrrole and polythiophene are of particular interest due to their high conductivity, stability in the oxidized state, interesting redox properties, and simplicity and accessibility of the preparation of the starting monomers, pyrroles and thiophenes [1–3]. The polypyrrole conductivity is 10^{-10} to 10^{-5} Cm cm^{-1}, the bandgap is 4 eV [4]. The introduction into its molecule of counterions (doping) leads to a manyfold increase in the conductivity, and the polymer can behave as a semiconductor (bandgap ≤ 2.5 eV) or metal [4, 5]. The polythiophenes conductivity is also high, bandgap 1.0–1.2 to 0.58 eV, and they are more stable. From this point of view it is interesting to obtain conjugated polymers that include both heterocycles simultaneously. This can be achieved in three ways [2]: preparation of thiophene and pyrrole copolymers from a mixture of the corresponding monomers, copolymerization of pyrrole and bi- or α-terthiophenes, and synthesis and further polymerization of substituted monomers incorporating in their structure both thiophene and pyrrole heterocycles, like substituted 2-(2-thienyl)pyrrole and 2,5-di(2-thienyl)pyrrole. The synthesis of unsubstituted and substituted 2,5-di(2-thienyl)pyrroles and the study of their electrochemical behavior were carried out by many authors. A review [2] comprises the methods of preparation, electrochemical behavior, and electrochemical and chemical polymerization of N-substituted 2,5-di(2-thienyl)pyrroles.

This paper describes the synthesis and properties of 2,5-di(2-thienyl)pyrroles containing a substituted benzene ring at the nitrogen atom. For the preparation we used the Paal–Knorr method. The *p*-nitrophenyl derivative **II** was synthesized and electrochemically investigated earlier [6, 7], but the chemical transformations of 2,5-di(2-thienyl)pyrrole were not described. By reduction of the nitro group in **II** with sodium sulfide we synthesized the amino derivative SNS-IV, previously synthesized by heating diketone **I** with 1,4-diaminobenzene in the medium of propionic acid and toluene [11]. By formylation of **II** in dichloroethane along the Vilsmeier–Haack method we isolated aldehyde **V** in a good yield.

In turn, by heating aldehyde **V** with 2 acetylthiophene in 10% NaOH solution in alcohol we synthesized new chalcone **VI**, a red-orange crystalline solid. The preparation and study of dithienylpyrrole **III** is of particular interest because its structure contains two polymerizable fragment, 2,5-di(2-thienyl)pyrrole and *N*-semidine, the latter being actually a dimer of aniline (>NC_6H_4NHPh). The structure of the compounds obtained was confirmed by ^{1}H NMR spectroscopy and the gas chromatography-mass spectrometry.

Electrochemical behavior of the compounds obtained in the work was studied using cyclic voltammetry, at the same time we obtained the electrochemical characteristics of the already described



compound **II** under the conditions used in this study. For the measurements potentiostats P8 and IPC Compact, three-electrode cell with the working electrode, reference silver chloride electrode, and auxiliary platinum electrode were used. The monomer concentration was 1×10^{-3} M, the concentration of supporting electrolyte 0.1 M, solvent acetonitrile. To determine the best conditions for the electrochemical polymerization of the compounds (monomers) we performed initial oxidation using a glassy carbon electrode changing the rate of the scanning potential (V_{scan}) in the range of 50–500 mV s^{-1}, as well as the composition of supporting electrolyte (Et_4NClO_4 or Bu_4NPF_6). After selecting optimum conditions using the glassy carbon electrode, Et_4NClO_4 as supporting electrolyte, and V_{scan} of 100 mV s^{-1} the further measurements were carried out with an ITO electrode (a glass plate covered with a layer of indium–tin oxide). Figures 1 and 2 are examples of cyclovoltammogramms obtained under these conditions, at V_{scan} = 100 mV s^{-1}. The comparison of Figs. 4a and 4b shows that the nature of the redox curves can vary significantly. All compounds were polymerized, and on the working electrodes a dark green or blue film formed.

The electrochemical polymerization proceeds most typically with dithienylpyrrole **III** containing at a nitrogen atom the *p*-semidine residue.

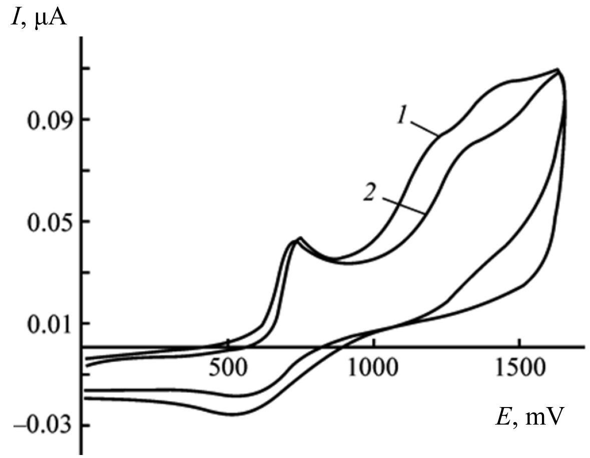


Fig. 1. Cyclovoltammogram of compound **III** (glassy carbon, 1 cycle, (*1*) Et_4NClO_4, (*2*) Bu_4NClO_4, V_{scan} 100 mV s^{-1} , MeCN).

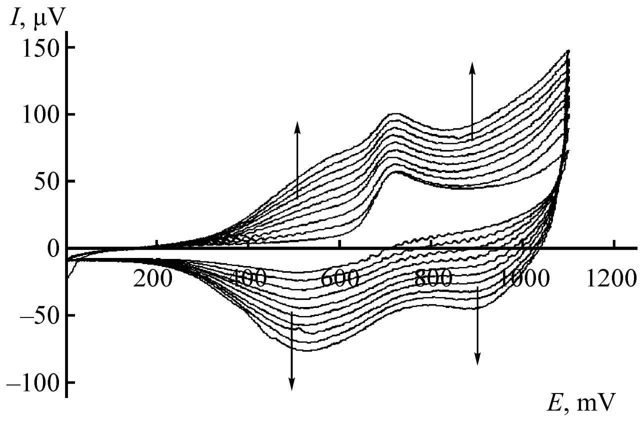


Fig. 2. Cyclovoltammogram of compound **III** (ITO, 10 cycles, Bu_4NClO_4, V_{scan} 100 mV s^{-1}, MeCN).

Figure 1 shows the cyclic voltammograms of **III** obtained with the glassy carbon electrode with different supporting electrolytes, Et_4NClO_4 (*1*) and Bu_4NPF_6 (*2*). Figure 2 shows the cyclovoltammograms obtained with the ITO-electrode (supporting electrolyte Bu_4NPF_6). As seen from Fig. 2, with increasing number of cycles the current density grows, which is due to the rapid growth of the polymer film on the electrode surface. In the voltammograms the reversible oxidation and reduction peaks (E^1_{ox} = 725 mV, E^1_{red} = 525 mV) and an irreversible reduction peak, E^2_{red} = 912 mV can be seen. We found that compound **III** exhibits electrochromic properties: in the process of electrochemical oxidation in the conditions of cyclic voltammetry (CVA) the color of the film at the working electrode changes (light → dark → light → dark). Figure 3 shows a view of the film formed on the ITO electrode, its reduced and oxidized states, as well as the photo of the oxidized film obtained with a Metam PB 21 microscope (6c).

The curves obtained in the electrospectrophotometric studies are shown in Fig. 4. We used a spectrophotometer SF2000, P8 potentiostat, a three-electrode cell (photometric cell) with a ITO working electrode, silver-silver chloride reference electrode, and platinum auxiliary electrode, monomer concentration $[c] = 3\times10^{-4}$ mol. A film of the polymer was pre-deposited electrochemically on the ITO-electrode before the registration of the photometric curves. The potential applied to the plate, increased abruptly as shown in Fig. 4. At high values of potential ($E_{\text{ox}} >$ 1000 mV), the film became almost black and its color did not change (irreversible oxidation). At low limiting potential ($E_{\text{ox}} <$ 1000 mV) a change in the film color was observed from colorless to green and back (reversible redox-transformation).

Figure 4 shows that with the growth of the potential the absorption of the film in the region of 700–950 nm increases dramatically. Also the absorption of film in the regions of 500–700 nm and 950–1000 nm slightly increases, which is probably due to an increase in the film thickness at the electropolymerization. The film of poly-**III** was studied by cyclic voltammetry in a solution of supporting electrolyte (Fig. 5). The arrows indicate the values of potentials $E_{\text{ox onset}}$ and $E_{\text{red onset}}$. Based on these values we calculated ionization potential *IP*, electron affinity *EA*, and the difference of the HOMO–LUMO energy levels in the resulting film by the method described in [15, 16]. $E^{\text{onset}}_{\text{ox}}$, 505 mV, $E^{\text{onset}}_{\text{red}}$ 480 mV, *IP* 4.86 eV, *EA* 3.87 eV; HOMO–LUMO 0.99 eV.

EXPERIMENTAL

^{1}H NMR spectra were obtained on a Mercury plus300 instrument, internal reference HMDS. Mass spectra were obtained on an Agilent GC 6890N MSD

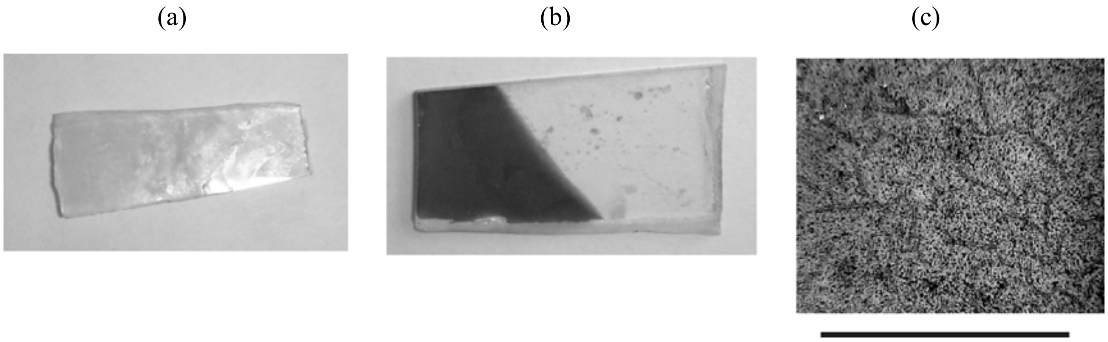


Fig. 3. Film of compound **III** grown electrochemiclly: (a) grown on ITO electrode, reduced state, (b) grown on ITO electrode, oxidized state, and (c) photo of oxidized film.

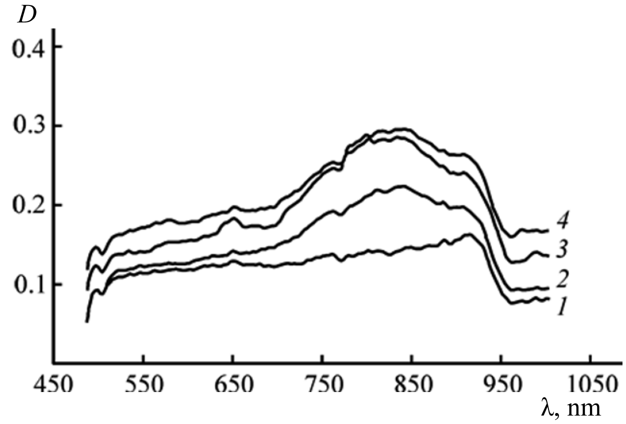


Fig. 4. Electron absorption spectrum of poly-**III** film at E_{ox} 500–1000 mV: (*1*) 500, (*2*) 700, (*3*) 900, (*4*) 1000 mV.

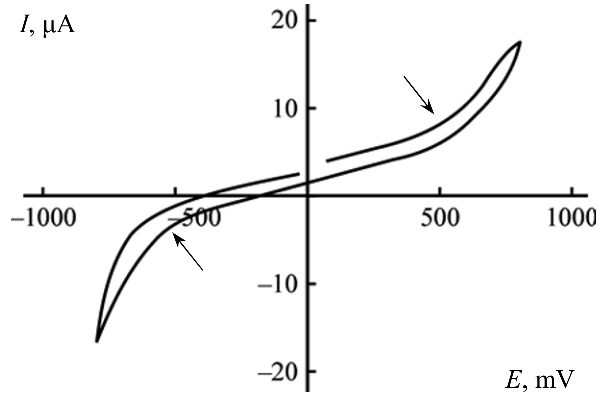


Fig. 5. Cyclovoltammogram of poly-**III** film.

5975B gas chromatography–mass spectrometer (EI, 70 eV). The monitoring of reactions was performed and purity of the obtained compounds was checked by TLC (Silufol, Cavalier). The separation of mixtures and purification of target products was performed on a column filled with silica gel (Lancaster, Silica gel 60, 0.060–0.2mm). Electrochemical studies were performed on potentiostat P8 (Elins) and IPC Compact (Volta), an electrochemical sensor module EM-04. The data were processed with the IPC-compact 8.60F software.

Succinyl chloride was obtained according to [12], 1,4-di(2-thienyl)butane-1,4-dione according to [13], 2-acetylthiophene was synthesized according to [14].

1-[4-(4-Phenyl)aminophenyl]-2,5-di(2-thienyl)-pyrrole (III). To a mixture of 0.5 g of 1,4-di(2-thienyl)butane-1,4-dione (2 mmol) and 1.47 g of *p*-semidine (8 mmol) was added a solution of 20 ml of toluene and acetic acid (1:1). The reaction mixture was refluxed for 72 h under argon, cooled, solvents were evaporated, the residue was purified by column chromatography (SiO_2, eluent methylene chloride). Yield 70%, white crystalline solid, mp 193–195°C. ^1H NMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 5.89 br.s (1H, NH), 6.53 s (2H, pyrrole), 6.65 d.d (2H, thiophene, J_1 = 3.6, J_2 = 1.2) , 6.84 m (2H, thiophene, J_1 = 3.6), 6.96–7.02 m (2H, thiophene), 7.04–7.8 m (4H, C_6H_4), 7.13–7.18 m (4H, C_6H_4), 7.31 m (1H, C_6H_4, J = 8.1). Mass spectrum (*m*/*z*, %): 400 (12.6) [M^+ +2H], 399 (28.5) [M^+ + H], 398.1 (100) [M^+]. $C_{24}H_{18}N_2S_2$. Mass-spectrum, *m*/*z* (*I*, %): 400 (12.6), $[M + H]^+$, 398.1 (100) [*M*]+, 197 (15).

1-(4-Aminophenyl)-2,5-di(2-thienyl)pyrrole (IV). A mixture of 2.7 g of 1-(4-nitrophenyl)-2,5-di(2-thienyl)pyrrole **II** (7.6 mmol) and 1.84 g of sodium sulfate (5 mmol) in 75 ml of ethanol was heated on a boiling water bath for 24 h. The residue obtained after evaporation of ethanol was purified by column chromatography (SiO_2, eluent, methylene chloride). Yield 30%, white crystalline solid, mp 160–161°C. ^1H NMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 3.87 br.s (2H, NH_2), 6.51 s (2H, pyrrole), 6.62 d (2H, thiophene, J = 3.6). 6.70, d (2H, phenyl, J = 8.4), 7.02, d (2H, thiophene, J = 5.1). 7.07, d (2H, phenyl, J = 8.4). Mass spectrum, *m*/*z*, (*I*, %): 324 (11), 323 (22) [M^+ + H], 322 (100), [M^+], 212 (22.5), 65 (13).

1-(4-Nitrophenyl)-2-(2-thienyl)-5-(5-formylthienyl)pyrrole (V). To a solution of 2.18 g of 1-(4-nitrophenyl)-2,5-di(2-thienyl)pyrrole (6 mmol) in 60 ml of water-free 1,2-dichloroethane at room temperature were added sequentially 0.47 ml of water-free DMF (0.44 g, 6 mmol) and 0.55 ml of $POCl_3$ (0.9 g, 6 mmol), and the reaction mixture was heated for 5 h at a temperature not exceeding 80◦C, cooled, poured into 300 ml of ice-cold water, carefully acidified with 10% HCl, extracted with CH_2Cl_2, then solvent was distilled off. The residue was separated by column chromatography (SiO_2, eluent methylene chloride) to give the **V** in the form of yellow crystals. Yield 44%, mp 1790–180°C. ^1H NMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 6.34 d.d (1H, thiophene, J_1 = 3.6 J_2 = 1.2), 6.8 t (1H, thiophene, J = 3,6), 6.96 d (1H , pyrrole, J = 3.6), 6.98 d (1H, pyrrole, J = 5.1), 7.03 d (2H, thiophene, J = 7.2), 7.20 d (1H, thiophene, J = 4.5), 7.34 d (2H, phenyl , J = 8.7), 7.38 d (1H, thiophene, J = 5.1). 8.20 d (2H, phenyl, J = 8.7), 9.84 s (1H, HCO). Mass spectrum *m*/*z* (*I*, %): 382 (12) $[M + 2H]^+$, 381 (24) $[M + H]^+$, 380 (100) $[M]^+$, 335 (14), 76 (10).

(2*E*)-3-[1-(4-Nitrophenyl)-2,5-di(2-thienyl)-1*H*-pyrrol-3-yl]-1-(3-thienyl)prop-2-en-1-one (VI). A mixture of 0.8 g of **V** (2 mmol) and 0.25 g of 2-acetylthiophene (2 mmol) in 120 ml of 2% alcohol solution of NaOH was refluxed for 12 h. After cooling, the reaction mixture was acidified to pH ~ 3, poured into cold water, extracted with methylene chloride, the solvent was removed, the residue was chromatographed on a column (SiO_2, eluent methylene chloride). Yield 70%, orange-red substance, mp (decomp) 222–224°C. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 6.56 d (2H, pyrrole, *J* = 3.3), 6.61 m (2H, thiophene), 6.84 m (2H, thiophene), 6.88 t (1H, thiophene, *J* = 4.5),. 6.99 t (1H, thiophene, *J* = 4.5), 7.21 d.d (1H, thiophene, J_1 = 5.4, J_2 = 1.5), 7.26–7.32 m (3H, 2H benzene + 1H CH=), 7.48 d.d (1H, thiophene, J_1 = 4.2, J_2 = 1.5), 7.51 d (1H, CH=, *J* = 15.9), 8.16 d (2H, phenyl, *J* = 9.3). Compound **VI** entered in the chromatographic column of the gas chromatography–mass spectrometer gave a single pek with the retention time 12.32 min. Mass spectrum did not contain the molecular ion peak, the observed peaks were attributable to peaks of molecular ions of the decomposition products of the chalcone. The presence of these fragments in the mass spectrum was an indirect proof of the chalcone structure. Mass spectrum, *m*/*z*, (*I*, %): 421 (26) $[M + H]^+$, 420 (100) $[M]^+$, 405 (11.7) 379 (10), 378 (20) [1-(4-nitrophenyl)-2-(thiophen-2-yl)-5-(5-vinylthiophen-2-yl)pyrrole + H]$^+$, 377 (84) [1-(4-nitrophenyl)-2-(thiophen-2-yl)-5-(5-vinylthiophen-2-yl)pyrrole − H]$^+$, 359 (21), 332 (10), 331 (36), 330 (18.5), 329 (12.5), 297 (12), 229 (12), 76 (10) [1-propanethiol]$^+$, 43 (13).

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