

Oligothiophenes. Part 4: Formation and characterization of stable radicals from novel bis- and tris-bithiophene methanes

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Abstract—Two star-shaped structures of the bis- and tris-thiophene methane types have been synthesized in a facile two-step synthesis. The resulting bis- and tris-thiophene methanes readily react with oxygen both as solids and in solution to yield stable radicals. The formed radicals, which were investigated using electron paramagnetic resonance (EPR), were found to be residing on the central carbons of the bis- and tris-thiophene methanes.

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Oligothiophenes continue to play an important role in the development of new electronic and optical materials. More than 200 papers were published last year in which oligothiophenes were investigated for these purposes.¹ The structures studied included both variously substituted linearly connected thiophenes^{2,3} as well as star-shaped forms.⁴ The latter structures have shown a great potential in the construction of nonlinear optical applications.⁵

In this letter we report the synthesis of two star-shaped structures of the bis- and tris-thiophene methane types that show unexpected radical properties.

On reacting the readily available 2,2'-bithiophene and 5-bromo-thiophene-2-carbaldehyde with perchloric acid in ethylene glycol at 50 °C, bis(2,2'-bithiophene-5-yl)-5-bromo-2-thienyl methane (**I**) was produced in a quantitative yield.⁶

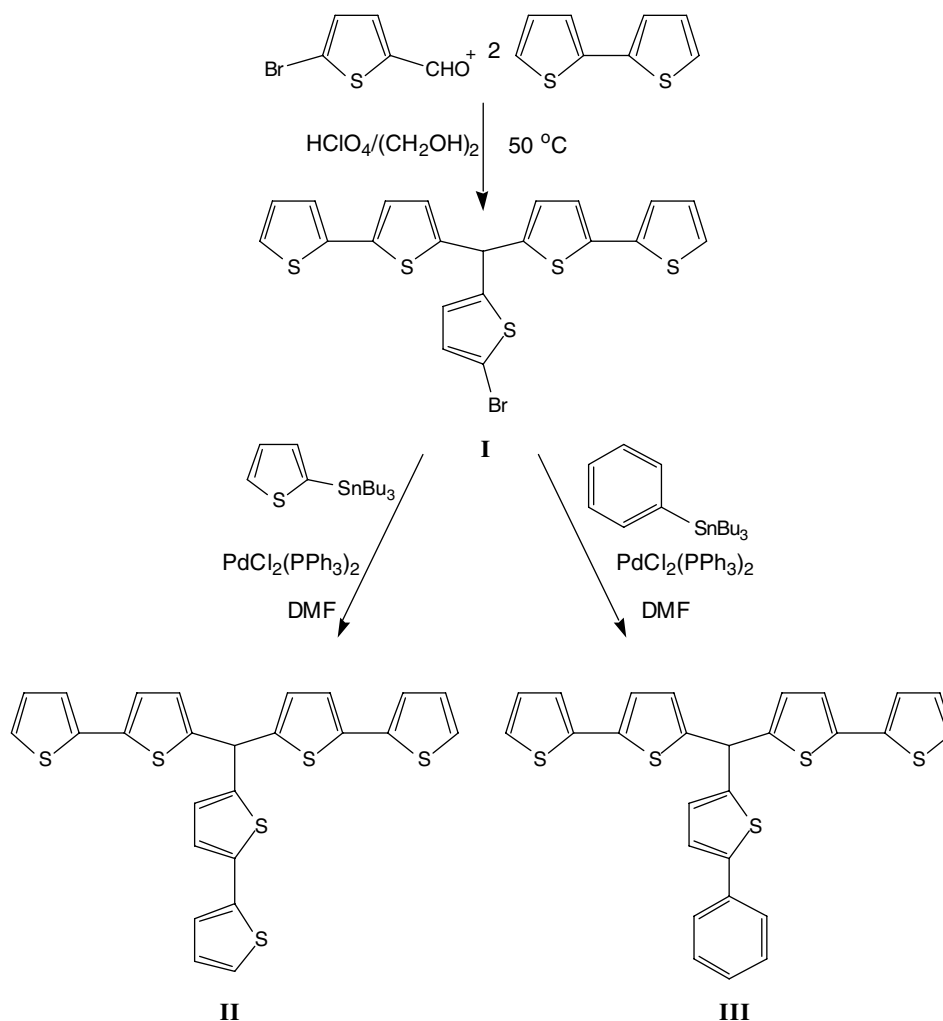
A Stille coupling of **I** with tributyl-2-thienyl stannane in dry dimethyl formamide at 100 °C in the presence of bis(triphenylphosphine)palladium chloride afforded tris(2,2'-bithiophene-5-yl) methane (**II**) as a white solid melting at 150–151 °C in a 70% yield.⁷ Compound **II** has previously been obtained by Krishnaswamy et al. as a product of a photochemical reaction.⁸ Similarly, a

Stille reaction between **I** and tributylphenyl stannane gave a 70% yield of bis(2,2'-bithiophene-5-yl)-5-phenyl-2-thienyl methane **III** as a white solid melting at 91–92 °C (Scheme 1).⁷ Both reactions were carried out under an atmosphere of argon to exclude oxygen from the reaction mixtures. When the reactions were ended, a saturated solution of potassium fluoride in methanol was added to the residue, still under argon. The mixture was stirred at an ambient temperature for 1 h and evaporated with a small amount of silica gel. The residue was eluted with degassed diethylether:hexane (8:1) on silica gel using flash chromatography with argon as the pressurizing gas. As long as oxygen is excluded, compounds **II** and **III** are stable as colourless solutions or as white solids. When exposed to air, however, they turned dark green. We believed this was due to oxidation to the corresponding radicals **II**[•] and **III**[•], which were confirmed by EPR measurements (passage below). When compounds **II** and **III** were incubated in water in the presence of oxygen, excess of potassium iodide, and starch, the solution turned blue due to the formation of a starch–iodine complex indicating that the production of peroxide has oxidized iodide to iodine.

The EPR experiments were carried out by dissolving the air-exposed compounds in toluene and keeping the solutions anaerobic in gas-tight EPR tubes before spectra were recorded at room temperature. The concentrations of the observed radicals were kept at 50 μM to avoid spin–spin interactions. The double integral of the signals of **II**[•] and **III**[•] were compared to that of a standard solution of DPPH (diphenylpicrylhydrazyl).

Keywords: Thiophenes; Stille coupling; EPR.

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Scheme 1.

The experimental EPR spectrum of **II \cdot** (Fig. 1) shows an isotropic signal with a *g*-factor of 2.0038. A satisfactory simulated fit (WINEPR SimFonia) to the experimental spectrum is obtained when the unpaired electron is coupled with three protons with a hyperfine splitting constant of 3.6 G, and with three protons with a hyperfine splitting constant of 0.91 G, and furthermore with three protons with a hyperfine splitting of 0.85 G, and a line width of 0.77 G. Such a coupling pattern is consistent with the C₃-symmetry of compound **II \cdot** . Additional hyperfine couplings cannot be resolved because their magnitude will be smaller than the line width of 0.6 G of the major peaks, whose presence are suggested due to the broadness of the EPR signal.

The experimental EPR spectrum of **III \cdot** (Fig. 2) shows an isotropic signal with an increased *g*-factor of 2.0044. A satisfactory fit to the experimental spectrum was simulated by coupling the unpaired electron with three protons with a hyperfine splitting constant of 3.5 G. The presence of a phenyl group in **III** lowers the symmetry compared to **II**. Other hyperfine interactions are therefore not obtained. Their presence are, however, suggested due to the broadness of the signals.

These tris-thienylmethyl radicals are heterocyclic analogs of the classical triarylmethyl radicals. The unsubstituted triphenylmethyl radical has a *g*-factor of 2.00266,⁹

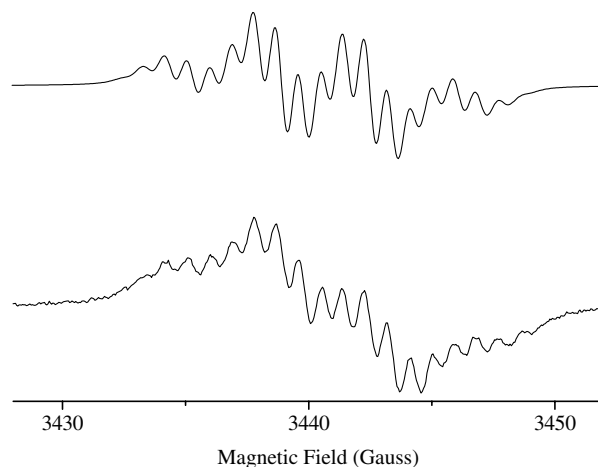


Figure 1. Depicted are simulated (top) and experimental (bottom) EPR spectra of **II \cdot** . Instrumental settings: frequency, 9.65 GHz; microwave power, 2.0 μ W; sweep time, 82 s; modulation frequency, 100 kHz; modulation amplitude, 0.5 G.

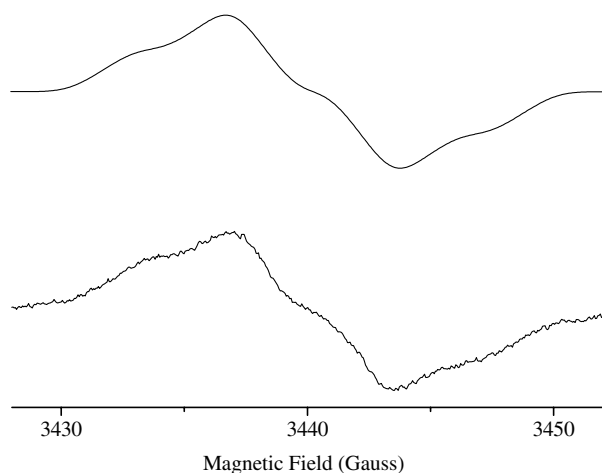


Figure 2. Depicted are simulated (top) and experimental (bottom) EPR spectra of **III**. Instrumental settings: microwave power, 2.0 μ W, sweep time, 82 s, modulation frequency, 100 kHz, modulation amplitude, 0.5 G.

close to that of the free electron (2.0023). Even the more similar tris-biphenylmethyl radical has been investigated using electron nuclear double resonance (ENDOR) with respect to assigning hyperfine coupling constants.¹⁰ In this work, the *g*-factor was not reported. Substitution with heavy halogens results in an increase in the *g*-factor to 2.0034 for tris(2,4,6-trichlorophenyl)methyl¹¹ and to 2.0038 for 4-iodotetradecachlorotriphenylmethyl.¹² In the same manner, the presence of sulfur in **II**[•] and **III**[•] increase the *g*-factor from that of the free electron to 2.0038 and 2.0044, respectively. The same trend is observed for the perhalogenated tris-thienylmethyl analogues tris(3,4,5-trichloro-2-thienyl)methyl (2.0037) and tris(3,4,5-trichloro-3-thienyl)methyl (2.0037).¹³ If the unpaired electrons in **II**[•] and **III**[•] were located directly at one of the sulfur atoms of the thiophene rings, the EPR signals would most likely have been either axial or rhombic, rather than isotropic, as seen for other organosulfur compounds.^{14–17}

There are several very interesting aspects of radicals **II**[•] and **III**[•], in particular the ease of their formation and their stability. In published syntheses, the reactions of the parent carbinols with trifluoromethanesulfonic acid/tetrabutylammonium iodide and perchloro acid/zinc powder have been used to form halogenated radicals tris(3,4,5-trichloro-2-thienyl)methyl and tris(2,4,5-trichloro-3-thienyl)methyl and the parent tris(thienyl)methyl radicals, respectively.¹³ While the published paper does not discuss the stability of the latter radicals, the former are reported to be stable between 10 and a few hours in solution. Compounds **II**[•] and **III**[•] are formed simply by an exposure to air either in solution or as solids. When kept as solids, the radicals appear to be stable even at room temperature. In toluene, the radicals are stable over a period of weeks as evidenced by EPR measurements.

Further work is underway to establish the reactivity pattern and other properties of these new radicals.

Acknowledgments

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